Difference in spin state and covalence between La$_{1-x}$Sr$_x$CoO$_3$ and La$_{2-x}$Sr$_x$Li$_{0.5}$Co$_{0.5}$O$_4$

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Abstract

We present a comparative study of the spin states and electronic properties of La$_{1-x}$Sr$_x$CoO$_3$ and La$_{2-x}$Sr$_x$Li$_{0.5}$Co$_{0.5}$O$_4$ using X-ray absorption near-edge structure spectroscopy at both the O-K and Co-L$_2$ thresholds. In the La$_{2-x}$Sr$_x$Li$_{0.5}$Co$_{0.5}$O$_4$ system the CoO$_2$,3$_{0.5}$ octahedra are isolated, the holes induced by Sr doping are trapped in the isolated Co(IV)O octahedra, and a low-spin state is found for the Co ions, which does not change upon Sr doping. In the La$_{1-x}$Sr$_x$CoO$_3$ system, the interconnected CoO octahedra, with a 180° Co–O–Co bond angle, give rise to a transition from low-spin to intermediate-spin state with a ferromagnetic alignment of the Co spins. The double-exchange, ferromagnetic coupling between Co ions mediated by the 180° bond angle is responsible for suppressing the low spin-state. We find that the branching ratio of spectral intensities at the L$_2$ and L$_3$ thresholds in the Co-L$_2$ X-ray absorption spectra is sensitive to the spin state of the Co ions allowing its direct spectroscopic determination.

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1. Introduction

The strongly correlated electronic structure of 3d transition-metal (TM) compounds has received substantial attention, particularly since the discovery of high-T$_c$ cuprate superconductors [1]. In this context, the Co oxides with their perovskite-type structure are of particular interest due to their unusual magnetic behavior originating from a subtle balance between the crystal-field splitting of the Co 3d levels, $\Delta_{cr}$, and the spin exchange energy, $J$, in the 3d manifold. For instance, the La$_{1-x}$Sr$_x$CoO$_3$ system exhibits a transition from low-spin (LS) to intermediate-spin state [2–7], a large negative magnetoresistance [8,9], the formation of localized magnetic polarons with an unusually high spin number [10], and the formation of a spin-glass state at low temperatures depending on the exact stoichiometry and temperature [4].

In the discussion of the magnetic and electronic properties of Co oxides, one finds many conflicting interpretations of the experimental data. LaCoO$_3$ undergoes a spin transition around 90 K from a nonmagnetic LS state to a magnetic state, which was interpreted as evidence for a LS to high-spin (HS) transition according to magnetic and neutron scattering measurements [3,7]. From magnetic and transport-property studies, Jonker proposed thermal excitations of HS Co ions in the temperature range from 50 to 300 K [11]. Alternatively, the transition at 90 K has been attributed to a LS to intermediate-spin (IS) transition [12,13], or an ordering of LS and HS cations through ferromagnetic superexchange via the intervening oxygen atoms [14]. Moreover, X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) studies indicated a transition from a LS to a HS state in the temperature range between 400 and 600 K [15].
The magnetic properties of La$_{1-x}$Sr$_x$CoO$_3$ as a function of Sr doping have also been discussed controversially. The occurrence of ferromagnetism in the mixed-valent La$_{1-x}$Sr$_x$CoO$_3$ system, with a 180° Co–O–Co bond angle, has been assigned to Zener’s double-exchange mechanism [16]. Based on the superexchange mechanism, it was concluded that Co(III) and Co(IV) ions are in a HS and a LS state, respectively [17]. In contrast to this, Goodenough proposed an intermediate-spin model to account for the observed magnetic moment of La$_{0.9}$Sr$_{0.1}$CoO$_3$ [18].

