Spin-lattice interaction in the insulator-to-metal transition of $\text{GdBaCo}_2\text{O}_{5+\delta}$

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We use electron paramagnetic resonance spectroscopy (EPR) and synchrotron radiation x-ray powder diffraction to study the temperature-induced insulator-to-metal transition (IMT) for $\text{GdBaCo}_2\text{O}_{5+\delta}$ samples in the δ range $0.54(1) \leq \delta \leq 0.63(1)$. The EPR linewidth markedly changes across IMT and its temperature evolution can be explained considering spin state transition involving Co ions. The temperature dependences of the EPR linewidth and of the a lattice parameter fairly overlap each other suggesting spin-lattice interaction along the same crystallographic direction of the reported Ising-like spin anisotropy [A. A. Taskin *et al.*, *Phys. Rev. Lett.* **90**, 227201 (2003)]. A possible mechanism describing the interplay between this strong spin-lattice interaction and IMT is proposed.

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I. INTRODUCTION

$\text{LnBaCo}_2\text{O}_{5+\delta}$ layered cobalt oxides (Ln is a rare earth element) exhibit very rich electronic and magnetic phase diagrams that involve many fascinating phenomena such as the magnetoresistance (MR) effect.^{1–3} The crystal structure of $\text{LnBaCo}_2\text{O}_{5+\delta}$ can be viewed as a sequence of square-lattice layers $[\text{CoO}_2][\text{BaO}][\text{CoO}_2][\text{LnO}_\delta]$ stacking along the c axis with alternation of two types of coordination environments for cobalt ions, i.e., CoO_5 pyramid (Co_{pyr}) and CoO_6 octahedra (Co_{oct}). The $\text{Co}_{\text{pyr}}/\text{Co}_{\text{oct}}$ ratio as well as their ordering along crystallographic directions can be modified by tuning the oxygen concentration δ in LnO_δ planes.² More importantly, δ affects the mean valence state of cobalt ions as Co^{3+} can exist in low-, intermediate-, or high-spin states (LS, IS, or HS) while Co^{2+} and Co^{4+} are stable in HS and LS configurations, respectively.² Then, the physics of these systems is driven by a complex interplay between charge, spin, orbital, and lattice degrees of freedom triggered, e.g., by temperature.

Such behavior is clearly demonstrated by the temperature-induced insulator-to-metal transition (IMT) found at $T_{\text{IM}} \approx 365$ K with $\text{GdBaCo}_2\text{O}_{5+\delta}$ when $\delta \approx 0.5$.^{1–5} However, despite a number of experimental and theoretical studies in layered cobaltites, great controversy has arisen regarding the Co spin state and the microscopic origin of IMT. In the year 2000, Moritomo *et al.*⁶ suggested that the IMT is induced by a spin-state transition (SST) from an orbital-ordered (OO) IS state to the HS state in both Co_{pyr} and Co_{oct} sites, basing their consideration on neutron powder diffraction of $\text{TbBaCo}_2\text{O}_{5.5}$. Later, a synchrotron radiation x-ray powder diffraction (XRPD) study of $\text{GdBaCo}_2\text{O}_{5.5}$ ruled out any OO, suggesting that the IMT should be related to a spin-state switch from LS to HS states at Co_{oct} . Conversely, the Co_{pyr} should remain in IS state at both sides of the IMT.⁴ This is consistent with *ab initio* calculations that verified the stability of pyramidal IS states in $\text{LnBaCo}_2\text{O}_{5.5}$ systems.⁷ Maignan *et al.*⁸ explained the interplay between IMT and SST using a model based on conversion of HS to LS state in Co_{oct} at $T < T_{\text{IM}}$ which would immobilize the electron charge carriers through a “spin blockade” mechanism between HSCo^{2+} and

