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Spin-state transition in $Pr_{0.5}Ca_{0.5}CoO_3$ analyzed by x-ray absorption and emission spectroscopies

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We present a study of the Co spin-state changes in $Pr_{0.5}Ca_{0.5}CoO_3$ across the metal-insulator transition by means of the analysis of two complementary synchrotron x-ray spectroscopic techniques. Recorded experimental and charge transfer multiplet–based calculated Co $L_{2,3}$ absorption spectra, in combination with Co $K\beta$ main emission lines, indicate that Co^{3+} ion spin state evolves from low in the insulating phase to a low:high mixed state in the metallic regime, close to a 1:1 ratio at ambient temperature. A pure high spin state can be discarded, while the occurrence of an intermediate state is also questioned.

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I. INTRODUCTION

Spin-state (SS) transitions in oxides containing Co^{3+} ions are attracting great interest since they are associated with a variety of interesting phenomena, for example, drastic changes in the electrical conductivity and magnetotransport properties and a nonconventional magnetic behavior.[1–4] A reference example is widely investigated, $LaCoO_3$, which presents magnetic (∼50–100 K) and insulator-metal (∼500–550 K) transitions. The local symmetry of Co ions in $LaCoO_3$ is O_h, adopting a low spin (LS, ${t_{2g}}^6$ and $S = 0$) configuration in the ground state. A thermal promotion of valence band Co $3d$ electrons into e_g states lifts the initial LS configuration. However, an accurate description of the reached magnetic state is still an object of debate.[5–12] Whereas a set of experiments were considered indicative of an intermediate spin (IS, ${t_{2g}}^5{e_g}^1$ and $S = 1$) lowest excited state,[5–9] other results suggest a LS-high spin (HS, ${t_{2g}}^4{e_g}^2$ and $S = 2$) scenario for the low temperature transition.[10,11] The first possibility would permit the existence of Co^{3+} Jahn-Teller (JT) active ions, which could be a source of enhanced electron-phonon coupling due to correlations with mobile charges. The possible presence of these local distortions and small JT polarons has been addressed by theory and different experimental techniques.[7–9,12] In summary, whether the magnetic activated state is due to IS or HS configuration remains controversial for $LaCoO_3$, highlighting the need for more conclusive investigations.

The ordered perovskites $LnBaCo_2O_{5.50}$ (Ln: lanthanide) are another example of Co^{3+}-based cobaltites in which the SS seems to determine the conducting properties. In compounds with a large Ln ion radius, the occurrence of a sharp LS-HS transition in $Co^{3+}O_6$ octahedra by increasing temperature is commonly accepted as the origin of the insulator-metal transition.[3,4] In this case, $Co^{3+}O_6$ octahedra alternate with $Co^{3+}O_5$ pyramids, which are thought to remain in the IS state across the conductivity transition.

In half-doped $Pr_{0.5}Ca_{0.5}CoO_3$ the understanding of the Co ions SS is fundamental for a correct description of the remarkable metal-insulator transition (MIT) observed on cooling at $T_{MI} \sim 75$ K.[13] In this case the presence of two Co ions (formally Co^{3+} and Co^{4+} in 1:1 ratio) represents a further complexity. The MIT is characterized by a sudden jump in the resistivity and a simultaneous drop of the magnetic susceptibility below T_{MI}.[13] In contrast with the M-O bond and volume expansion observed in Mott oxides when entering the insulating phase, $Pr_{0.5}Ca_{0.5}CoO_3$ displays a large volume contraction.[14,15] This, in combination with the striking susceptibility drop, has been usually interpreted as the signature of a spin-crossover phenomenon. Accordingly, a sudden LS-IS or LS-HS transition in Co^{3+} ions was proposed as the origin of the metallic phase.[13,16,17] However, this scenario has recently been questioned following the discovery of changes in the oxidation state of praseodymium ions, from Pr^{3+} to Pr^{4+} on cooling across T_{MI}.[15,18–21] X-ray absorption spectroscopy (XAS) at the Pr $M_{4,5}$ and L_3 edges demonstrates the presence of a 85:15 admixture of localized $4f^2$ states (Pr^{3+}) and further oxidized Pr^{4+} atoms at 10 K.[21] The anomalous shortening of some Pr-O bondlengths accounts for the observed unit cell volume reduction and Co-O-Co bending, whereas the expected shrink of the $Co^{3+}O_6$ octahedra due to the stabilization of a lower Co SS has not been observed.[15] Diffraction studies describing the evolution of mean Co-O distances in CoO_6 octahedra below room temperature did not detect signs of coherent JT distortions (from JT active Co ions) at any side of the transition.[15,22]