The spin-state transition was attributed to lattice expansion induced by the dopant Sr ions [4]. However, the Co–O bond length makes a jump from $x=0$ to 0.1, and is scarcely influenced by a further increase of Sr concentration up to $x=0.3$ [19]. It was also argued that the LS state of Co(IV) is stable in the ground state of La$_{2-x}$Sr$_x$Li$_{0.25}$CoO$_3$, while Co(III) ions can transform to an IS state as a consequence of a large D$_{4h}$ elongation of the CoO$_6$ octahedra [20]. Conflicting interpretations have also been reported in the context of the electronic properties. Bhide et al. interpreted Mössbauer spectra in terms of a charge disproportionation above 200 K in LaCoO$_3$ [2], while no evidence for a valence transition had been found in the Co–L$_{2,3}$ XAS spectra [15]. Previous studies of O–K XAS spectra of La$_{1-x}$Sr$_x$CoO$_3$ system were concentrated on the assignment of the hole character upon Sr-doping in analogy to La$_{2-x}$Sr$_x$Cu(Ni)O$_4$ by subtracting the undoped parent compound LaCoO$_3$ [23,24]. However, this procedure is questionable, since the spin state of the Co(III) ion changes upon Sr-doping. The new pre-edge peak in the O–K XAS spectrum of LaCoO$_3$ (at 529 eV) found upon increasing temperature was assigned to a transition to a HS state by Abbate et al. [15] and alternatively a hole peak appearing near the temperature where metallic conduction appears [23].

In the present work we present a detailed, comparative study of the O–K and Co–L$_{2,3}$ XAS spectra of two different systems, La$_{1-x}$Sr$_x$CoO$_3$ and La$_{2-x}$Sr$_x$Li$_{0.25}$CoO$_3$. In the latter compounds, the CoO$_6$ octahedra are isolated, while in the former the CoO$_6$ octahedra are interconnected by oxygen atoms with a 180° Co–O–Co bond angle. The significant differences observed in the O–K and Co–L$_{2,3}$ XAS spectra between the two systems provide valuable insight into differences in magnetic properties and the electronic structure, and help to pin down the spin states of the various compounds. Especially, the branching ratio in the Co–L$_{2,3}$ XAS is expected to be sensitive to the spin state, the combined theoretical and experimental study is very instructive.

The XAS measurements were performed at the SX700/II beamline at BESSY. The O–K and Co–L$_{2,3}$ XAS spectra were taken in the total-electron-yield (TY) detection mode. The O–K XAS spectra were corrected for the energy-dependent incident flux and were normalized at 60 eV above the absorption threshold. The total experimental resolution was 0.3 and 0.5 eV at the O–K and Co–L$_{2,3}$ threshold, respectively. Prior to the measurements, the sample surfaces were scraped in-situ with a diamond file at a base pressure of $1 \times 10^{-10}$ mbar. For the high-temperature measurements on LaCoO$_3$, we first heated the sample to 580 K, then scraped it just prior to the measurements in order to minimize the loss of oxygen with time from the sample surface.

The compounds La$_{1-x}$Sr$_x$CoO$_3$ were prepared by the nitrate method in the Indian Institute of Science, Bangalore. The starting materials were pre-dried La$_2$O$_3$, CoC$_{2}$O$_4$·2H$_2$O, and SrCoO$_3$. The required proportions of the reactants were dissolved in concentrated nitric acid. The mixture was dried and then decomposed at 400 K after which it was heated to 900 °C for 1 day. The powder obtained was then ground, pelletized, and heated to 900 °C for 1 day. After that, the pellets were crushed, ground, and again pelletized before being heated to 1400 °C for 1 day. The compounds La$_{2-x}$Sr$_x$Li$_{0.25}$CoO$_3$ were prepared at the Philipps-Universität Marburg, according to the experimental procedures in Ref. [21], which starts from a mixture of La(OH)$_3$, SrCoO$_3$, and Co$_3$O$_4$; brownish black single-phase products result. The average oxidation state was determined by iodometric titration. SrCoO$_3$ was obtained under high pressure as described in Ref. [22]. The O–K TY XAS spectra of La$_{1-x}$Sr$_x$CoO$_3$, obtained directly after scraping in this work, are very similar to those from fluorescence yield (FY) measurements reported by Moodenbaugh et al. [23] and those from TY by Okamoto et al.; therefore, the very weak pre-edge peak from TY XAS measurements, reported in Ref. [23], might be due to insufficient handling of the sample surface.

3. Results and discussion

3.1. O–K XAS spectra

In O–K XAS spectra, the effects of intra-atomic Coulomb correlation are normally much weaker than in transition-metal L$_{2,3}$ XAS spectra, i.e. an agreement between the experimental spectra and the results of band structure calculations is plausible [15,25,26]. Therefore, O–K XAS spectra are usually studied in order to explore the amount of O-$2p$ holes induced by covalence or doping in the ground state.

