

## Surprising Cobaltates: A Spectroscopic Perspective

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The layered Co oxides have attracted considerable attention recently, since the discovery of superconductivity in the  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ , giant magneto-resistance as well as metal-insulator (MIT) and antiferro-ferro-para-magnetic transitions in  $\text{REBaCo}_2\text{O}_{5.5}$ . Moreover, these compounds possess the so-called spin state degree of freedom, i.e. the  $\text{Co}^{3+}$  ions can be in a low spin (LS,  $S = 0$ ), high spin (HS,  $S = 2$ ) and even intermediate spin (IS,  $S = 1$ ) state [1]. This spin state degree of freedom is generally considered to play a key role for the unconventional magnetic and transport properties of the cobaltates. A spin-blockade mechanism [2,3] has been recently proposed as the driving force for the MIT in  $\text{REBaCo}_2\text{O}_{5.5}$  [2, 4].

### (I) Polarization dependent effects in the Co- $L_{2,3}$ XAS spectra of $\text{Na}_x\text{CoO}_2$

$\text{Na}_x\text{CoO}_2$  consists of alternating layers of  $\text{CoO}_2$  and Na along the  $c$  axis. The edge-sharing  $\text{CoO}_6$  octahedra in the  $\text{CoO}_2$  layers have their threefold (111) axis oriented parallel to the  $c$  axis and show a compression along  $c$ . The local symmetry of the Co is close to  $D_{3d}$ , which splits the  $t_{2g}$  states into a two-fold degenerate  $e_g^\pi$  and a nondegenerate  $a_{1g}$ , while the  $e_g$  states remain doubly degenerate, now called  $e_g^\sigma$ . A  $\text{Co}^{3+}/\text{Co}^{4+}$  charge ordering was proposed for  $\text{Na}_x\text{CoO}_2$  [5], where the  $\text{Co}^{4+}$  ion is claimed to attract the neighboring oxygens and to cause a local symmetry lower than  $D_{3d}$  for its adjacent  $\text{Co}^{3+}$  ions. This then would split the  $e_g^\sigma$  doublet and stabilize the IS state. Moreover, a strong polarization dependence of the Co- $L_{2,3}$  XAS spectra of  $\text{Na}_x\text{CoO}_2$  was observed and interpreted as a symmetry lower than  $D_{3d}$  [6]. It was also concluded that the samples used in these XAS studies showed  $\text{Co}^{3+}/\text{Co}^{4+}$  spectral ratios which were inconsistent with their nominal Na contents [6].

Figure 1 shows our experimental polarization dependent Co  $L_{2,3}$  edge XAS spectra of  $\text{Na}_{0.5}\text{CoO}_2$  and  $\text{Na}_{0.75}\text{CoO}_2$ . (a) and (e) are the spectra measured at the Dragon beamline at the NSRRC in

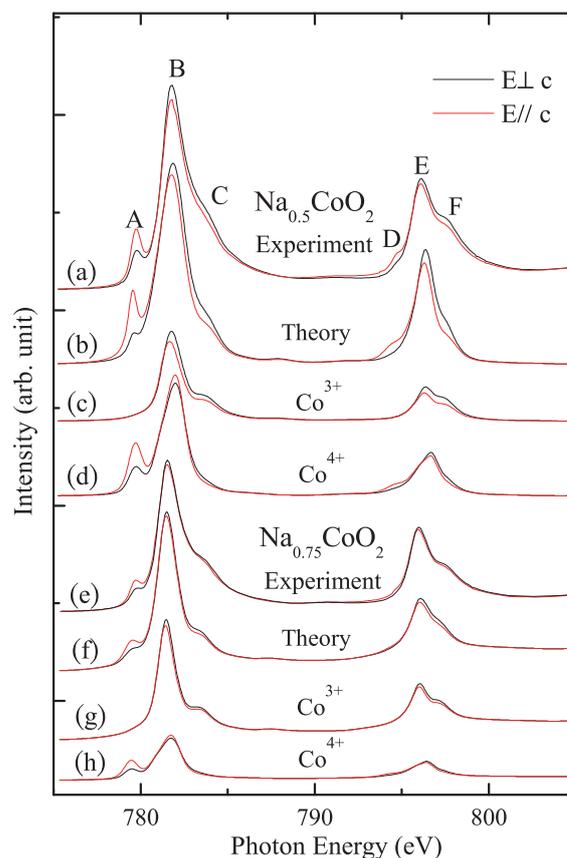


Fig. 1: The experimental and theoretical Co  $L_{2,3}$  edges XAS spectra of  $\text{Na}_{0.5}\text{CoO}_2$  and  $\text{Na}_{0.75}\text{CoO}_2$