In addition, $Pr_{0.5}Ca_{0.5}CoO_3$ is one of the first strongly correlated oxides able to offer a large and ultrafast photoresponse in the insulating state. As reported by Okimoto *et al.*, metallic domains can be induced by laser stimulation.[23] In order to understand the photoinduction of the MIT it is crucial to study the ground and excited electronic and SSs that can be switched by means of a light source. For instance, the susceptibility drop below T_{MI} may be simply attributed to changes in the magnetic moment of Pr due to the reported Pr^{3+}/Pr^{4+} valence transition instead of to a Co SS change.[20]

In this paper we investigate the electronic configuration and the nature of the SS of Co ions across the MIT in $Pr_{0.5}Ca_{0.5}CoO_3$ by Co $L_{2,3}$, Co K and O K edge XAS, and $1s3p$ nonresonant x-ray emission spectroscopy (XES). We conclude that a Co SS transition indeed takes place across the MIT, in addition to the Pr→Co charge transfer quantified in a recent work.[21] We discuss the different scenarios in the metallic phase that would be compatible with our x-ray spectroscopic experimental observations and calculations.

II. EXPERIMENTAL

$Pr_{0.5}Ca_{0.5}CoO_3$ samples were prepared by solid-state reaction in air. A high-pressure oxygen treatment after sintering permitted us to obtain the correct stoichiometry.[15] Details on the electric transport and magnetic behavior, and structural properties of $Pr_{0.5}Ca_{0.5}CoO_3$ samples used, can be found in Refs. 15,20, and 21. In Fig. 1 their resistivity (ρ) and magnetization (M) curves are shown as measured in cooling and heating processes. Simultaneous changes in ρ(T) and M(T) take place in the interval 50–90 K, the inflection point being ~70 K on cooling (75 K on heating). A weak hysteretic behavior can be appreciated in the resistivity, where the temperature shift is ~8 K. Soft x-ray absorption measurements across the Co $L_{2,3}$ and O K edges were performed at the PGM-3 beamline at the synchrotron radiation source of the Helmholtz-Zentrum in Berlin with a flux of $\sim 10^{10}$ photon/s and energy resolution of ~0.1 eV at 530 eV. X-ray $K\beta$ main emission lines and high-energy resolution fluorescence detection (HERFD) spectra at the Co K edge (recorded at the maximum of the $K\beta$ emission) were acquired at the ID26 beamline at the European Synchrotron Radiation Facility. The data collection interval was 0.3 and 0.1 eV, respectively. A Si (311) monochromator was used, and the overall resolution was 0.9 eV. The total flux (or per unit area) on the samples was $\sim 2 \times 10^{12}$ photon/s. Nonresonant XES was performed at 7800 eV incident energy. The emitted x-rays were analyzed using the Ge (444) Bragg reflection of four spherically bent (1 m radius) crystals arranged in a vertical Rowland geometry. A He-flow cryostat was also used. The integral of the spectral area between 7620 and 7730 eV was normalized to one in all recorded emission spectra. Charge transfer multiplet (CTM) calculations to simulate Co $L_{2,3}$ XAS spectra were performed with the CTM4XAS code.[24]