Fig. 1 shows the O–K XAS spectra of La$_{2-x}$Sr$_x$Li$_{0.25}$CoO$_3$O$_4$ ($x=0$ and 0.2); for comparison, we also show the spectrum of CoO as a well-known HS Co(II) reference with a 3d$^7$ configuration in the ground state, and the spectrum of LaFeO$_3$ (shifted by $-2$ eV) as a HS 3d$^5$ reference. Here, we are interested in the pre-edge region below 533 eV, which is assigned to the hole fraction with...
O-2p character in the unoccupied $t_{2g}$ and $e_g$ orbitals in $O_h$ local symmetry arising from TM-3d/O-2p mixing [26]. The double peak in the CoO reference sample is well known to arise from $1s(t_{2g}^{-1})(e_g)^0$ and $1s(t_{2g}^{-1})(e_g)^1$ final states, reached from the $(t_{2g}^{-1})(e_g)^0$ ground state [27], where-for simplicity-the fully occupied spin-up state $(t_{2g}^{-1})(e_g)^2$ is not given (for notation, see Fig. 2). The 1.6-eV splitting of the pre-edge doublet is then essentially due to the energy difference between $t_{2g}$ and $e_g$ states, and is primarily governed by the bare crystal-field splitting, 10 $Dq$, due to a difference in the electrostatic potential as well as anisotropic hopping strengths of these orbitals with oxygen p states. Similarly, the double peak in the O–K XAS spectrum of LaFeO is assigned to $1s(t_{2g}^{-1})(e_g)^0$ and $1s(e_g)^1(t_{2g}^+)^0$ final states reached from the $(e_g)^0(t_{2g}^0)^0$ ground state. The spectral weight of the lower-energy feature increases with decreasing 3d occupancy from CoO to LaFeO. In contrast to the doublet features in CoO and LaFeO, La$_2$Li$_{0.5}$CoO$_{1.5}$ exhibits a single narrow peak at 530.1 eV. Since the spectral profile of this single peak is the same as that in the well-known LS Co(III) oxide, LiCoO$_2$ [27], it can be assigned to the only possible transition leading to a $1s(t_{2g}^{-1})(e_g)^1$ final state from a $t_{2g}^0$ configuration in the LS ground state, as shown in the energy scheme of 3d configurations with $O_h$ symmetry in Fig. 2(a). This observation is in agreement with the LS state derived from earlier EPR measurements [21,28]. Since the CoO$_6$ octahedra are isolated, the holes induced

![Energy schemes for a 3d<sup>6</sup> configuration in O<sub>h</sub> symmetry](image)

Fig. 2. Sketch of energy schemes in $O_h$ symmetry for a 3d<sup>6</sup> configuration. 10 $Dq$ and $J$ are the crystal-field splitting and exchange splitting, respectively.
by Sr-doping are expected to be confined to the resulting Co(IV)O₆ units. In La₂₋ₓSrₓLiₓCo₃O₅, both isolated Co(IV)O₆ octahedra, with an additional hole, and isolated Co(III)O₆ octahedra, without doped holes exist, i.e. a mixed-valent state (called here inhomogeneously mixed-valent). We consequently expect that the O–K spectra are the sum of spectra from Co(IV)O₆ and Co(III)O₆ units. In addition, it had been shown previously that the pre-edge peaks in the O–K XAS spectra of the late TM oxides are shifted by ~1 eV to lower energies when the TM valence increases by 1 [29,30]; therefore, spectral features from the two different valence states can be well resolved in this case. For x = 0.2, the spectral feature observed at the same energy as the single peak for x = 0 is thus easily recognized as a transition to the e₈ state of the remaining 60% Co(III)O₆ octahedra, while the other two structures at lower energies originate from the doping-induced 40% Co(IV)O₆ units. Based on the LS state known from EPR measurements [21,28], we can reasonably well assign the stronger peak at 529 eV to transitions to a configuration (indicated with an arrow in Fig. 1) and the weaker peak at 528 eV to transitions to a configuration with only one hole (denoted as t₂g in Fig. 1), both arising from the 40% Co(IV)O₆ units in the sample.