Taiwan; and (b)-(d) and (f)-(h) are the corresponding simulated spectra together with the individual  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  contributions. The excellent agreement between theory and experiment demonstrates that a strict  $D_{3d}$  local symmetry for both  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions in a LS state is sufficient to explain the observed spectral features and polarization dependence, refuting the need for a local symmetry lower than  $D_{3d}$  for the  $\text{Co}^{3+}$  ion as claimed in [5,6]. The reason for suggesting a local symmetry lower than  $D_{3d}$  for the  $\text{Co}^{3+}$  ion in previous polarization dependent XAS studies is that the authors were still using cubic wavefunctions in their  $\text{Co}^{3+}$  simulations in  $D_{3d}$  symmetry [6], thus essentially neglecting the anisotropic mixing of the  $t_{2g}$  with the  $e_g$  states due

to the trigonal crystal field. Also in contrast to previous studies is our finding, that the  $\text{Co}^{3+}/\text{Co}^{4+}$  spectral fractions used to reproduce our spectra match the nominal Na concentrations. This indicates that the samples are of proper stoichiometry.

We find that the polarization dependence of the main peak B and E is due to the mixing between  $e_g^\pi$  and  $e_g^\sigma$ . The polarization dependence of the peaks A and D can be rather directly linked to the hole occupation in the  $a_{1g}$  vs.  $e_g^\pi$  orbital.

From the cluster calculations which yield the excellent simulation of the experimental polarization dependent spectra, we find that the  $\text{Co}^{4+}$  has a hole density of about 0.58 in the  $a_{1g}$  and 0.42 in the  $e_g^\pi$  orbital. These numbers apply for both, the  $\text{Na}_{0.5}\text{CoO}_2$  and  $\text{Na}_{0.75}\text{CoO}_2$  composition. Band structure calculations [7] predict that for low Na contents, i.e.  $x < 0.67$ , the  $t_{2g}$  hole has indeed a mixed  $a_{1g}$  and  $e_g^\pi$  character. However, for high x contents, i.e.  $0.67 < x < 1$ , the hole should reside only in the  $a_{1g}$  band. This is in contradiction to our findings. If the hole were of pure  $a_{1g}$  character, the linear dichroism of peak A would be larger by a factor of 2 – 3 than what is experimentally observed.

## (II) Co valence in bilayer hydrated superconducting $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$

The bilayer hydrated  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  ( $x \sim 0.35$ ,  $y \sim 1.3$ ) (BLH) is one of the exotic superconductors with a superconducting transition temperature ( $T_c$ ) of about 5 K [8]. BLH has attracted tremendous research interest since this compound was discovered as the first Co-based superconducting oxide. It has two-dimensional Co-oxygen planes analogous to the Cu-oxygen planes in the high- $T_c$  cuprate superconductors. It was found that varying the Na content in BLH results in the same type of out-of-plane chemical doping control of the in-plane electronic charge as found in the high- $T_c$  cuprates [9].

Since the existence of an optimal doping for a maximum  $T_c$  is thought to be an important characteristic of the cuprate superconductors, the relationship between doping and  $T_c$  has also been examined intensively for the BLH system [8–10]. At the time of discovery, the BLH was regarded as an electron-doped system in which a low spin  $\text{Co}^{4+}$  lattice would acquire an electron density of about 0.35 per Co atom on the basis of the Na content. In

other words, the Co valence state  $V_{\text{Co}}$  would be close to +3.65 [8,9]. In the BLH phase diagram, the superconductivity was then found to lie in the narrow region from  $V_{\text{Co}} = +3.65$  to +3.75, with an optimum  $T_c$  for  $V_{\text{Co}} = +3.7$  [9].