LSCo^{3+} . In strong contrast with SST, a muon-spin relaxation study on $\text{LnBaCo}_2\text{O}_{5+\delta}$ $\delta \approx 0.5$ suggested that the HS state of Co^{3+} is retained at $T < 300$ K.⁹ Recently thermal expansion measurements on $\text{GdBaCo}_2\text{O}_{5.5}$ confirmed the SST as the driving force for IMT excluding the occurrence of stepwise SST at lower temperatures.⁵ Another model based on density functional theory calculations¹⁰ and supported by photoemission¹¹ and isotope-effect neutron diffraction data¹² suggested that the IMT is due to hole delocalization in the Co^{3+} HS state rather than to SST.^{10,12}

In this paper we present a EPR study on $\text{GdBaCo}_2\text{O}_{5+\delta}$ combined with synchrotron XRPD as a function of δ and of the temperature across the IM transition. EPR spectroscopy allows direct access to the spin-environment interactions through the investigation of the spin relaxation behavior.¹³ The EPR signal markedly changes with increasing temperature for $\delta = 0.54(1)$ and $\delta = 0.57(1)$ samples, indicating that the spin exchange frequency increases above T_{IM} in both cases. By comparing EPR and XRPD T -dependent experimental results we clearly demonstrate that the interplay between Co spin state and crystal lattice plays a central role in the IM mechanism of this layered cobaltite.

II. EXPERIMENTAL PROCEDURES AND RESULTS

$\text{GdBaCo}_2\text{O}_{5+\delta}$ was synthesized by a conventional solid-state reaction technique¹⁴ and the desired oxygen content was adjusted on three aliquots according to annealing conditions and thermal treatments reported by Taskin *et al.*² The oxygen content was determined by the procedure described in Ref. 15; $\delta = 0.54(1)$, $\delta = 0.57(1)$, and $\delta = 0.63(1)$ were found for the three prepared samples.

XRPD patterns were collected at the ID31 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble. For each sample, 40 diffraction patterns were collected in the $0 < 2\theta < 20^\circ$ range from 300 to 400 K selecting a wavelength of $\lambda = 0.39620(5)$ Å. Moreover, some high-quality diffraction patterns were collected at $\lambda = 0.35422(1)$ Å for a total counting time of 1 h at selected T between 300 and

FIG. 1. (a), (b) Selected region of XRPD patterns as collected at different temperatures for the $\delta = 0.54(1)$ and $\delta = 0.57(1)$ samples, respectively. The black dots are the experimental data while the continuous lines are the results from Rietveld refinements. The Miller indexes of the diffraction peaks are also reported. Typical agreement factor $R(F^2)$ between observed and calculated XRPD patterns range from 0.06 to 0.08.

400 K depending on sample composition. Data were analyzed using the Rietveld method as implemented in GSAS software suite.¹⁶ All the data sets have been refined against the $Pmmm$ model derived from the cubic perovskite by doubling along the b and c axes ($a_c \times 2a_c \times 2a_c$ unit cell, where a_c stands for the cell parameter of the cubic perovskite lattice).⁴ To account for the actual δ values in structural models, we located the extra oxygen ions (with respect to $\delta = 0.5$) at the $1c$ $(0,0,1/2)$ position considering the $1g$ $(0,1/2,1/2)$ fully occupied. This is equivalent to considering an ordered alternation of Co_{pyr} and Co_{oct} along the $[010]$ direction for $\delta = 0.5$.^{1,4,6,17} The Rietveld refinements in selected portions of the diffraction patterns collected at various temperatures for $\delta = 0.54(1)$ and $\delta = 0.57(1)$ samples are shown in Fig. 1. Refined lattice parameters are shown for all the samples in Fig. 2.