In Fig. 3 we present O–K XAS spectra of the La₁₋ₓSrₓCoO₃ system. A single pre-edge peak is observed in the spectrum of LaCoO₃ taken at 300 K. However, this peak is relatively broad. The comparison of these two materials will therefore allow us to assess the impact of additional delocalization effects (nonlocal effects) that arise from the interaction between neighboring CoO₆ clusters in LaCoO₃. Delocalization depends on the degree of covalence as well as the TM–O–TM bond angle; it should be very strong for a 180° bond angle due to the large hopping integral in this case [31,32]. This leads to considerable broadening of e₈ derived bands and an energy shift of 0.5 eV to lower energy in LaCoO₃ as compared to La₂₋ₓSrₓLiₓCo₃O₅. A similar effect had been observed previously when comparing La₃₋ₓLiₓNi₆O₁₅ and La₀.₉₋ₓSrₓNi₆O₉₅ [30]. Furthermore the pre-edge peak in LaCoO₃ exhibits a large asymmetry at the leading edge (indicated with an arrow in Fig. 1). LDA + U calculations have predicted that for LaCoO₃, the LS state is the ground state only for very low temperatures, while at room temperature it is mixed with the IS state, with a configuration [12], that lies slightly above the LS state. As shown in the schematic energy diagram of Fig. 2b, the contribution from a configuration will develop with increasing temperature, and this will be responsible for the asymmetry at the leading edge. In the 580 K spectrum, where one expects substantial thermally populated higher spin states, this asymmetry has further developed to a peak at 528.5 eV marked by an arrow, in agreement with previous magnetic studies [4,6,11,33]. The spectral change with increase in temperatures is schematically shown in Fig. 2 from (a) to (d), but the difference between (c) and (d) cannot be distinguished on the basis of O–K XAS spectra alone, since in both cases a ratio of 2:2 is expected for the holes of the two peaks, one has to perform full-multiplet cluster-model calculations [34], or study branching ratio in the Co–L₃,₅ XAS spectra.

The spectral features of La₁₋ₓSrₓCoO₃ compounds are obviously different from those of the system La₂₋ₓSrₓLiₓCo₃O₅. If we assume that upon Sr-doping the spin state of the Co(III) ion is not changed, one expects for low Sr-doping levels of x = 0.1 a dominant pre-edge peak that originates to 90% from Co(III)O₆ units at the same energy as observed for LaCoO₃, while the 10% Co(IV)O₆ units would contribute to the rest of the spectrum. The experimental results, however, are entirely different, with the pre-edge feature for x = 0.1 being split into a poorly resolved double-peak structure. The observed spectral features of La₀.₉₋ₓSrₓCoO₃ are similar to those of LaCoO₃ taken at 580 K, which indicates that the spin state of most Co(III) ions is changed either by heating or by doping. A similar conclusion has been obtained previously from the conductivity and the magnetic results: the electronic structure of LaCoO₃ at 800 K is similar to that of the Sr-doped compound with x = 0.3 [33].

For doping levels x < 0.2, each Co(IV) ion couples with neighbors via double-exchange interaction, resulting in

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Fig. 3. O–K XAS spectra of the La₀.₉₋ₓSrₓCoO₃ system. For x = 0 the spectrum obtained at 580 K is also given.
strong ferromagnetic short-range correlations. This situation has been observed by magnetic neutron scattering [4] that also showed the occurrence of a spin-glass ground state. Within this short range, the doping-induced holes tend to distribute homogeneously. In the perovskite structure of La$_{1-x}$Sr$_x$CoO$_3$, the La/Sr ions occupy pseudo-body-centered positions, while the Co ions are located at the corners of the cube. Thus, the doped hole delocalizes over all nearest-neighbor CoO$_6$ octahedra, affecting the electronic structure (and consequently, the spin state) of a large number of Co sites. This is the origin of the significant changes observed in the O–K XAS spectrum for $x = 0.1$. Even at such low doping levels, the LS state is destroyed, and the spin-transition transition from LS to IS around 90 K does no longer occur, as known from magnetic measurements [7]. This clearly demonstrates the high sensitivity of the O–K XAS spectra to the spin state [15]. With increasing Sr-doping, ferromagnetic coupling develops in the solid, and conductivity increases until Co(IV)–O–Co(III) units distribute homogeneously in the solid, which then can be called a homogeneous mixed-valent compound. Due to strong covalence and large hopping via the 180$^\circ$ Co–O–Co bond angle in the La$_{1-x}$Sr$_x$CoO$_3$ system, the difference in 3d occupancies between nominally Co(IV) and Co(III) ions is small.

