Spin-state order/disorder and metal–insulator transition in GdBaCo$_2$O$_{5.5}$: experimental determination of the underlying electronic structure

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Abstract. We have investigated the electronic structure of GdBaCo$_2$O$_{5.5}$ across the metal–insulator transition (MIT) using soft x-ray absorption and photoelectron spectroscopy. For the low-temperature insulating phase, we find that half of the Co$^{3+}$ ions at the octahedral sites are in the low spin (LS) and the other half in the high spin (HS) state, while the Co$^{3+}$ ions at the pyramidal sites are in the HS configuration. Upon increasing the temperature across the MIT, part of the LS octahedral Co$^{3+}$ undergoes a spin-state transition into the HS configuration. We infer that this destroys the spin-state ordering and thus explains the decrease in resistivity. We observed that the band gap is reduced but not closed in the high-temperature phase.

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The layered cobaltates $R$BaCo$_2$O$_{5.5}$ ($R =$ rare earth) have attracted considerable attention of the scientific community in recent years because of their peculiar magnetic and transport properties, showing giant magneto-resistance as well as metal–insulator (MIT) and antiferro–ferro-ferromagnetic transition phenomena [1–27]. Moreover, these compounds possess the so-called spin-state degree of freedom, i.e. the possibility of the Co$^{3+}$ ions to be in a low spin (LS, $S = 0$), high spin (HS, $S = 2$) and even intermediate spin (IS, $S = 1$) state [28, 29]. This spin-state degree of freedom is generally considered to play a key role for the unconventional transport properties of the cobaltates, and a spin-blockade mechanism [13, 30] has recently been proposed [13, 16] as the driving force for the MIT in $R$BaCo$_2$O$_{5.5}$.

The crystal lattice of $R$BaCo$_2$O$_{5.5}$ is composed of an equal number of CoO$_6$ octahedra and CoO$_5$ pyramids and the valence of all the Co ions is 3+. These materials exhibit a series of magnetic orders, namely, a ferromagnetic-like phase below $T_C \sim 290$ K, an antiferromagnetic phase below $T_{N1} \sim 260$ K which is accompanied by the appearance of strong magneto-resistive effects and a second antiferromagnetic phase below $T_{N2} \sim 200$ K. Despite a large number of neutron diffraction studies, the nature of these magnetic orderings is still unresolved [7, 18–20, 22]. One main reason for the disagreement is the confusion about the spin state of the Co$^{3+}$ ions in both octahedral (Co$^{3+}_{\text{oct}}$) and pyramidal (Co$^{3+}_{\text{pyr}}$) coordination. This is particularly evident in the discussion about the sharp drop in the resistivity, the so-called MIT, occurring in the paramagnetic phase at $T_{\text{MIT}} \sim 360$ K. This MIT is commonly attributed to a sudden spin-state switch of Co$^{3+}_{\text{oct}}$, but its modality is controversial and intensely debated. Contradictory scenarios have been proposed, including full or partial LS→IS or LS→HS state transitions for the Co$^{3+}_{\text{oct}}$ and IS or HS configurations for the Co$^{3+}_{\text{pyr}}$ [1–6–26]. It is noteworthy that at present there is, in fact, no direct evidence for any of the claimed spin-state transitions. There is therefore a pressing need to address the issue of the spin state of the Co ions and its evolution as a function of temperature. We have performed experiments utilizing soft x-ray absorption spectroscopy (XAS) at the Co-$L_{2,3}$ and O-$K$ edges, a method proven to be extremely sensitive to the spin state of transition metal ions in general [31, 32] and 3d$^b$ systems in particular [30, 33–35]. We have also carried out valence band photoelectron spectroscopy.
Twinned single crystals of GdBaCo$_2$O$_{5.5}$ were grown from a high-temperature flux melt. The purity and cation composition of the crystals were checked by x-ray diffraction and fluorescence analysis, respectively. The oxygen content was determined by iodometric titration to be 5.48(2). Co-$L_{2,3}$ spectra in the total-electron-yield mode and O-K XAS spectra in the total-fluorescence-yield mode were measured at the Dragon beamline of the NSRRC in Taiwan with a photon-energy resolution of 0.45 and 0.25 eV, respectively. XAS spectra of CoO were measured simultaneously as energy calibration for the Co-$L_{2,3}$ and O-K edges, respectively. The O-K and Co-$L_{2,3}$ XAS spectra of two reference compounds LaCoO$_3$ and Sr$_2$CoO$_3$Cl were collected under the same conditions. The PES spectra were recorded at the ID08 beamline of the ESRF in Grenoble, using a photon energy of 700 eV and a Scienta SES200 electron analyser. The overall experimental resolution was 110 meV and the Fermi level was calibrated using polycrystalline silver.