The presence of splitting in the diffraction profile of (040), (020), and (002) peaks is evident for $\delta = 0.54(1)$ and $\delta = 0.57(1)$ in a narrow T range (~ 7 – 8 K) below $T_{\text{IM}} \approx 365$ K^{1–5} as shown in Fig. 1. This phase transition in the proximity of IMT is well known to occur in $\text{LnBaCo}_2\text{O}_{5.5}$ ^{4,6,12,18} and the presence of peak splitting in the XRPD patterns is related to coexistence of the low- and high- T structural phases. The latter finding provides evidence for the first order of the transition.¹⁸ As shown in Fig. 2, with increasing T toward IMT, both the b and c lattice parameters exhibit a steplike increase while a suddenly shrinks for both $\delta = 0.54(1)$ and $\delta = 0.57(1)$ samples. No phase coexistence was evidenced by the XRPD patterns of the $\delta = 0.63(1)$ sample, since b and c linearly increase in $300 \leq T \leq 400$ K range and a decreases up to $T \sim 325$ K. The anisotropic thermal expansion of the unit cell parameters results in a variation of the unit cell volume. By comparing unit cell volume values as a function of T and δ reported in the insets of Fig. 2, we note that the discontinuity which holds for first-order transition is apparent only for $\delta = 0.54(1)$. This provides an indication that the order of the structural phase

FIG. 2. (a)–(c) Lattice parameters a (filled squares), $b/2$ (empty circles), and $c/2$ (filled circles) as a function of temperature are displayed for $\delta = 0.54(1)$, $0.57(1)$, and $0.63(1)$, respectively. Insets: the temperature dependence of the unit cell volume for selected temperature range.

transition may change from the first to second order upon increasing δ .

EPR measurements were performed on a Bruker ELEXSYS spectrometer equipped with an ER4102ST standard rectangular cavity at X band (9.4 GHz) frequency in the temperature range 305–450 K every 5 K. Powdered samples were placed into quartz tubes and the derivative dP/dH of power P absorbed was recorded as a function of the static magnetic field H .

In Fig. 3 we show EPR spectra as a function of temperature for $\delta = 0.54(1)$ sample, as an example. The signal consists of a single broad resonance line. It is well known that the Co^{3+} EPR signal cannot be observed because of a too-short relaxation time¹⁹ so that the EPR signals in $\text{GdBaCo}_2\text{O}_{5+\delta}$ can be originated from the shift and/or broadening of the Gd^{3+} resonance caused by exchange interaction $J_{fs}S \cdot s$ between localized $4f$ electron spin (S) and the spins (s) of the transition metal.¹³

At each T , the spectra were well fitted by a single Dysonian lineshape²⁰ shown as a solid line in the inset of Fig. 3. However, meaningless negative dispersion-to-absorption α contributions were evaluated in these EPR features. By comparing our spectra with the Dysonian line reported in the literature for other perovskitic systems,²¹ we found that the EPR features measured by us correspond only to a part of the literature-reported line.²¹ In particular, the left lobe of the EPR spectrum shown in the inset of Fig. 3 is too broad to be fully observable. This leads to unreliable numerical values of the x_0 (peak position), α , or w (linewidth) parameters. Another possible reason could be the presence of multiple

FIG. 3. (Color online) EPR spectra of the $\delta = 0.54(1)$ sample as a function of temperature. The arrow outlines their trend with increasing temperature and in particular at the critical temperature $T_c \approx 365$ K. In the inset an example of fit using a Dysonian line shape is shown (open circles: observed data; solid line: fit).

signals as reported for other Co-based oxides.²² However, attempts by linear combinations of Lorentzian and Gaussian functions gave no improvement to the lineshape description. We decided to extract the peak-to-peak linewidth (ΔH_{pp}) by direct observation of the experimental patterns as indicated in the inset of Fig. 3. The trend of ΔH_{pp} with temperature is shown in Figs. 4(a)–4(c) for all the samples. It should be noted that in our spectra the base line is not well defined and, hence, we cannot determine directly the peak position.