Despite the same formal valence of +3.4, the pre-edge peaks in the XAS spectrum of La$_{0.06}$Sr$_{0.4}$CoO$_3$ are totally different from those of the LS compound La$_{1.8}$Sr$_{0.2}$Li$_{0.5}$Co$_{0.5}$O$_4$; the origin of this lies in the different spin states. In the XAS spectra of La$_{1-x}$Sr$_x$CoO$_3$, the lower-energy pre-edge component is dominant, while the higher-energy spectral features in the pre-edge region have lower spectral weight and are only observed as broad shoulders. Considering that the pre-edge peaks are shifted to lower energies with increasing Co valence, the lowest energy peak should be related to Co(IV)O$_6$ units. The missing similarity between the lower-energy components and the pre-edge peaks in SrCoO$_3$ indicates that the O–K spectrum of La$_{0.06}$Sr$_{0.4}$CoO$_3$ cannot simply consist of one from Co(IV)O$_6$, as in SrCoO$_3$, and another one from Co(III)O$_6$, as in LaCoO$_3$. Moreover, magnetic measurements and X-ray magnetic circular dichroism studies of the Co–L$_{2,3}$ XAS spectra indicate that the magnetic moment per Co ion increases significantly with increasing hole doping (i.e. when replacing La by Sr) in LaCoO$_3$ or with electron doping (i.e. replacing Sr by La) in SrCoO$_3$ [39]. Thus, the single-peak structure for the doping-induced hole states in La$_{1-x}$Sr$_x$CoO$_3$, obtained recently by subtracting a LaCoO$_3$ spectrum, is problematic [23]. Since the spin state of the Co(III)O$_6$ unit changes upon Sr-doping, the subtraction process leads to negative spectral weight at the energy position of the prepeak in the spectrum of LaCoO$_3$. Furthermore, the intensity of the hybridization peak (i.e. of the prepeak in LaCoO$_3$), which can be associated with the upper Hubbard band (UHB), was assumed to be proportional to $1-x/2$, which means that the subtraction procedure might have underestimated the spectral weight of the hole peak. The reason for this is that when going from isolated to connected octahedra [35–37] or from a 90$^\circ$ to a 180$^\circ$ TM–O–TM angle [29], an additional dynamical spectral-weight transfer from the hybridization (UHB) peak to the hole peak should occur [35,36]. This is also one of the reasons for the very weak higher-energy pre-edge peak observed for La$_{0.8}$Sr$_{0.2}$CoO$_3$.

From a comparison of the O–K XAS spectra of LaFeO$_3$ and SrCoO$_3$, we can exclude a HS state for SrCoO$_3$. Based on an effective spin of $\mu_{eff} \sim 3\mu_B$, the Co–L$_{2,3}$ XAS spectrum of SrCoO$_3$ was simulated by assuming an IS state [38]. For later TM oxides in high valence states, e.g. Fe(IV), Co(IV), and Cu(III), the charge-transfer energy is known to be negative, and the ground state is dominated by ligand-hole character. From an ionic LS 3d$^5$ configuration, we expect one unpaired spin-up electron in $t_2g$ orbitals. As covalence and long-range coupling are switched on in SrCoO$_3$, the Co-3d($t_2g$) states get occupied with electrons from ligand O-2p states. The parallel arrangement of two unpaired spins exhibits a situation as shown in Fig. 2(b) and 2(c): an ‘IS’ state for 3d$^4$ with one hole in an O-2p state. Theoretical studies of XPS and XAS spectra of SrCoO$_3$ suggested 3d occupation numbers of 5.8–5.9 [38,39]. These numbers are in better agreement with the results of recent magnetic measurements, which yielded $\mu_{eff} \sim 2\mu_B$ [22,39], as compared to the assumption of a 3d$^6$ configuration with four unpaired spins plus one O-2p hole, as supposed previously [38]. In view of the strong electron delocalization and the strong covalence in SrCoO$_3$, the observed main peak and the lower-energy shoulder cannot be assigned to any pure orbital character. Detailed theoretical and experimental studies are required to reach an improved understanding of the spin state in SrCoO$_3$.

