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High spin, hole delocalization and electron transfer in $\text{LBaCo}_2\text{O}_{5.5}$ ($\text{L} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Y}$)

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Abstract

By means of electron-correlation-corrected density functional calculations for $\text{GdBaCoO}_{5.5}$, it has been found that the $\text{pd}\sigma$ hole delocalization in the ‘almost high-spin’ state is responsible for the antiferromagnetic–ferromagnetic-like transition and insulator–metal transition in isostructural $\text{LBaCo}_2\text{O}_{5.5}$ ($\text{L} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Y}$), and that the simultaneous octahedral $\text{Co1 } 3z^2 - r^2/x^2 - y^2$ (pyramidal $\text{Co2 } x^2 - y^2$) \rightarrow Co1 (Co2) yz electron transfer gives rise to the lattice anomaly at T_{IM} . The present study, supporting the author’s prior work (Wu H 2001 *Phys. Rev. B* **64** 092413), provides a unified explanation for a number of experimental findings for $\text{LBaCo}_2\text{O}_{5.5}$.

1. Introduction

Very recently, a class of layered double perovskites $\text{LBaCo}_2\text{O}_{5+\delta}$ ($\text{L} = \text{Y}$ or lanthanides; $0 \leq \delta \leq 1$) were synthesized in the search for cobalt analogues of both the layered cuprate superconductors and the perovskite colossal-magnetoresistance (CMR) manganites; they exhibit a rich variety of phases depending on both the L species and the oxygen content [1–10]. Most important among this class are the isostructural cobaltites of the intermediate lanthanides $\text{LBaCo}_2\text{O}_{5+\delta}$ ($\text{L} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Y}$; $\delta \approx 0.5$), because they exhibit an antiferromagnetic (AFM)–ferromagnetic (FM)-like transition at $T_i \approx 220$ –270 K, an insulator–metal transition (IMT) at $T_{\text{IM}} \approx 310$ –360 K, and a giant MR effect near T_i [2, 6, 8–10], as well as anomalous lattice distortions at T_{IM} [6, 9, 10].

It is well known that the physical properties of cobalt oxides are closely related to the Co spin state and the corresponding electronic structure. However, great controversy has arisen regarding the issue of the Co spin state of $\text{LBaCo}_2\text{O}_{5.5}$ and the explanation of the rich physical properties. Maignan *et al* [2] proposed, on the basis of the measured effective magnetic moments, that a spin-state ordering is most probable in $\text{LBaCo}_2\text{O}_{5.5}$ below T_{IM} with low-spin (LS) octahedral Co1 and intermediate-spin (IS) pyramidal Co2, while both the spin states evolve towards a high-spin (HS) state above T_{IM} . Moritomo *et al* [6] suggested, on the basis of an investigation of the varying crystal structure of $\text{TbBaCo}_2\text{O}_{5.5}$ with temperature (T), that

the IMT is induced by a spin-state transition from the $3x^2 - r^2/3y^2 - r^2$ orbital-ordered IS state below T_{IM} to the HS state above T_{IM} . However, a later structural study of $\text{GdBaCo}_2\text{O}_{5.5}$ performed by Frontera *et al* [9] ruled out orbital ordering and indicated that the IMT is driven by a sudden electron excitation in the octahedral Co1 ions from the LS to the HS states, while the pyramidal Co2 ions remain in their IS state. Meanwhile, the lattice anomaly at T_{IM} was ascribed to the Co1 LS–HS transition.

In strong contrast, the present author argued, on the basis of density functional calculations, that the AFM–FM-like transition and IMT originate from the $\text{pd}\sigma$ hole delocalization in the almost HS state [7]. In this work, the author finds some more evidence to support this distinct mechanism of the AFM–FM transition, IMT, and lattice anomaly in $\text{LBaCo}_2\text{O}_{5.5}$ ($\text{L} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Y}$), by conducting LSDA + U (the local spin-density approximation plus electron-correlation correction) calculations for $\text{GdBaCo}_2\text{O}_{5.5}$ (for which structural data are available and the results applicable to the isostructural $\text{LBaCo}_2\text{O}_{5.5}$ class). The present study provides a unified explanation for a number of experimental findings on $\text{LBaCo}_2\text{O}_{5.5}$ as seen below.