ΔH_{pp} shows three different temperature-dependent regions for $\delta = 0.54(1)$ and $\delta = 0.57(1)$: (i) It is roughly constant or decreases smoothly between 300 and 330 K; (ii) it decreases steeply with increasing T toward a critical temperature T_c for $\sim 330 < T < \sim 360$ K; (iii) it exhibits a distinct kink at $T_c = 360 \pm 5$ K, then approaches constant values up to $T = 450$ K. The behavior of ΔH_{pp} is rather different for the $\delta = 0.63(1)$ sample, showing a smaller ΔH_{pp} value at $T = 300$ K with just a weak decrease at $T_c \sim 325$ K. All the samples display a similar ΔH_{pp} value at $T > T_c$. In Fig. 4(d) we compare the T_c with the T_{IM} values determined by Taskin *et al.* for $\delta = 0.50$ and $\delta = 0.65$ from resistivity measurements.² The good agreement between the two critical temperatures as a function of δ indicates that the EPR linewidth change at T_c is consistent with the IM transition. $T_c = T_{IM}$ will be considered hereinafter.

III. DISCUSSION AND CONCLUSION

According to magnetization measurements performed by Respaud *et al.*¹⁷ on a $\text{GdBaCo}_2\text{O}_{5.54(3)}$ sample, a drastic change in the Weiss-Curie temperature Θ_{WC} and effective cobalt magnetic moment was observed above T_{IM} . In order to estimate the strength of the magnetic interactions involved, we calculated the value of the isotropic exchange constants (J)

FIG. 4. (a)–(c) ΔH_{pp} against temperature for $\delta = 0.54(1)$, $\delta = 0.57(1)$, and $\delta = 0.63(1)$, respectively. (d) The T_c (filled circles) highlighted in panels (a)–(c) are compared with T_{IM} reported by Taskin *et al.* (Ref. 2) (open squares).

using the molecular field theory for three-dimensional (3D) systems. To compute J from the molecular field equation,²³ we assumed the model proposed by Taskin *et al.*^{1,2} in which the magnetic interactions are generated by IS- Co^{3+} and we used the modulus of the values of Θ_{WC} reported below and above the IMT.¹⁷ By considering $S = 1$ for IS- Co^{3+} and $Z = 3$, i.e., by counting only for nearest neighbors, we estimated $|J_{ins}|/k_B \approx 69$ K and $|J_{met}|/k_B \approx 150$ K in the insulating and metallic phases, respectively. This corresponds to a ratio of $|J_{met}|/|J_{ins}| \sim 2$ indicating that the isotropic exchange interactions between cobalt ions increase above T_{IM} .

In the case of strong isotropic exchange interactions the Gaussian EPR linewidth is narrowed into a Lorentzian line with ΔH_{pp} given by^{23–25}

$$\Delta H_{pp} = \frac{\hbar M_2}{g\mu_B\omega_{ex}}, \quad (1)$$

where $\omega_{ex} \approx J/\hbar$ is the frequency of the isotropic exchange interactions caused by the Heisenberg Hamiltonian $H_{ex}^{ij} (=J s_i \cdot s_j)$ between neighboring spins s_i and s_j . It should be

noted that, in the case of an asymptotic regime as observed at $T \rightarrow 300$ K and at $T \rightarrow T_{IM}$ for $\delta = 0.54(1)$ and $\delta = 0.57(1)$ samples, both the second moment M_2 and the exchange frequency ω_{ex} are temperature independent. Basically, Eq. (1) can be employed to explain that the ΔH_{pp} asymptotic value at $T > T_{IM}$ in the metallic phase is smaller than that reached at $T \rightarrow 300$ K in the insulating phase. According to the equation, above T_{IM} the decreasing of ΔH_{pp} can be justified by an increase of the frequency of the isotropic exchange interactions ω_{ex} and/or by a decrease in the second moment M_2 . As a matter of fact, M_2 parameter depends on anisotropic exchange interactions and can be determined by measuring the angular dependence of EPR linewidth or g factor as a function of several orientations of a single crystal sample in the external magnetic field.²⁶ As we deal with powdered samples, we cannot resolve the anisotropy of the EPR spectra and, hence, we cannot say anything about the influence of such parameter to explain the strong narrowing. On the other hand, from $\omega_{ex} \approx J/\hbar$ we can scale the J ratio accordingly and deduce that $\omega_{ex}^{met} > \omega_{ex}^{ins}$. Thus, the observed temperature decreasing of the ΔH_{pp} above T_{IM} is compatible with an enhancement of the isotropic exchange frequency term in the metallic phase.