3.2. Co–L$_{2,3}$ XAS spectra

Fig. 4 shows the Co–L$_{2,3}$ XAS spectra of both the La$_{2-x}$Sr$_x$Li$_{0.5}$Co$_{0.5}$O$_4$ and the La$_{1-x}$Sr$_x$CoO$_3$ materials studied. Going from the isolated CoO$_6$ octahedra in La$_{1.8}$Sr$_{0.2}$Li$_{0.5}$Co$_{0.5}$O$_4$ to the interconnected CoO$_6$ octahedra in LaCoO$_3$, the Co–L$_{2,3}$ XAS spectrum gets broader, a change that can be associated with the larger bandwidth in the latter. A further difference is the enhanced spectral weight of the shoulders below and above the main peak in the latter compound.

The changes in the spectral features between the two Co oxides, La$_{1.8}$Sr$_{0.2}$Li$_{0.5}$Co$_{0.5}$O$_4$ and La$_{0.8}$Sr$_{0.2}$CoO$_3$, with a formal valence of +3.4, are more pronounced than those between the two Co(III) oxides discussed above. A new higher-energy structure, marked by arrows in the Co–L$_3$ and Co–L$_2$ spectra, is clearly observed in the spectrum of La$_{1.8}$Sr$_{0.2}$Li$_{0.5}$Co$_{0.5}$O$_4$. The spectrum of LaCoO$_3$ taken at 580 K is very similar to the one obtained before by Abbate et al. [15], exhibiting enhanced shoulder intensities; this is
that the BR is sensitive to the spin state of TM ions \[40\]. In practice, however, the error bars in the experimental data induced by contributions from the absorption process, the continuum as well as background, might wipe out the small intensity difference between LS and HS states. Furthermore, for late 3\textit{d} TM oxides in high oxidation states, e.g. TM(III) and TM(IV) oxides, the differences in BR between HS and LS states become small due to strong covalence and configuration interaction, a fact that limits the applicability of this method. Fortunately, when going from 3\textit{d} to 3\textit{d} compounds, the difference of the BR between LS and HS states is rather large and far beyond the experimental uncertainties, which makes it usable for determining the spin states in the ground states of these compounds. To this purpose, we substract the background and normalize all spectra at the Co–\textit{L}\textsubscript{XAS} spectra. In this way, we can directly read off the differences in BR from the intensities of the Co–\textit{L}\textsubscript{XAS} spectra. In Fig. 5,

again due to a thermally populated high-spin state \[11,15\]. With increase of formal valence, we observe a shift to higher energies by 0.4 eV from LaCoO\textsubscript{3} to La\textsubscript{0.8}Sr\textsubscript{0.2}CoO\textsubscript{3} and by 1 eV from LaCoO\textsubscript{3} to SrCoO\textsubscript{3}. In contrast, no such shift is observed for LaCoO\textsubscript{3} when the temperature is increased \[15\]. This observation contradicts the idea of charge disproportionation into Co(II) and Co(IV) as claimed previously \[2\].

Since the multiplet splitting is large in the TM–\textit{L}\textsubscript{2,3} XAS spectra, a full theoretical description of mixed-valent systems is beyond the capability of the present approach. One useful method, however, to obtain information on the spin state of a mixed-valent system is based on the branching ratio (BR) of the intensities, I(\textit{L}\textsubscript{1}) and I(\textit{L}\textsubscript{2}), of the \textit{L}\textsubscript{3} and the \textit{L}\textsubscript{2} XAS spectra, respectively, defined by:

\[
\text{BR} = \frac{I(\textit{L}\textsubscript{1})}{I(\textit{L}\textsubscript{1}) + I(\textit{L}\textsubscript{2})}
\]

It is known from theoretical model calculations that the HS state has a larger BR than the LS state, which means...
we directly compare the XANES spectra of two Co(III) compounds, LaCoO$_3$ and La$_2$Li$_{0.5}$Co$_{0.5}$O$_4$ (Fig. 5(a)), and LaFeO$_3$ and SrCoO$_3$, with a formal 3d$^5$ configuration (Fig. 5(b)) as well as those of the compounds La$_{0.6}$Sr$_{0.4}$CoO$_3$ and La$_{1.8}$Sr$_{0.2}$Li$_{0.5}$Co$_{0.5}$O$_4$ with the formal valence +3.4 (Fig. 5(c)). Without a quantitative analysis, one can clearly see that the largest difference in BR occurs for the Co(3.4 +) compounds, with $\Delta$BR = 0.08; this BR difference decreases to $\Delta$ = 0.05 for the Co(III) pair.