2. Computational details

The crystal structure of $\text{LBaCo}_2\text{O}_{5.5}$ is illustrated in figure 1. For convenience, the octahedral and pyramidal cobalts are called Co1 and Co2, respectively. O1 (in the LO layer) and O2 (in the BaO layer) represent two c -axis apical oxygens of the CoO_6 octahedron, and O3 (in the BaO layer) stands for the one apical oxygen of the CoO_5 pyramid, O4 (O5) for the planar corner oxygen linking the CoO_6 octahedra (CoO_5 pyramids) along the a -axis, and O6 for the planar corner oxygen linking the CoO_6 octahedron and the CoO_5 pyramid along the b -axis. Owing to both the smaller size of the L^{3+} ion (compared with the large Ba^{2+} ion) and the apical oxygen deficiency in the CoO_5 pyramid, the CoO_4 basal square and, especially, the basal oxygens move towards the oxygen-deficient L layer. As a result, a considerable base corrugation occurs in the CoO_2 layer. The structural data for $\text{GdBaCo}_2\text{O}_{5.5}$ at 300 K (below $T_{\text{IM}} \approx 350$ K [9]) are used in the present calculations.

The full-potential linearly combined atomic orbital band method [11] based on LSDA + U [12] is adopted. In order to study the Co spin state and the corresponding electronic structure, spin-polarized calculations are performed for the hypothetical AFM and FM states. Gd 5p5d6s, Ba 5p5d6s, Co 3d4s, and O 2s2p orbitals are treated as valence states¹. The Hartree potential is expanded in terms of lattice harmonics up to $L = 6$, and an exchange–correlation potential of von Barth–Hedin type is adopted [13]. The Co 3d electron correlation $U = 5$ eV and the exchange parameter $J = 0.9$ eV are used as in the previous work [4, 7]. 64 special k -points in an eighth of the irreducible Brillouin zone are used in the self-consistent calculations.

3. Results and discussion

3.1. AFM state

The AFM state is insulating with a gap of 0.38 eV lying between the O 2p valence bands and Co 3d conduction bands, as seen in figure 2. This O 2p–Co 3d charge-transfer (CT) gap compares well with the onset value (≈ 0.2 eV) of the measured optical gap in $\text{SmBaCo}_2\text{O}_{5.6}$ [14]. The

¹ The Gd 4f orbital turns out to be strongly localized and has a full spin moment ($6.39 \mu_{\text{B}}$ from the LSDA and $6.96 \mu_{\text{B}}$ from LSDA + U calculations with $U = 8$ eV and $J = 0.7$ eV for the Gd 4f electrons in a hypothetical FM state). Therefore the Gd^{3+} ($4f^7$) ions are believed to form a paramagnetic (PM) sublattice, and the 4f orbital can be treated as a core one in the present calculations.

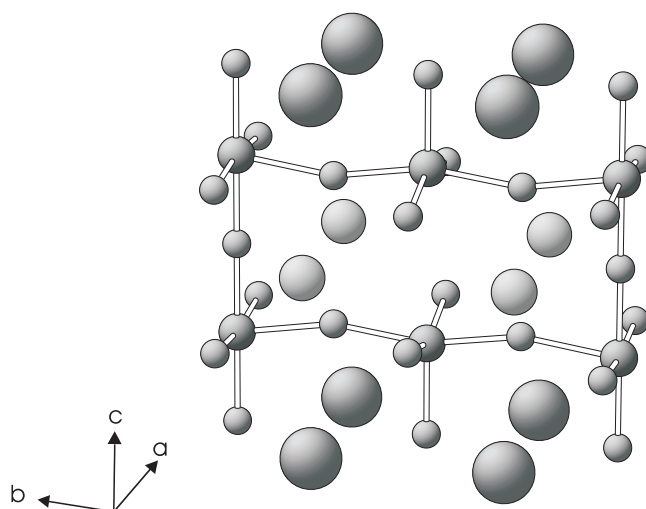


Figure 1. The crystal structure of $\text{LBaCo}_2\text{O}_{5.5}$ with an ' $a_p \times 2a_p \times 2a_p$ '-type unit cell (a_p being the cell parameter of a cubic perovskite). The spheres with size going from largest to smallest denote Ba, L, Co, and O, respectively. There is a considerable base corrugation in the CoO_2 layer. See more details in section 2.