According to the model proposed by Maignan *et al.*,⁸ the increase of spin-spin exchange frequency observed at $T > T_{IM}$ in $\delta = 0.54(1)$ and $\delta = 0.57(1)$ samples can be easily understood as an increasing of hopping probability of $3d$ electrons between nearest-neighbor Co ions. The metallic state is interpreted as the motion of an extra electron from an excited $HSCo^{2+}$ ion to a HS or to an $ISCo^{3+}$ ion.⁸ However, this model does not explain how Co^{2+} ions are created and does not consider that a motion of one e_g electron from $HSCo^{3+}$ to $ISCo^{3+}$ would generate an unstable non- $LSCo^{4+}$. To avoid the production of such cobalt species, we suppose that the Co_{oct}^{3+} sites in the metallic phase of an ideal $\delta = 0.5$ sample display the IS state together with a T -independent $ISCo_{pyr}^{3+}$.⁴ It should be noted that an e_g electron hopping from an $ISCo_{oct}^{3+}$ to the next $ISCo_{oct}^{3+}$ along the a and c axes and/or to the next $ISCo_{pyr}^{3+}$ along the b axis generates, in any case, a couple of $LSCo^{4+}$ and $HSCo^{2+}$ stable species. For example, the electron transfer along the b axis from Co_{pyr} to Co_{oct} and vice versa can be sketched as $t_{2g}^5 e_g^1 - ISCo_{pyr}^{3+} + t_{2g}^5 e_g^1 - ISCo_{oct}^{3+} \rightarrow t_{2g}^5 e_g^0 - LSCo_{pyr}^{4+} + t_{2g}^5 e_g^2 - HSCo_{oct}^{2+}$ (Fig. 5). This process justifies high ω_{ex} above T_{IM} since the presence of $LSCo_{pyr}^{4+}$ and $HSCo_{oct}^{2+}$ implies double exchange (DE) interaction between $LSCo_{pyr}^{4+}$ and $HSCo_{oct}^{2+}$ and $ISCo_{oct/pyr}^{3+}$ ions occurring along the b axis. At the same time, the formation of e_g conduction band of IS character gives rise to the observed metallic ground state since DE paths formed by the 3D network of $ISCo_{oct/pyr}^{3+}$ account for electronic delocalization in all directions. Upon cooling below T_{IM} , a SST from IS to LS state can occur solely at Co_{oct}^{3+} while the Co^{3+} in pyramid remains in IS state.⁴ Within this spin configuration, t_{2g} electron hopping from $LSCo_{oct}^{3+}$ to $ISCo_{pyr}^{3+}$ produces a couple of $LSCo_{oct}^{4+}$ and $HSCo_{pyr}^{2+}$. Conversely e_g electron hopping from $ISCo_{pyr}^{3+}$ to $LSCo_{oct}^{3+}$ ions generates stable $LSCo_{pyr}^{4+}$ but unstable $ISCo_{oct}^{2+}$ (Fig. 5). This latter process accounts for the decreased ω_{ex} value since the above sketched model to produce Co^{4+} - Co^{2+} pairs would be no longer valid.

FIG. 5. Schematic electronic level diagram of Co in $GdBaCo_2O_{5.5}$ showing the processes of e_g electron hopping. On the left-hand side of (a), (b) the e_g electron transfers from pyramidal to octahedra Co sites are displayed in the metallic and insulating phases, respectively. On the right-hand side of the same panels the diagram related to cobalt species generated after the hopping processes are shown.