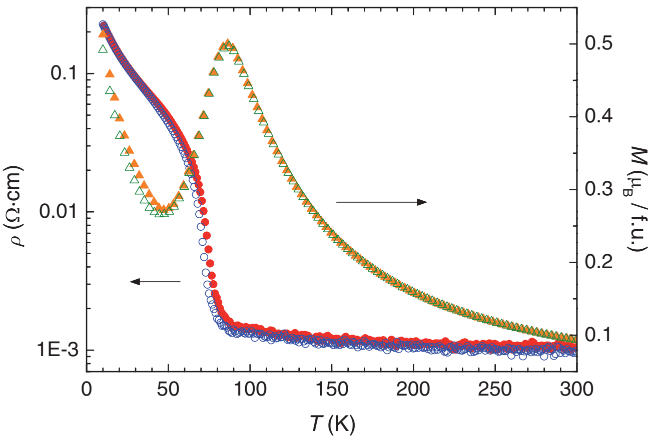

FIG. 1. (Color online) Electrical resistivity (circles) and magnetization under an applied field of 0.1 T (triangles) of $Pr_{0.5}Ca_{0.5}CoO_3$ as a function of temperature, for a cooling (empty symbols)–heating (filled symbols) cycle.

III. RESULTS AND DISCUSSION

In Fig. 2 we show the experimental Co $L_{2,3}$ absorption spectra of $Pr_{0.5}Ca_{0.5}CoO_3$ at 10 and 295 K and theoretical simulations we have performed based on the CTM theory. We have considered Co^{3+} and Co^{4+} ions in an octahedral local environment with different valence band electronic filling configurations (low, intermediate, or high SS) as they might appear in $Pr_{0.5}Ca_{0.5}CoO_3$. This is achieved by an adequate choice of the crystal field and charge transfer parameters.[25] The individual Co $L_{2,3}$ spectra thus resulting from each calculation are similar to others reported in literature.[11,26–28] In $Pr_{0.5}Ca_{0.5}CoO_3$ at 10 K, calculated Co density of states (DOS) confirms that $3de_g$ states lie above a bandgap responsible of the insulating character.[18] So, Co^{3+}, and Co^{4+} are expected to be in a LS state. At $T < T_{MI}$ a small charge transfer from Pr ions produces an unbalance of Co^{3+} and Co^{4+} ions (1:1 at $T > T_{MI}$).[18,20,22] The Co L_3 edge spectral evolution of $Pr_{0.5}Ca_{0.5}CoO_3$ across T_{MI} was initially ascribed solely to the electron donation by Pr atoms.[20] However, the differences observed between 10 and 295 K seem very large to be accounted for by the ~0.15 e^-/Pr atom estimated to be transferred to the Co sublattice by a recent theoretical analysis of Pr $M_{4,5}$ and L_3 absorption data.[21] After stoichiometry, this means an excess of ~0.08 Co^{3+} ions per formula unit at 10 K.

Hence, the 10 K experimental spectrum was simulated by the weighted addition of Co^{3+} LS and Co^{4+} LS calculations in a 58:42 ratio, the agreement being quite satisfactory, as seen in Fig. 2. If we assume that no SS change occurs across the MIT, the differences between the simulated 10 and 295 K spectra are much smaller than those found in the experiment. The occurrence of a SS transition in $Pr_{0.5}Ca_{0.5}CoO_3$ at T_{MI} concomitant with the changes in the electrical conductivity

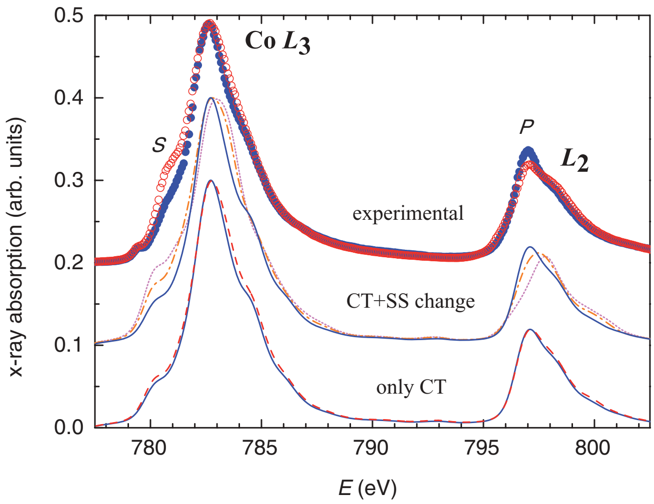

FIG. 2. (Color online) (Top) Experimental Co $L_{2,3}$ XAS spectra of $Pr_{0.5}Ca_{0.5}CoO_3$ at 10 K (filled circles) and 295 K (empty circles); (middle) weighted addition of CTM calculations depicting the spectral effects of the CT and the SS change at the MIT: 58:42 addition of Co^{3+} LS and Co^{4+} LS (solid line), 50:50 of Co^{3+} IS:Co^{4+} LS (dotted line), and 25:25:50 of Co^{3+} HS:Co^{3+} LS:Co^{4+} LS (dotted-dashed line); (bottom) 58:42 (solid line) as compared to 50:50 (dashed line) of Co^{3+} LS: Co^{4+} LS. Spectra are vertically shifted for clarity.