latter was ascribed to the $t_{2g}-e_g$ Co 3d interband transition in the LS state [14], whereas the present results clearly indicate the CT transition in the HS state (due to a complete filling of the majority-spin Co1/Co2 3d orbitals) which is discussed below. Moreover, the present calculation reproduces a main spectral feature observed at 3 eV [14], which is due to the transition from O 2p bands centred around -2 eV to the Co 3d bands below 1 eV. The present results, except for the strongly localized and fully polarized L^{3+} 4f orbital, are nearly the same as those for $\text{TbBaCo}_2\text{O}_{5.5}$ (for a comparison see figures 2 and 3 in this paper and figure 2 in [7]), which indicates their relevance to the isostructural $\text{LBaCo}_2\text{O}_{5.5}$ class. The small quantitative difference between them, e.g., 4% in the calculated Co^{3+} spin moment, is due to the slightly different structural parameters [6, 9].

Owing to a finite pd covalence effect, the ideal HS Co^{3+} spin moment of $4 \mu_B$ is reduced to $-3.16 \mu_B$ at Co1 and $3.14 \mu_B$ at Co2, and a non-negligible oxygen spin moment of $0.09 \mu_B$ appears at the O6 site which is 0.08 \AA [9] closer to Co2 than to Co1. The intralattice and interlattice couplings in and between the Co1 and Co2 sublattices are expected to be AFM due to strong superexchange (SE) couplings [15] between the HS Co^{3+} ions, thus leading to an expected G-type AFM ordering. The O6 spin moment and, especially, a possible spin canting as discussed below account for the measured weak magnetization of $0.095 \mu_B/\text{Co}$ in $\text{SmBaCo}_2\text{O}_{5.6}$ [14], $0.2 \mu_B/\text{Co}$ in $\text{YBaCo}_2\text{O}_{5.5}$ [10], and $0.45 \pm 0.1 \mu_B/\text{Co}$ in $\text{GdBaCo}_2\text{O}_{5.5}$ [8].

The Co2 ion sees a weak crystal field (CF; a maximal CF splitting of ≈ 0.8 eV between the lowest xz level and the highest $x^2 - y^2$ one as indicated by the PM calculation is not shown here) in $\text{GdBaCo}_2\text{O}_{5.5}$ due to the apical oxygen deficiency and a large base corrugation (an average distance $D \approx 0.35 \text{ \AA}$ between the Co and O_4 base [9]). Thus the dominant Hund coupling forces it to take a localized HS state, as previously found in YBaCo_2O_5 [4]. In the Co1O_6 octahedron there also exists a notable base corrugation—the Co1 and basal O4/O6 have respective atomic displacements of 0.02, 0.18, and 0.32 \AA [9]. As a result, the xy orbital drops to the lowest level among the Co1 3d orbitals, and the xz and yz levels rise, while the higher-lying $x^2 - y^2$ level drops considerably and the highest $3z^2 - r^2$ level drops a little; all of

these features are due to the notable O4/O6 displacements. Thus the Co1 ion sees a weaker CF (an average t_{2g} – e_g splitting of about 1.0 eV—the PM-state result) in $\text{GdBaCo}_2\text{O}_{5.5}$ than in the pseudocubic LaCoO_3 . In LaCoO_3 a larger CF splitting of about 1.2 eV between the $t_{2g}(xz, yz, xy)$ and higher $e_g(3z^2 - r^2, x^2 - y^2)$ levels restricts a spin polarization and leads to the Co^{3+} LS ($3d^6, t_{2g}^6 e_g^0$) non-magnetic ground state [4]; while strong $pd\sigma$ hybridizations and a small CT gap (about 0.1 eV between the broad e_g conduction bands and the top valence bands) make the excitation energy between the LS and IS states smaller, and also lead to a smaller difference between the actual electronic structures [16]. As a result, the localized t_{2g} electrons in the LS state can be thermally excited into the empty e_g bands with increasing T , thus giving rise to a LS–IS transition at about 90 K [17]. Similarly, an IS state is stabilized in the cubic perovskite SrCoO_3 (a FM metal) by a strong $pd\sigma$ covalent effect [18]. Compared with the cases of LaCoO_3 and SrCoO_3 , in $\text{GdBaCo}_2\text{O}_{5.5}$ the Co1 ion sees a reduced CF and has weaker $pd\sigma$ hybridizations due to the notable base corrugation [19]. It is therefore not surprising that the Co ions take an (almost) HS state in $\text{GdBaCo}_2\text{O}_{5.5}$ by Hund coupling, since the mechanism of forming the LS (IS) state in LaCoO_3 via a strong CF (via the strong $pd\sigma$ hybridizations, and also for SrCoO_3) seems less effective in $\text{GdBaCo}_2\text{O}_{5.5}$.