Within 1 year from the discovery, however, chemical analysis studies using redox titration methods claimed that the value of  $V_{\text{Co}}$  must be in the +3.3 to +3.4 range [10–14]. It was proposed that the charge compensation is achieved by the intercalation of oxonium ions ( $\text{H}_3\text{O}^+$ ) along with the water. Yet, spectroscopic studies in the same period and afterwards, provide the standard Na doping picture. Electron energy loss [15], high-energy photoemission [16], NMR [17], hard X-ray absorption [18,19], and angle-resolved photoemission [20] all conveyed the message that the superconducting BLH has a Co valence of about +3.7 consistent with the Na content. Also a more recent study using a chemical postreduction method [21] found a similar value. This message is in clear conflict with the earlier chemical titration results, and this issue has not yet been resolved to the best of our knowledge.

The debate about the Co valence causes considerable uncertainty about the size and shape of the Fermi surface and has, in turn, far reaching consequences for the modeling of the superconductivity in this system. A Co valence of about +3.7 would lead to the existence of six  $e_g^\pi$  hole pockets in addition to the large  $a_{1g}$  cylindrical Fermi surface according to standard band structure calculations [22,23]. This then leads to multiorbital models claiming the superconductivity driven by magnetic spin correlations with even the possibility of triplet pairing [24–27]. A scenario with a Co valence of +3.3, on the other hand, does not have the six  $e_g^\pi$  hole pockets and requires quite different approaches for the superconductivity, e.g., involving electron-phonon mechanisms and unconventional s-wave pairing [28–31].

The confusion about the Co valence and the Fermi surface has not been settled yet. An angle-resolved photoemission study did not find the presence of the six  $e_g^\pi$  hole pockets [20], but there is also considerable debate whether this due to correlation effects [22,32] or surface effects [33]. By contrast, a more recent study using Compton scattering claimed to have observed these pockets [34]. Also a recent specific heat experiment has been interpreted as to support the existence of two types of hole pockets [35].

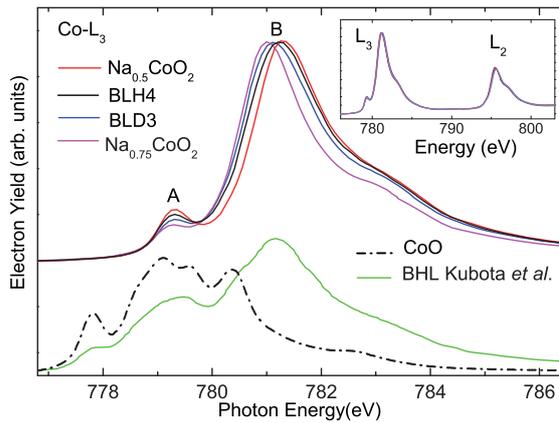


Fig. 2: The Co- $L_3$  XAS spectra of the BLH4 and BLD3 samples together with  $\text{Na}_{0.5}\text{CoO}_2$  and  $\text{Na}_{0.75}\text{CoO}_2$ , as well as  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  from Ref. [41], and CoO for comparison. Inset: complete view of the Co- $L_{2,3}$  edges of the samples studied.

Here we utilize soft X-ray absorption (XAS) spectroscopy at the Co- $L_{2,3}$  ( $2p \rightarrow 3d$ ) and O- $K$  ( $1s \rightarrow 2p$ ) edges as the preferred method to determine the valence state of the Co ions. The Co ( $2p \rightarrow 3d$ ) transitions involve directly the relevant valence shell, and are extremely sensitive to the charge state: not only do the energy positions depend on the valence but also the spectral line shape can be used as fingerprints for the valence [36–38]. In addition the O  $1s \rightarrow 2p$  transitions reach final states which are directly hybridized with the empty Co  $3d$  orbitals. We have explicitly proven recently that this method is suitable for the cobaltates [2,39,40]. In particular, we have shown that soft XAS provides not only element specific information but also quantitative information on how much of the Co ions are in the  $4+$ ,  $3+$  or  $2+$  states as they are present in the material. This is obviously more specific than obtaining only the average charge number for entire multicomponent system when using chemical titration methods.