Hence, we can say that the proposed mechanism identifies the SST from $LSCo_{oct}^{3+}$ to $ISCo_{oct}^{3+}$ as a possible origin for the IMT. The temperature-induced SST is corroborated by the sudden unit cell volume expansion observed for $\delta = 0.54(1)$ sample. Indeed the transition to a higher spin state in Co^{3+} implies bigger ionic radius with respect to $LSCo^{3+}$.^{4,5}

Dealing with $\delta > 0.5$ samples, the role of the increased amount of $LSCo^{4+}$ induced by increasing δ must be taken into account in the above mechanism. As suggested by Taskin *et al.*,^{2,3} the presence of $LSCo^{4+}$ can imply double exchange (DE) interaction between $LSCo^{4+}$, $ISCo^{3+}$, and $LSCo^{3+}$. These exchange channels are active even at room temperature and can be considered to enlighten the gradual improvement in the conductivity that blurs the IMT with increasing δ .^{2,3} We argue that the δ dependence of EPR results reported here can be understood considering the interplay between SST and DE. Looking at the ΔH_{pp} temperature dependences, distinct transitions were found for $\delta = 0.54(1)$ and $\delta = 0.57(1)$ samples and we can suggest that the DE contribution is negligible for $\delta \leq 0.57$ (i.e., $Co^{4+}/Co^{3+} \leq 7.5\%$). Conversely, the weak effect observed in the temperature dependence of ΔH_{pp} for $\delta = 0.63(1)$ (i.e., $Co^{4+}/Co^{3+} \approx 15\%$) can be explained considering a strong contribution of DE that accounts for high ω_{ex} value even at room temperature. Moreover we observe a gradual decrease of ΔH_{pp} value increasing δ above 0.54(1) at 305 K. This is a further confirmation that the narrowing of the EPR line with increasing Co^{4+} concentration can be fully explained by the DE channel between $LSCo^{4+}$ and $LS/ISCo^{3+}$ active at $T < T_{IM}$.

To compare the XRPD and EPR results, in Fig. 6(a) we plot the normalized change of ΔH_{pp} , $\delta \Delta H_{pp} / \Delta H_{pp} = [\Delta H_{pp}(305) - \Delta H_{pp}(T)] / \Delta H_{pp}(305)$, together with the normalized changes of the lattice constants for $\delta = 0.54(1)$ sample,

FIG. 6. (Color online) (a) The normalized ΔH_{pp} (open squares) values are reported together with the normalized a (filled circles), $b/2$ (open circles), and $c/2$ (filled squares) axes for $\delta = 0.54(1)$ sample. (b) The normalized data (a axis and ΔH_{pp}) are reported for $\delta = 0.57(1)$. The activation model proposed (solid line) is superimposed in panels (a), (b) to experimental data.

$\Delta L/L = [L(305) - L(T)]/L(305)$ where $L = a, b, c$. In the biphasic region we considered an average lattice parameter value calculated as $F_1 L_1 + F_2 L_2$, where L is the lattice parameter and F is the relative phase fraction. Indices 1 and 2 stand for low- T and high- T phases, respectively.

As shown in Fig. 6(a), it is clear that the temperature dependences of $\delta\Delta H_{pp}/\Delta H_{pp}$ and $\Delta a/a$ fairly overlap each other and the change of ΔH_{pp} is much larger than that of the latter parameter; e.g., at $T = 400$ K, $\delta\Delta H_{pp}/\Delta H_{pp} \approx 15\%$ and $\Delta a/a \approx 0.5\%$. In particular, $\Delta a/a$ is the only normalized lattice parameter that increases as a function of T and saturates above T_{IM} in a manner remarkably similar to $\delta\Delta H_{pp}/\Delta H_{pp}$. This could give evidence that the Co-O-Co interatomic distances along the $[100]$ direction contract with increasing T giving rise to the enhancement of the spin-spin exchange frequency along this direction and the decreasing of ΔH_{pp} . These results suggest spin-lattice interaction along the a axis.