The trivalent Co1/Co2 HS states and especially their fully filled majority-spin e_g orbitals mediate strong SE–AFM couplings and are responsible for the high $T_N \approx 240$ –270 K (which is partly masked by the successive FM-like state at 260–300 K) of $\text{LBaCo}_2\text{O}_{5.5}$ ($L = \text{Sm, Eu, Gd, Tb, Dy, Y}$) [2], and even higher $T_N \approx 330$ –340 K of the AFM insulators LBaCo_2O_5 ($L = \text{Y, Tb, Dy, Ho}$) [3, 5]. In contrast, any other spin-state combination, due to decreasing number of channels (mainly related to the occupied e_g orbitals) for SE couplings, seems to make it somewhat hard to account for the high T_N . This is supported by a recent study on the layered trivalent Co compound $\text{TlSr}_2\text{CoO}_5$ for which an IS–HS combination gives rise to the lower $T_N \approx 150$ K [20]. Like for this low- T IS–HS ordered system, T_N is about 100 K for layered $\text{LaBaMn}_2\text{O}_5$ containing the charge-ordered (CO) Mn^{2+} ($3d^5, t_{2g}^3 e_{g\uparrow}^2$) and Mn^{3+} ($3d^4, t_{2g\downarrow}^3 e_{g\downarrow}^1$) ions [21].

Ultrahigh-resolution synchrotron diffraction data for $\text{GdBaCo}_2\text{O}_{5.5}$ [9] indicate that in the distorted lattice, the ab -planar Co–O bond-length difference is about 0.07 (0.05) Å for the Co1 (Co2) ion at 300 K, and about 0.11 (0.06) Å at 400 K. These distortions are much smaller than the corresponding ones for the e_g half-filled Jahn–Teller (JT) ions, e.g., 0.29 Å in LaMnO_3 ($\text{Mn}^{3+}, t_{2g}^3 e_g^1$) [22], 0.38 Å for the IS Co^{3+} ($t_{2g}^5 e_g^1$) ion in $\text{TlSr}_2\text{CoO}_5$ [20], and 0.3 Å for the octahedral Mn^{3+} ion in $\text{LaBaMn}_2\text{O}_{5.5}$ [23]; while they compare well with the observed JT distortion of 0.06 Å for the Ti^{3+} (t_{2g}^1) ion in YTiO_3 and for V^{3+} (t_{2g}^2) ion in YVO_3 and LaVO_3 [24]. In a sense, the JT distortion observed in $\text{GdBaCo}_2\text{O}_{5.5}$ is not related to the e_g electrons but to the t_{2g} electrons which commonly see a much weaker JT distortion than the former. Therefore the IS state seems unlikely for the Co^{3+} ions in $\text{GdBaCo}_2\text{O}_{5.5}$, and the LS ($t_{2g}^6 e_g^0$) state can be ruled out also, since the LS Co^{3+} ions (being non-magnetic and non-JT ions) cannot yield a magnetic structure. As a result, the present HS ($t_{2g}^4 e_g^2$) model is the best candidate for describing the Co^{3+} ions with a one-third filling of the minority-spin t_{2g} orbitals.