and the crystal structure has been long discussed.[16,29] The metallic behavior at high temperatures is associated with a partial occupation of Co $3de_g$ states. This is a consequence of the Co-O bandgap closure.[18] Modifications in the DOS and consequently in the symmetry of the electronic occupation can be ascribed to the structural changes taking place at the transition, such as the Co-O-Co angle variations and the volume reduction.

Concerning the spectroscopic discussion, a Co^{3+}:Co^{4+} picture (including crystal field and charge transfer effects providing a more realistic approach to a solid-state system) can be kept at $T > T_{MI}$ since the Co $L_{2,3}$ XAS process is faster ($\sim 10^{-15}$ s) than the characteristic time of the double exchange interaction, believed to be responsible of the electric conduction mechanism. Then, assuming a SS change of Co^{3+} ions across the MIT, the question arises whether the electronic configuration of Co^{3+} ions at $T > T_{MI}$ better fits a $3dt_{2g}{}^5\, e_g{}^1$ (HS) or $t_{2g}{}^4\, e_g{}^2$ (IS) single particle model. In both cases, a change in the SS of trivalent Co ions results in a release of empty t_{2g} symmetry orbitals where $2p$ electrons can jump in, two of the most evident fingerprints in the Co^{3+} $L_{2,3}$ XAS spectrum being (i) a contribution in the low energy side of the main structure at the L_3 edge (S), and (ii) a shift to higher energies (by ∼1–2 eV) and a reduction of the main structure at the L_2 edge (P), as can be seen in Fig. 2.

In the middle part of Fig. 2 we show the simulation resulting after a full transformation of Co^{3+} LS into IS, and that considering a mixed state composed of half Co^{3+} LS and Co^{3+} HS ions, in a similar manner as argued for $LaCoO_3$ by Haverkort *et al.*[11] A comparison to the simulation for the insulating state at 10 K reveals that in both cases we see an enhancement of the S feature just below the Co L_3 edge at ∼780.5 eV. Also, the L_3 edge main structure gets wider. These changes show a good agreement with experimental observations. At the L_2 edge the comparison becomes more qualitative, but we can nevertheless affirm that the mixed Co^{3+} LS/HS configuration yields a better agreement to the 295 K experimental spectrum. Indeed, looking at the experimental spectra we see that the peak ∼797 eV, which is typical of Co^{3+} LS, does not completely disappear at room temperature. Our theoretical analysis thus demonstrates that the effect on the Co $L_{2,3}$ absorption spectrum of a spin state transition is much greater than that of the Pr→Co CT across the MIT. This has two direct implications. First, the Co L_3 absorption spectrum cannot be taken as a good indicator to estimate the magnitude of the Pr-Co charge transfer mechanism in $Pr_{0.5}Ca_{0.5}CoO_3$.[21] Second, the large change observed in these spectra across the MIT requires a SS transition to be considered. The existence of changes in the symmetry of the electronic filling in the valence band, most likely associated to Co^{3+} ions, would help to explain the Co $L_{2,3}$ XAS thermal evolution.