Anisotropic interactions involving Co^{3+} spin and crystal structure are not new in the $\text{GdBaCo}_2\text{O}_{5+\delta}$ system. In particular, Taskin *et al.*¹ found Ising-like behavior of spins along the a axis in the ferromagnetic (FM) phase of

$\text{GdBaCo}_2\text{O}_{5.5}$ single crystal below the Curie temperature $T_{\text{Curie}} \sim 275$ K.^{1,2} According to the proposed model,¹ the insulating FM ground state is generated from the interaction of ISCo^{3+} ions forming two-leg ladders extended along the a axis. These ladders are separated from each other, along the b axis, by ac CoO_2 layers composed by nonmagnetic LSCo^{3+} .^{1,2} Above T_{Curie} a clear FM-to-paramagnetic (PM) transition is observed in the magnetization curve of $\delta \approx 0.5$ sample composition.¹ Basically, two contrasting explanations can be given for such transition: (1) Cobalt spins keep their spin easy axis in the direction of the a axis but the interaction between FM ladders becomes weaker than the PM contribution of Gd^{3+} ; (2) the orientation FM order of Co^{3+} Ising-like spins is completely destroyed above T_{Curie} .

Ising-like behavior of spins and the observed $\delta\Delta H_{pp}/\Delta H_{pp}$ and $\Delta a/a$ scaling behavior shows that the a axis is the preferred crystallographic direction for distinct phenomena related to the FM and the PM phases. According to Taskin *et al.*^{1,2} in the FM phase the a axis is the preferred direction for magnetization which precludes the formation of magnetic moments along the b and c axes. Above T_{Curie} , in the PM phase, the a axis is the preferred direction for the spin-lattice interaction which is connected mainly to spin-spin exchange channels. In order to make a link between the two distinct phenomena occurring along the same crystallographic direction, we might suggest that something related to the nature of spins of the FM phase is retained along the a axis even when the phase is PM. This could support explanation (1) given above and, more importantly, the bridge between FM and PM could be useful to figure out the interplay between the spin-lattice interaction and SST. Indeed, with increasing T and by approaching the IMT from the FM phase, the SST from LS to ISCo^{3+} occurs in the octahedral ac layers stacked along the b axis. On the other side, we suggest that the generation of the ISCo^{3+} state, holding to lattice deformation, can be significantly influenced by the nature of spins of the FM phase along the a axis. Hence, strong coupling between spin-spin exchange interactions and the a lattice parameter can be made explaining the observed $\Delta a/a$ and $\delta\Delta H_{pp}/\Delta H_{pp}$ scaling.

In our model the SST is linked with an increasing of spin-spin exchange frequency which is the driving force of IMT. The formation of the metallic phase could be then explained by thermally activated hopping of spins between neighboring Co sites where the SST from $t_{2g}^6 e_g^0$ -LS state to a cobalt high-spin state enhances the number of electrons in the e_g conduction band.⁴ To account for such behavior we consider that the change of ΔH_{pp} can be described by $\delta\Delta H_{pp}/\Delta H_{pp} \approx K \exp[-E(T)/k_B T]$ where K is a constant and $E(T)$ is a temperature-dependent energy gap. The energy $E(T)$ is given by the parametrized power function $E(T) = E_0[1 - (T/T_{\text{IM}})^{3.39}]$ used to model the temperature dependence of energy splitting between ground and excited spin states of Co in GdCoO_3 system.²⁷ Using the optical band-gap width $E_g = 0.26$ eV given in Ref. 28, we calculated the solid lines shown in Figs. 6(a) and 6(b). The good agreement between model and observed data proves the role of excited Co spin states and, thus, SST in the IMT dynamics of the $\delta = 0.54(1)$ sample. These considerations are still valid for the $\delta = 0.57(1)$ sample, as shown in Fig. 6(b). Conversely, just a weak

FIG. 7. (Color online) (a), (b) The ab planar bond length difference (D_{ab}) values as a function of T for $\delta = 0.54(1)$ (circles), to $\delta = 0.57(1)$ (squares) and $\delta = 0.63(1)$ (triangles) are reported in the octahedral and pyramidal environment, respectively.

correlation between the $\Delta a/a$ and $\delta \Delta H_{pp}/\Delta H_{pp}$ trends was found for $\delta = 0.63(1)$ up to ~ 325 K.