The author's prior work on LBaCo_2O_5 ($L = \text{Y, Ho}$) indicated a HS $\text{Co}^{2+}/\text{Co}^{3+}$ CO state [4], whereas a different HS $\text{Co}^{2+}/\text{IS Co}^{3+}$ state was reported by Kwon *et al* [25]. Neutron diffraction measurements at 25 K [3] suggest that in the low- T CO state of YBaCo_2O_5 , the Co^{2+} (Co^{3+})

² Instead of the ab -planar Co–O bond-length difference of about 0.07 (0.1) Å for Co1 (Co2) ions in the 270 K phase of $\text{TbBaCo}_2\text{O}_{5.5}$ (see the first of [6]), a significantly increasing difference about 0.25 (0.17) Å around 400 K was reported in the second of [6]. The weak (strong) JT distortion below (above) $T_{IM} = 340$ K would be a signal of a transition into the high- T IS state, but the correlation with low- T (high- T) insulating (metallic) behaviour is rather unexpected.

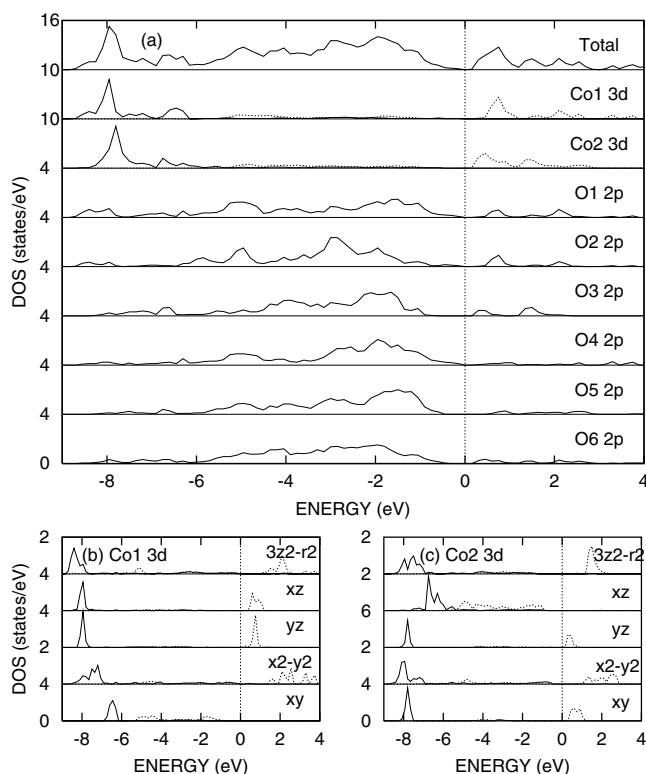


Figure 2. The density of states (DOS) of the AFM insulating state with an O 2p–Co 3d CT gap of 0.38 eV from LSDA + U calculation. A complete filling of the majority-spin Co1/Co2 3d orbitals indicates the HS state. For the Co 3d DOS curves, the solid (dashed) curve denotes the majority (minority) spin. The Fermi level is set at zero.

ion lies above the ab -planar O_4 base by $D = 0.28$ (0.51) Å and has an average basal Co–O bond length of 2.02 (1.95) Å. The Co^{3+} $3d_{x^2-y^2}$ level should be lower than the Co^{2+} $3d_{x^2-y^2}$ level [4], in view of both the Co^{3+} ion having a much larger D (but slightly smaller bond length) and one fewer 3d electrons than the Co^{2+} ion. It is therefore hard to understand why, in the above HS Co^{2+} /IS Co^{3+} model, the majority-spin Co^{2+} $3d_{x^2-y^2}$ orbital is occupied whereas the majority-spin Co^{3+} $3d_{x^2-y^2}$ orbital is unoccupied [25]. Note that this discrepancy is most probably due to the simple atomic sphere approximation (for the charge density and potential) made in their band-structure calculations [25]. A full-potential method (no shape approximation adopted), as used in the author's prior and present work, should be preferable for descriptions of distorted-lattice materials such as $\text{LBaCo}_2\text{O}_{5+\delta}$. Moreover, it is worth noting that the HS $\text{Co}^{2+}/\text{Co}^{3+}$ CO state and a prediction of a small gap (see figure 3 in [4]) are supported, respectively, by unrestricted Hartree–Fock calculations [26] and an observation of an excitation gap about 0.05–0.1 eV in $\text{HoBaCo}_2\text{O}_5$ [5].