We find that the valence state of the Co lies in a narrow range from  $+3.3$  to  $+3.4$  for all studied  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  samples and their deuterated analogue (BLD) with  $T_c$ 's ranging from 3.8 K to 4.7 K, see Figure 2. These valence values are far from the often claimed  $+3.7$ , the number based on the Na content only. We propose to modify the phase diagram accordingly, see Figure 3, where the basic electronic structure of the superconducting phase is very close to that of the  $\text{Na}_{0.7}\text{CoO}_2$  system, suggesting that the presence of in-plane spin fluctuations could play an important role for the superconductivity.

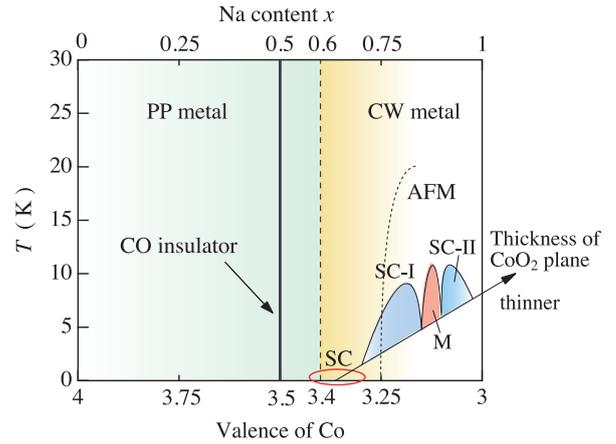


Fig. 3: Electronic phase diagram of the  $\text{Na}_x\text{CoO}_2$  against both the Co valence ( $V_{\text{Co}}$ ) and the Na content  $x$ , reproduced from Ref. [42]. The BLH lies within the CW metal phase of the  $\text{Na}_x\text{CoO}_2$  (circled area).

### (III) Spin state order/disorder and metal-insulator transition in $\text{GdBaCo}_2\text{O}_{5.5}$

The crystal structure of  $\text{REBaCo}_2\text{O}_{5.5}$  is composed of an equal number of  $\text{CoO}_6$  octahedra and  $\text{CoO}_5$  pyramids and the valence of all the Co ions is  $3+$ . A sharp drop of the resistivity, the so-called MIT, at  $T_{\text{MI}} \sim 360$  K is commonly attributed to a sudden spin-state switch of  $\text{Co}_{\text{oct}}^{3+}$  [2,4]. Contradictory scenarios have been proposed, including full or partial  $\text{LS} \rightarrow \text{IS}$  or  $\text{LS} \rightarrow \text{HS}$  state transitions for the  $\text{Co}_{\text{oct}}^{3+}$ , and  $\text{IS}$  or  $\text{HS}$  configurations for the  $\text{Co}_{\text{pyr}}^{3+}$ .

Figure 4(a) displays our isotropic O- $K$  XAS measured on  $\text{GdBaCo}_2\text{O}_{5.5}$  (GBCO) at 78 K (black), 285 K (blue) and 400 K (red) at the Dragon Beamline (NSRRC). The spectral structures from 528 eV to 532 eV are due to transitions from the O  $1s$  core level to the O  $2p$  orbitals which are hybridized with the unoccupied Co  $3d$   $t_{2g}$  and  $e_g$  states.

In determining the spin-state configurations for GBCO at 78 K, we assume that the  $\text{Co}_{\text{pyr}}^{3+}$  ions are in the HS state like in  $\text{Sr}_2\text{CoO}_3\text{Cl}$  [43] and we first start by investigating the LS scenario for the  $\text{Co}_{\text{oct}}^{3+}$  ions as proposed in several studies [2,4]. To this end we summed the  $\text{Sr}_2\text{CoO}_3\text{Cl}$  (HS) and the  $\text{LaCoO}_3$  at 20 K (LS) spectra. The result is displayed in Figure 4(c) (green). One can clearly observe that this is very different from the GBCO spectrum in Figure 4(a). The LS  $\text{Co}_{\text{oct}}^{3+}$  scenario can thus be safely ruled out. Next we take the  $\text{LaCoO}_3$  at 650 K corresponding to 50% LS and