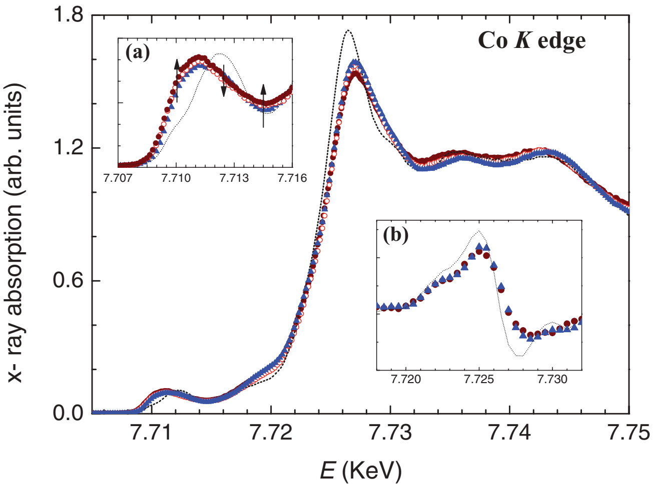

FIG. 3. (Color online) HERFD spectra at the Co K absorption edge of $Pr_{0.5}Ca_{0.5}CoO_3$ at 10 K (blue triangles), 100 K (red empty circles), and 295 K (red filled circles), and $PrCoO_3$ (Co^{3+}) at 10 K (dotted line). Insets: (a) zoom of the pre-edge region sensitive to Co $3d$ empty orbitals via quadrupole or nonlocal dipole allowed transitions; (b) reduced region of the first derivative spectra at the main edge showing minimal changes in the average oxidation state of cobalt ions in $Pr_{0.5}Ca_{0.5}CoO_3$ between 10 and 295 K after comparison to reference $PrCoO_3$.

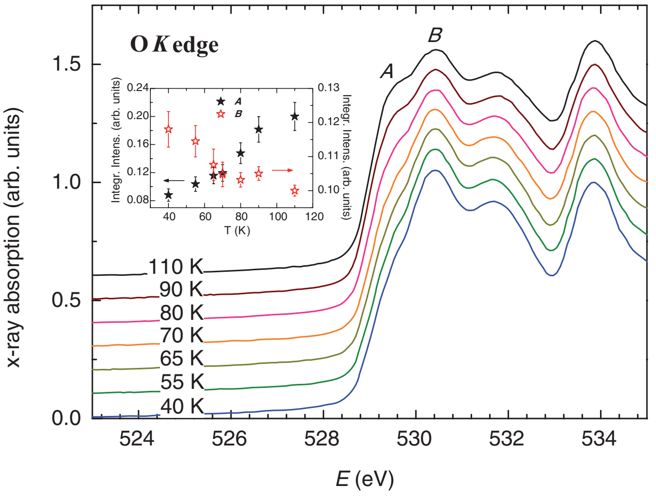

FIG. 4. (Color online) Experimental O K pre-edge absorption in $Pr_{0.5}Ca_{0.5}CoO_3$ at different temperatures around T_{MI}. The inset shows the T evolution of the A (filled stars) and B (empty stars) features intensity: B was fitted to a single Gaussian peak, then the background subtracted by a straight line between 529.9 and 531.2 eV. The A intensity was calculated as the difference between the experimental curve and the Gaussian fit of B in the energy range between 528.5 and 529.9 eV. Spectra have been vertically shifted to facilitate their comparison.

A further proof of the small variation of the average oxidation state of Co ions in $Pr_{0.5}Ca_{0.5}CoO_3$ with temperature is provided in Fig. 3. The HERFD Co K edge spectra of $Pr_{0.5}Ca_{0.5}CoO_3$ at 10 and 295 K show minimal changes at the first momentum position ($E \sim 7725$ eV) [Fig. 3(b), inset]. Moreover, the bare spectral differences of the white line (at ∼7727 eV) width between low and high temperature also justify the treatment of the metallic phase in terms of two ionic Co species. The SS changes can also be studied looking at the Co K [Fig. 3(a), inset] and O K pre-edge structures, as shown in Fig. 4. In Fig. 3 the prepeak region between approximately 7708 and 7715 eV mainly reflects the density of empty Co $3d$ orbitals via hybridization with oxygen atoms. After the comparison to the low temperature spectrum of $PrCoO_3$ (Co^{3+} LS), we can conclude that the lowest unoccupied states in $Pr_{0.5}Ca_{0.5}CoO_3$ at 10 K correspond to Co^{4+}, with t_{2g} symmetry. The $Pr_{0.5}Ca_{0.5}CoO_3$ spectrum at room temperature reflects an increase of the spectral weight in the low energy side of the broad prepeak structure, which can be due to the partial release of Co^{3+} t_{2g} orbitals. At the same time there is a small reduction of the absorption cross section at ∼7712 eV and an enhancement at 7714.5 eV. Both of them could be related to a partial conversion of Co^{3+} LS into IS or HS.[30] The observations at the O K pre-edge allow us to extract similar conclusions. In Fig. 4 the effect of increasing temperature across the MIT is mainly reflected on a spectral transfer from B- to A-labeled features (see inset), just above the Fermi energy, which may also be correlated to the appearance of a t_{2g} symmetry density of empty states due to an electron transfer to e_g orbitals in trivalent Co ions.[31,32] Nevertheless, and likewise at the Co K pre-edge, this analysis shall remain qualitative since the presence of a comparable quantity of Co^{4+} and an intraatomic d-d electronic exchange energy similar to the octahedral crystal field effect in $Pr_{0.5}Ca_{0.5}CoO_3$ hinders a more detailed interpretation.