3.2. FM state

Now we turn to the LSDA + U calculation for the FM state. The FM state differs from the AFM state most significantly (see the total DOS in figures 2 and 3) in that the FM DOS intensity around -2 eV and below 1 eV decreases and, instead, a considerable DOS appears at the

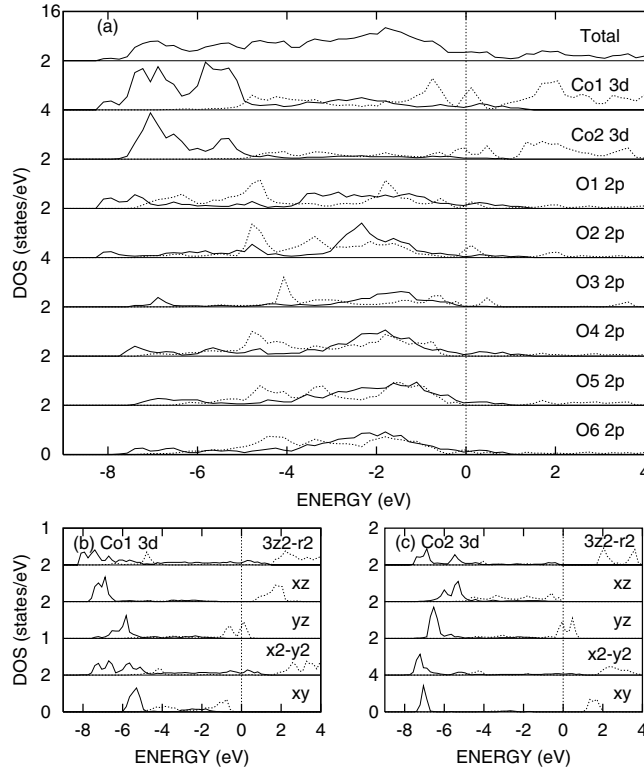


Figure 3. The DOS of the almost HS FM metallic state from LSDA + U calculation. The delocalized $pd\sigma$ holes are created, and an electron transfer leads to a partial filling of the weakly delocalized minority-spin Co1/Co2 yz orbitals.

Fermi level. This FM metallic solution takes an almost HS state. Coupled to the itinerant O 2p orbitals, the Co1 $e_g(3z^2 - r^2, x^2 - y^2)$ and Co2 $x^2 - y^2$ orbitals become delocalized, and thus the net spin at the Co sites is reduced to $2.74 \mu_B/\text{Co1}$ and $3.02 \mu_B/\text{Co2}$. Owing to a smaller base corrugation in the Co1O₆ octahedra ($D \approx 0.25 \text{ \AA}$) than in the Co2O₅ pyramids ($D \approx 0.35 \text{ \AA}$) as shown above, the Co1 $x^2 - y^2$ orbital is more delocalized than the Co2 $x^2 - y^2$ one, while the Co1 $3z^2 - r^2$ orbital has a highest 3d level and is most delocalized, as seen in figure 3. As a result, the majority-spin $pd\sigma$ conduction bands in total contribute 0.88 delocalized holes per formula unit. These $pd\sigma$ holes have mainly O 2p character due to the CT nature of LBaCo₂O_{5.5}, and they contain 0.64 mobile holes (0.32 holes per CoO₂ basal ‘square’ on average) within the ab -plane. And the remaining 0.24 holes are mobile along the c -axis Co1–O chain. The mobile O 2p majority holes are antiferromagnetically coupled to the Co local spins, and thus they induce an effective FM coupling (between the Co spins) and a metallic-like behaviour via the p - d exchange [27, 28]; while the (almost) HS coupled SE–AFM insulating behaviour is inherent and competes with the above FM metallicity, thus probably giving rise to a non-metallic spin-canted structure in LBaCo₂O_{5.5}. This possible spin-canted structure (with a finite FM metallic-like signal due to a gradual delocalization of the $pd\sigma$ holes with increasing T) can consistently account for the observed AFM–FM-like transition at $T_i \approx 220\text{--}270 \text{ K}$, a weak magnetization even in the so-called FM state, and a sudden drop of the insulating resistivity at T_i [2, 6, 8–10]. As T increases further, the $pd\sigma$ holes delocalize completely in the high- T PM phase, thus leading to the IMT at $T_{IM} \approx 310\text{--}$

360 K. The $\text{pd}\sigma$ hole delocalization behaviour has been shown by the present calculations and also clearly seen in the observed optical spectra of $\text{SmBaCo}_2\text{O}_{5.6}$ [14]—the reflectivity and conductivity below 1 eV increase up to T_{IM} and saturate above T_{IM} ; this is accompanied by a decrease of the spectral intensity centred at 3 eV.