In order to understand this difference, we compare the experimental data with theoretical results. TM–L$_2$XAS spectra of formally divalent late TM compounds can be well reproduced by atomic multiplet calculations [41], however, for trivalent late TM compounds, the covalent mixture between TM 3d and O-2p becomes important [29,30,42]. Considering covalent effects, we have simulated the Co–L$_2$XAS spectrum of La$_2$Li$_{0.5}$Co$_{0.5}$O$_4$ using a charge-transfer multiplet calculation [30,42], which includes both intra-atomic multiplet interaction and interatomic covalence. The Co–L$_2$XAS spectrum of La$_2$Li$_{0.5}$Co$_{0.5}$O$_4$ is reproduced with $\Delta$ = 3 eV, 10 Dq = 1.3 eV, and U$_{sd}$–U$_{dd}$ = 2 eV. The Slater integrals have been reduced to 75% of the atomic Hartree–Fock values, which yields a considerably better agreement with the experimental spectrum of La$_2$Li$_{0.5}$Co$_{0.5}$O$_4$. Considering an increase in covalence when going from isolated to interconnected CoO$_6$ octahedra, one has to decrease $\Delta$ to simulate the Co–L$_2$XAS spectrum of LaCoO$_3$. However, in the theoretical calculation using the parameters suitable for La$_2$Li$_{0.5}$Co$_{0.5}$O$_4$, the BR decreases as $\Delta$ is decreased, while the experimental BR increases from BR = 0.67±0.01 for La$_2$Li$_{0.5}$Co$_{0.5}$O$_4$ to BR = 0.71±0.01 for LaCoO$_3$. Besides the difference in covalence, there is also a difference of the Co spin state in the two compounds. Since the spin state is sensitive to subtle changes of the balance between crystal-field and exchange interaction, we select the crystal-field parameter 10 Dq as a free parameter to simulate the influence of the spin state on the spectral feature. The spectral features and the BR are very sensitive to a slight change of 10 Dq as shown in Fig. 6. We have found that the Co is close to a minimum BR = 0.61 for 10 Dq = 1.3 eV, representing a LS state, and close to a maximum BR = 0.7 for 10 Dq = 1.1 eV, i.e. for a HS state. The BR observed for the LS state in La$_2$Li$_{0.5}$Co$_{0.5}$O$_4$, which is larger than the one calculated, is in agreement with previous results, where it was shown that theoretical branching ratios are systematically smaller than experimental numbers [40,43,44]. The difference in BR between HS and LS states, BR(HS)–BR(LS), however, is consistent for experiment and theory, which suggests to shift theoretical results by $\sim$ 0.05 in order to match the experimental numbers.

When going from La$_2$Li$_{0.5}$Co$_{0.5}$O$_4$ to LaCoO$_3$, the broadening of the spectra is reflected also in the theoretical IS spectrum in Fig. 6, where the multiplet structures are poorly resolved. For the La$_{2-x}$Sr$_x$Li$_{0.5}$Co$_{0.5}$O$_4$ system, the BR does not change upon Sr doping, while it increases to 0.74±0.01 in the La$_{1-x}$Sr$_x$CoO$_3$ system for a doping level of $x$ = 0.4. We summarize the BRs of the compounds studied in this work and those from the literature in Fig. 7 [40,43,44]. Note that the La$_{0.6}$Sr$_{0.4}$CoO$_3$ system has not quite arrived at a HS state, in agreement with magnetic measurements [11,39]. For the 3d$^2$-compound LaFeO$_3$, a BR of 0.78±0.01 is obtained, which is slightly smaller than that in previous studies [43]; it decreases to 0.72±0.01 in SrCoO$_3$, which is close to the IS state of LaCoO$_3$. The difference in the BRs between LaFeO$_3$ and SrCoO$_3$ is very significant, as shown in Fig. 5(c), but it is still smaller than the theoretical difference $\Delta$BR = 1.1 between LS and HS states obtained with a 75% reduction of the Slater integrals from their atomic values [40]. This result excludes a HS state and supports our interpretation of an ‘IS’ 3d$^2$L state for SrCoO$_3$.

4. Summary

We have shown that the O–K and Co–L$_2$XAS spectra are very sensitive to spin state, valence and covalence in
ent configurations. Both Co(III) and Co(IV) ions are in a LS state in La$_{2-x}$Sr$_{x}$Li$_{0.5}$Co$_{0.5}$O$_{4}$.

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