In order to confirm the hypothesis of Co^{3+} SS changes at the MIT we have performed Co K-shell nonresonant XES measurements. This technique allows us to indirectly probe the 3d valence levels by the (3p, 3d) exchange interaction. In more detail, in the one electron picture the XES process can be viewed as a second order excitation–deexcitation–optical process. The incoming photon creates a hole in the 1s level that recombines with a 3p electron, and the associated emitted photon reflects the exchange interaction of the secondary hole in the 3p orbitals with the electrons in the 3d band.[34,35] This leads to the splitting of $K\beta$ main line emission into a sharp $K\beta_{1,3}$ and a broad $K\beta'$ feature. The intra-atomic origin of the strongest interactions in the $K\beta$ main lines is well established by comparison between spectra obtained on free metal atoms and solid-state systems.[36]

In Fig. 5 we show the Co $K\beta$ main lines of $Pr_{0.5}Ca_{0.5}CoO_3$ at 10, 100, and 295 K, compared to $PrCoO_3$ also measured at 10 K, with no unpaired spins (or a negligible fraction) expected in the Co 3d shell ($t_{2g}{}^6\, e_g{}^0$, $S = 0$). In $Pr_{0.5}Ca_{0.5}CoO_3$ we observe a clear thermal evolution, larger between 10 and 100 K than between 100 and 295 K. This mainly responds to the SS transition at T_{MI}. In addition, we have also plotted the spectrum of $LaMn_{0.98}Co_{0.02}O_3$ containing only Co^{2+} in a HS state ($t_{2g}{}^5 e_g{}^2$, $S = 3/2$), as reproduced from Ref. 33. In $LaMn_{0.98}Co_{0.02}O_3$ $K\beta$ main emission we see a noticeable transfer of spectral weight from the $K\beta_{1,3}$ to the $K\beta'$ lines and a larger splitting in the energy scale between them due to the presence of more half-occupied Co 3d levels than in $PrCoO_3$ and $Pr_{0.5}Ca_{0.5}CoO_3$. Qualitatively speaking, while the $Pr_{0.5}Ca_{0.5}CoO_3$ spectrum at 10 K ($S = 1/4$) resembles $PrCoO_3$, the intensity and position of the $K\beta_{1,3}$ and $K\beta'$ lines in the $Pr_{0.5}Ca_{0.5}CoO_3$ spectrum at 295 K turn out to be kind of intermediate between the latter and $LaMn_{0.98}Co_{0.02}O_3$. At this point, the integral of the absolute values of the difference spectra (IAD) appears as a robust quantitative indicator of the thermal evolution of the SS.[30,33,37–39]

Within this differential method between a compound matter of study and a reference with a known oxidation and SS, a direct relation (approximately linear, provided a similar local structure around the photoabsorbing ion in both compounds) relates the difference in the number of unpaired spins per photoabsorbing ion (ΔS) in the valence band with the IAD values, crossing the origin of the plot ($\Delta S = \mathrm{IAD} = 0$). We have tested the IS and the HS state models for Co^{3+} ions at 295 K. The vertical axis coordinate in data points in Fig. 6 corresponds to the integral of the absolute difference between two measured $K\beta$ main lines emission spectra. Meanwhile, the x axis coordinate gives the expected ΔS value depending on the SS model assumed. We observe that the IS model nicely fits the experimental data. We have included the CT effect across the MIT, but this contribution barely produces any substantial modification, as in Co $L_{2,3}$ XAS. In this case, and assuming