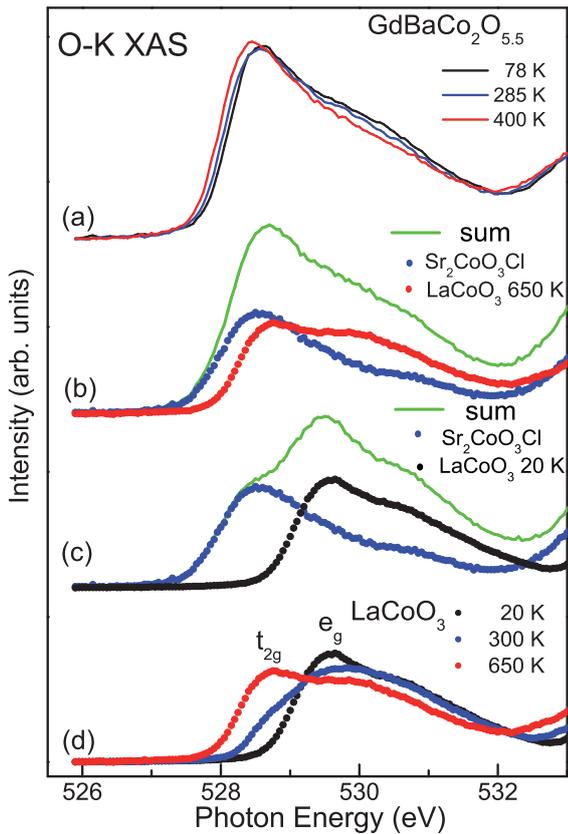


Fig. 4: The O-K XAS of GBCO taken at 78 K (black), 285 K (blue) and 400 K (red), superposition (green) of  $\text{Sr}_2\text{CoO}_3\text{Cl}$  (blue) and  $\text{LaCoO}_3$  at 650 K (red)(b) or at 20 K (black)(c), (d)  $\text{LaCoO}_3$  taken at 20 K (black), 300 K (blue) and 650 K (red).

50% HS for the  $\text{Co}_{\text{oct}}^{3+}$  part [44]. The superposition is shown in Figure 4(b) (green). Surprisingly, this superposition reproduces very well the GBCO spectrum at 78 K. This strongly suggests that GBCO in the low temperature phase has 50% of its  $\text{Co}_{\text{oct}}^{3+}$  ions in the LS state and 50% in the HS. All of its  $\text{Co}_{\text{pyr}}^{3+}$  ions are HS. Remarkable is also the very modest temperature dependence in the GBCO spectra, when compared to the canonical spin state transition in  $\text{LaCoO}_3$ , which leads to a significant spectral-weight transfer from 529.5 eV to 528.5 eV when going from 20 K to 650 K. This suggests that only a small part of the  $\text{Co}_{\text{oct}}$  ions participates in a spin state transition and disproves the claims of a massive spin-state transition across the MIT made in a large number of publications.

Recent diffraction data showed at  $T_{\text{MI}}$  the onset of a structural transition towards a checkerboard modulated structure with two inequivalent  $\text{Co}_{\text{oct}}^{3+}$  sites [45]. Our results showing a 50%-50% mixture of LS/HS  $\text{Co}_{\text{oct}}^{3+}$  ions provide direct evidence that this superstructure is caused by a LS/HS spin-state ordering of the  $\text{Co}^{3+}$  ions at the octahedral sublattice.

We now investigate the effect of the spin-state configurations on the band width and band gap of GBCO. Figure 5 shows the valence band PES measured at the synchrotron research facility ESRF in Grenoble at temperatures both below and above  $T_{\text{MI}}$ . Surprisingly and in contradiction with a previous report [46], the