Co^{3+} in IS state is a Jahn-Teller (JT) active ion, so that we expect an increased JT distortion across T_{IM} . Aiming to account for Q_2 -type JT distortion, we calculated the differences between ab -planar long and short Co-O bond lengths¹⁰ (D_{ab}) obtained by Rietveld refinements against the high-quality XRPD data.²⁹ In Fig. 7 the D_{ab} values related to octahedra and pyramids are plotted as a function of T for all the samples.

In the former case, D_{ab} increases linearly with increasing temperature for $\delta = 0.54(1)$, indicating that the Q_2 -type distortion of the basal plane increases when heating above T_{IM} . Interesting features come out with increasing δ . At $T \approx 300$ K, the D_{ab} values are very similar for $\delta = 0.54(1)$, $\delta = 0.57(1)$, and $\delta = 0.63(1)$. This indicates that increasing δ well above 0.5 does not significantly affect the Co-O distances in the octahedra. D_{ab} seems to increase linearly with increasing T for $\delta = 0.57(1)$, approaching a constant value above T_{IM} . Conversely, D_{ab} remains practically unchanged for $\delta = 0.63(1)$. In the pyramid, the D_{ab} parameters were weakly δ

dependent and they did not change significantly with T . This is in agreement with the assumption of T -independent $\text{ISCo}_{\text{pyr}}^{3+}$ states.

The increasing of D_{ab} distortion observed by the XRPD analysis of the $\delta = 0.54(1)$ sample corroborates the occurrence of the proposed SST through the gradual population of the JT-active IS state. On the other hand we have suggested that the DE interactions between LSCo^{4+} and $\text{LSCo}_{\text{oct}}^{3+}$ and $\text{ISCo}_{\text{pyr}}^{3+}$ (Ref. 1) strengthens with δ increasing above $\delta \geq 0.54(1)$ giving rise to a blurred IMT.² We then expect that the strong DE contribution can also restrain the temperature-induced SST by making the $\text{LSCo}_{\text{oct}}^{3+}$ species less available for the transition. This leaves the high-temperature ISCo^{3+} states less populated and destroys the JT effect at $\text{Co}_{\text{oct}}^{3+}$ sites. Such effects are supported by the absence of a sudden unit cell volume expansion across IMT and the saturation of D_{ab} above T_{IM} for $\delta = 0.57(1)$ sample as shown in Fig. 7. In addition, the lack of phase coexistence and the temperature-independent behavior of the D_{ab} parameter for $\delta = 0.63(1)$ further confirms the removal of the JT with increasing δ . These structural effects give evidence to the occurrence of a transition from low-spin to JT-active intermediate spin state and should support the mechanism proposed to explain IMT.

In conclusion, the increasing of electron hopping probability between Co in different spin states can be identified as the main driving force for IMT in $\text{GdBaCo}_2\text{O}_{5+\delta}$ system. EPR data are consistent with this model and the increasing of ω_{ex} with increasing T can be explained by taking into account the SST from $\text{LSCo}_{\text{oct}}^{3+}$ to $\text{ISCo}_{\text{oct}}^{3+}$. XRPD and EPR results give evidence about a strong coupling between the SST and the crystal structure. To figure out the nature of this coupling and its connection with IMT two ingredients are needed: (i) spin-lattice interaction along the a axis; (ii) JT distortion induced by $\text{ISCo}_{\text{oct}}^{3+}$ which is removed with increasing δ giving rise to a blurred IMT.

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