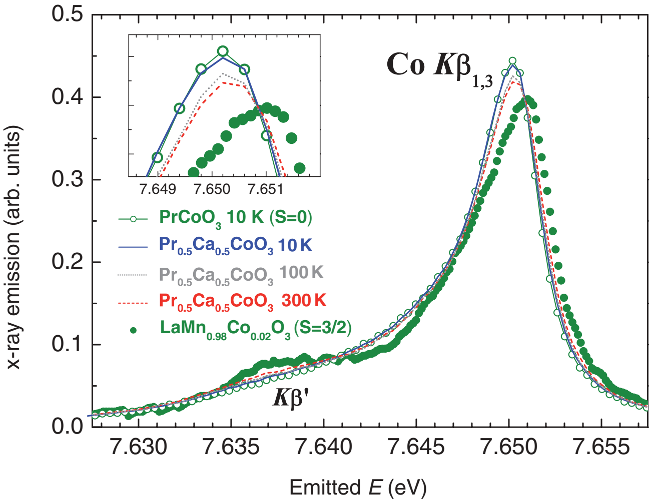

FIG. 5. (Color online) Co $K\beta$ emission spectra of $Pr_{0.5}Ca_{0.5}CoO_3$ at 10 ($T < T_{MI}$) and 100 and 295 K ($T > T_{MI}$), as compared to $PrCoO_3$ and $LaMn_{0.98}Co_{0.02}O_3$ (Ref. 33) references.

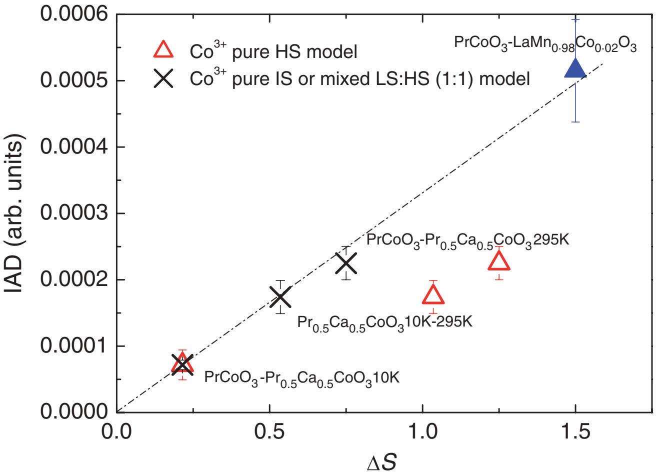

FIG. 6. (Color online) IAD analysis of Co $K\beta$ main emission lines under three hypotheses for the SS of Co^{3+} ions in $Pr_{0.5}Ca_{0.5}CoO_3$ at 295 K: (i) pure IS or (ii) mixed LS:HS in a 1:1 ratio (crosses), which would produce the same IAD data points, and (iii) pure HS (empty triangles). We see that either the first or the second model fit the expected linear dependence (dashed line). For $LaMn_{0.98}Co_{0.02}O_3$ we assume the Co^{2+} are in HS state (filled triangle). The dotted-dashed line is an eye guide.