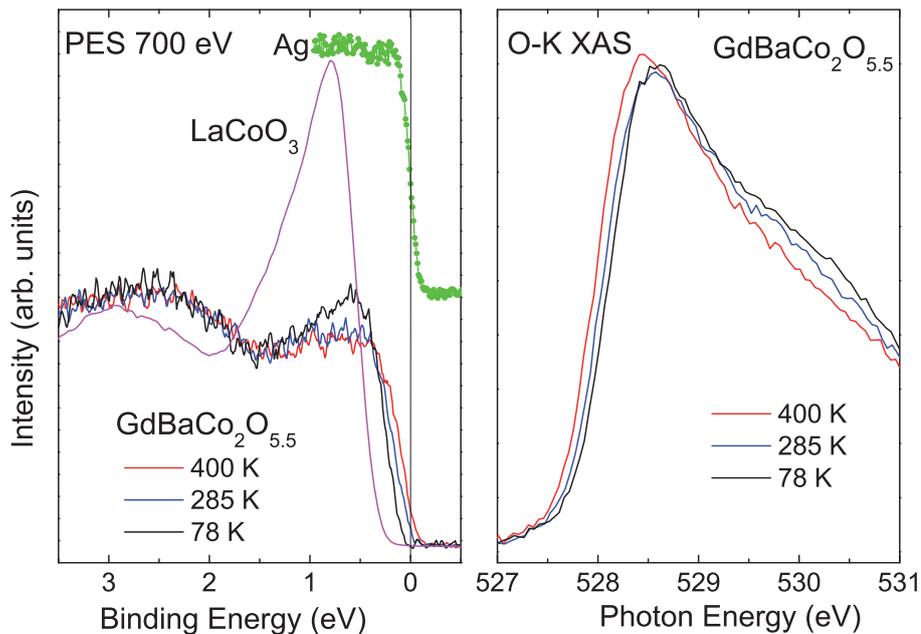


Fig. 5: The valence band PES (left) and O-K XAS (right) of GBCO taken at 78 K (black), 285 K (blue) and 400 K (red),  $\text{LaCoO}_3$  taken at 65 K (magenta), and Ag (green).

valence band PES of  $\text{GdBaCo}_2\text{O}_{5.5}$  reveals that the spectral weight at the Fermi level is negligible not only at 78 K (black) and 285 K (blue) but also at 400 K (red), so that we have to conclude that actually the material is an insulator or semiconductor even above  $T_{\text{MI}}$ . What we found is that the band gap is indeed reduced when the temperature is increased: the top of the valence band (Fig. 5 left panel) moves up by about 60 meV in going from 285 K to 400 K, while the bottom of the conduction band (Fig. 5 right panel) shifts downwards by 70 meV from 285 K to 400 K. So in total, the band gap is reduced by about 130 meV across  $T_{\text{MI}}$ . With the energy scale of the  $T_{\text{MI}}$  being about 30 meV, using the formula  $\rho \propto e^{E_g/k_B T_{\text{MI}}}$ , this gap narrowing well accounts for the observed reduction of resistivity by two orders of magnitude at  $T_{\text{MI}}$ . From Figure 5 one can see that there is no pronounced LS peak at 0.8 eV as found in the spectrum of  $\text{LaCoO}_3$  at 65 K, where the  $\text{Co}^{3+}$  ions are basically in LS state [44]. However, we see that the weak feature at 0.6 eV in GBCO corresponding to 50% LS  $\text{Co}^{3+}_{\text{oct}}$  ions loses spectral weight with increasing temperature.

The following picture now emerges from our electronic structure measurements concerning the MIT in this system. In the low temperature phase, a superstructure associated with the 50% LS – 50% HS spin-state ordering of the  $\text{Co}_{\text{oct}}^{3+}$  ions stabilizes the insulating state of the  $\text{GdBaCo}_2\text{O}_{5.5}$  system. Upon increasing the temperature across the  $T_{\text{MI}}$ , part of the LS  $\text{Co}_{\text{oct}}^{3+}$  ions undergoes a transition to the HS state, thereby destroying the superstructure as shown by X-ray diffraction [45]. This loss of order has the direct consequence that the band gap gets reduced. In converting a HS-LS (left-right) neighboring pair into an antiferromagnetic HS-HS pair by a rise in temperature, one can transfer an  $e_g$  electron both ways instead of only from left to right, thereby increasing the amount of charge fluctuations.

Yet, the band gap does not vanish since the hopping of an extra hole or electron is energetically quite costly in such an antiferromagnetic state. Conversely, the observation that the changes in the widths of the valence (PES) and conduction (O-K XAS) bands are very modest excludes an IS state scenario: the presence of IS  $\text{Co}_{\text{oct}}^{3+}$  ions would allow for a free propagation of an extra hole or electron in a ferromagnetically aligned  $e_g$  band.

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