Some of the previous studies suggested the LS and/or IS model for $\text{LBaCo}_2\text{O}_{5.5}$ given by Kusuya *et al* [6], Respaud *et al* [8], and Saito *et al* [14], on the basis of the measurements of the weak magnetization or a simple (but inappropriate, as discussed above [19]) analogy with LaCoO_3 . As indicated above, however, the LS and/or IS model seems to make it hard to account for the high T_{N} . In addition, a spin-canted structure of the (almost) HS Co^{3+} ions can reasonably account for the weak magnetization observed in $\text{LBaCo}_2\text{O}_{5.5}$, as is the case for $\text{LaMnO}_{3+\delta}$ ($0 \leq \delta \leq 0.18$) [29]. In the latter, a spin-canted or glassy structure formed by the Mn^{3+} (spin = 2) and Mn^{4+} (spin = 3/2) ions, due to a competition between the AFM and FM couplings, gives rise to a magnetization notably weaker than the expected one of about $4 \mu_{\text{B}}$.

It can be seen in figure 3 that, accompanying the Co e_{g} electron delocalization, a considerable electron transfer occurs from the majority-spin Co1 e_{g} ($\text{Co}2 x^2 - y^2$) orbitals to the minority-spin Co1 (Co2) yz orbitals. The occupation number of the minority-spin Co1 yz orbital (0.69) is larger than that of the Co2 yz orbital (0.56), since two delocalized Co1 e_{g} ($3z^2 - r^2/x^2 - y^2$) orbitals contribute to the electron transfer, while only one delocalized Co2 $x^2 - y^2$ orbital does so. The partly occupied yz orbitals coupled to the O 2p ones form narrow conduction bands crossing the Fermi level. Owing to the e_{g} electron delocalization in the almost HS state, the a -axis shrinks at the IMT; whereas the more than half-filling of the weakly delocalized Co1/Co2 yz orbitals forces an elongation of both the b - and c -axes, which prevails over a tendency towards b - and c -axis contraction induced by the e_{g} electron delocalization. As a result, the b - and c -axis elongation and the volume expansion occur at the IMT [9]. Moreover, owing to the Co1 yz orbital being more occupied than the Co2 one, the b -axis Co1–O6 (Co2–O6) bond is elongated (shortened). The lattice stress in the Co_2O_5 pyramid (due to the shrinking a - and b -axis Co2–O bonds) is relieved by elongating the c -axis Co2–O bond, as observed.

4. Conclusions

This study supports the author's prior work [7] on $\text{LBaCo}_2\text{O}_{5.5}$. The present LSDA + U calculations for $\text{GdBaCo}_2\text{O}_{5.5}$ reproduce well the main spectral features and their T -variations observed for $\text{SmBaCo}_2\text{O}_{5.6}$. Detailed analyses of both the present results and the available experimental findings for $\text{LBaCo}_2\text{O}_{5.5}$ ($L = \text{Sm, Eu, Gd, Tb, Dy, Y}$) and for some relevant compounds lead to a proposal: that a gradual delocalization of the $\text{pd}\sigma$ holes in the almost HS state of $\text{LBaCo}_2\text{O}_{5.5}$ with increasing T is responsible for the successive AFM–FM-like transition (which is probably accompanied by a spin reorientation in a spin-canted structure) and IMT, and that the simultaneous octahedral Co1 $3z^2 - r^2/x^2 - y^2$ (pyramidal Co2 $x^2 - y^2$) \rightarrow Co1 (Co2) yz electron transfer gives rise to the lattice anomaly at T_{IM} .

Acknowledgments

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