that Co^{4+} remains in the LS state in the studied thermal range, $S = 0.5 \times 1 + 0.5 \times (1/2) = 3/4$ for $Pr_{0.5}Ca_{0.5}CoO_3$ at 300 K. At 10 K we find instead $S = 0 + 0.42 \times (1/2) = 0.21$. In contrast, following Fig. 6, a full conversion of Co^{3+} ions into a HS state should be completely discarded. However, we also see that a mixed LS:HS model for trivalent Co ions in a 1:1 ratio would yield an indistinguishable result with respect to a pure IS state following the IAD method and therefore shall be considered. Regarding the possibility of a mixed SS, multiplet calculations show that thermal excitation effects expressed via a Boltzmann distribution may also drive the partial occupation of Co^{3+} $3de_g$ states across the MIT. For this to occur, the crystal field value used in the calculations yielding a LS ground state needs to produce an electronic states energy distribution where first excited unoccupied levels are found at energies of the order of K_BT beyond the Fermi level (at T_{MI}). For comparison, values ∼20–30 meV have been theoretically found for $LaCoO_3$.[11] We have checked that the spectral effect is equivalent to that of a mixed LS/IS configuration neglecting thermal excitation effects. This is so because in the code employed, the succession of SSs (by increasing the crystal field energy) is high–intermediate–low by default, although real solid-state systems do not necessarily obey this rule.[11,40,41] A thermal population of excited configurations should behave monotonically with T. Then, in $Pr_{0.5}Ca_{0.5}CoO_3$, sharp XAS and XES spectral variations observed across the MIT could be explained by the concomitant structural changes, enough to induce little modifications in the electronic states distribution allowing a rapid variation of the population of excited configurations. In any case, it is convenient to note that a mixed SS is a quantum-chemical single state (e.g., in $Pr_{0.5}Ca_{0.5}CoO_3$ at $T > T_{MI}$ the SS would be neither low nor high) and not a thermal population of excited configurations. At the moment, in view of our x-ray spectroscopic results, we cannot conclude which of these two possibilities should be taken as the most likely one.

IV. CONCLUSIONS

Very recently XAS measurements at the Pr L_3 and $M_{4,5}$ edges[20,21] confirmed the specific heat[19] and neutron indications[15] of abrupt changes in the valence of praseodymium as a consequence of an electron transfer to cobalt sites at T_{MI} thus entering the insulating state. This exotic intersite Pr-Co charge migration, shown to spontaneously occur in $Pr_{0.5}Ca_{0.5}CoO_3$, is a key ingredient for the MIT in this compound with a simple perovskite structure. However, the evidence of changes in the electronic density around the Pr and Co atoms needed to be complemented with specific investigations of the changes in the Co spin density. This was the aim of the present work, which focused on the fingerprints of the charge localized and metallic phases of $Pr_{0.5}Ca_{0.5}CoO_3$ on the x-ray absorption and emission spectra from cobalt atoms.

The Pr→Co electronic charge transferred (∼0.08 e^- per Co atom after Ref. 21) is rather small and suggests that the charge migration due to a strong Pr $4f$-O $2p$ interaction is only one of the ingredients at play, but alone it cannot account for the unconventional electronic properties of the system. Hence, we have here presented x-ray spectroscopic experimental and theoretical results that evidence the importance of another basic component of its puzzling behavior, namely the spin-crossover phenomenon.

We have shown that despite the spectroscopic effects of a charge transfer and a LS-IS or LS-HS state changes may be similar, a separate analysis of both phenomena is feasible. The comparison of experimental and CTM-based calculated Co $L_{2,3}$ x-ray absorption spectra of $Pr_{0.5}Ca_{0.5}CoO_3$ in the metallic and insulating states indicates that a SS transition is concomitant with the charge migration. The analysis of Co $K\beta_{1,3}$ emission lines confirms this conclusion. While XAS and XES results neither prove nor disprove that the Co^{3+} HS is the lowest energy excited state, an inhomogeneous mixed LS:HS state model for trivalent Co ions seems to work somewhat better than a pure intermediate state consisting of JT active ions for the metallic phase. The largest evolution in $K\beta$ main emission lines takes place at $T \sim T_{MI}$, although little spectral changes are further seen up to 295 K, which supports the model of a mixed SS in a variable ratio, determined not only by the MIT but also by temperature. The IS state in the metallic phase cannot be categorically ruled out according to x-ray emission results, but these allow us to discard the presence of a pure HS state of Co^{3+} ions at room temperature. Also, presented Co and O K edge spectra support our interpretations, particularly regarding the reduced Co formal valence change at the MIT.

The confirmation and the details of the spin-crossover phenomenon in $Pr_{0.5}Ca_{0.5}CoO_3$ are of particular relevance for our understanding of the exceptional photoresponse capabilities recently reported in this oxide.[23] Thus, the correlation of the MIT with the SS changes here shown would be responsible for the generation of metallic domains in the sample after photoirradiation in the nonconducting state (below T_{MI}). A comparative study with better known photoinduced transitions and spin dynamics in spin-crossover organometallic complexes containing transition metals would be very convenient.

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