Figure 1(a) displays the isotropic O-K XAS measured on GdBaCo$_2$O$_{5.5}$ at different temperatures. The spectral structures from 528 to 532 eV are due to transitions from the O 1s
core level to the O 2p orbitals that are mixed with the unoccupied Co 3d t$_{2g}$ and e$_g$ states. In the XAS of GdBaCo$_2$O$_{5.5}$ we observe a very modest spectral weight transfer from the broad feature at 530 eV to the dominant peak at 528.4 eV. These spectra are the sum of two contributions related to the Co$^{3+}_{\text{pyr}}$ and Co$^{3+}_{\text{oct}}$ sites. To explain their line shapes we will make use of Sr$_2$CoO$_3$Cl as a reference compound containing Co$^{3+}_{\text{pyr}}$ ions [34, 37], and of LaCoO$_3$ as a reference material having Co$^{3+}_{\text{oct}}$ ions which undergo a spin-state transition as a function of temperature [35, 38].

The O-K XAS of Sr$_2$CoO$_3$Cl is reported in figures 1(b) and (c) as the curve of blue dots. The Co$^{3+}_{\text{pyr}}$ ions here have the HS configuration [34, 37]. The O-K spectra of LaCoO$_3$ are displayed in figure 1(d) for $T = 20$ K (black), 300 K (blue) and 650 K (red). Figure 1(d) shows a significant spectral-weight transfer from the higher energy structure at around 529.4 eV to the lower energy one at around 528.4 eV when going from 20 to 300 K and further to 650 K. The LaCoO$_3$ data demonstrate that O-K XAS is also very sensitive to the spin-state transition of Co$^{3+}$ ions, which can be explained as follows. At low temperatures, the LS Co$^{3+}_{\text{oct}}$ has its t$_{2g}$ shell completely occupied [35] and only transitions to the higher lying empty e$_g$ states are possible. At higher temperatures, with part of the Co ions in the HS state [35], the t$_{2g}$ states become partially unoccupied; then transitions to lower lying t$_{2g}$ states are also allowed, leading to the feature at around 528.4 eV. As the temperature increases this lower energy feature gains gradually spectral weight at the expense of the higher energy feature. From the Co-$L_{2,3}$ XAS, it was estimated that at 650 K, 50% of the Co ions are in the HS state and 50% in the LS [35].

In determining the spin-state configurations for GdBaCo$_2$O$_{5.5}$ at 78 K, we assume that its Co$^{3+}_{\text{pyr}}$ ions are in the HS state like in Sr$_2$CoO$_3$Cl and we start by investigating the LS scenario for the Co$^{3+}_{\text{oct}}$ ions as proposed in several studies [12, 13, 16]. To this end we sum the Sr$_2$CoO$_3$Cl spectrum (blue) and the LaCoO$_3$ at 20 K (black). The result is displayed in figure 1(c) (magenta). One can clearly observe that this is very different from the GdBaCo$_2$O$_{5.5}$ spectrum in figure 1(a). The LS Co$^{3+}_{\text{oct}}$ scenario can thus be safely ruled out. Next, we take the LaCoO$_3$ at 650 K (red) as ansatz for the Co$^{3+}_{\text{oct}}$ part. The sum is shown in figures 1(b) and (a) (green). Surprisingly, this sum reproduces the GdBaCo$_2$O$_{5.5}$ spectrum at 78 K very well. This strongly suggests that GdBaCo$_2$O$_{5.5}$ in the low-temperature phase has 50% of its Co$^{3+}_{\text{oct}}$ ions in the LS state and 50% in the HS. All of its Co$^{3+}_{\text{pyr}}$ ions are HS. Remarkable is also the very modest temperature dependence in the GdBaCo$_2$O$_{5.5}$ spectra, i.e. very much unlike the LaCoO$_3$ case, suggesting that only a small part of the Co$_{\text{oct}}$ ions participate in a spin-state transition across the MIT.

More support for the above results can be found from Co-$L_{2,3}$ spectroscopy. Figure 2(a) depicts the isotropic Co-$L_{2,3}$ XAS spectrum of GdBaCo$_2$O$_{5.5}$ at 78 K. The Co 2p core-hole spin–orbit coupling splits the spectrum roughly into two parts, namely the $L_3$ (at 780.5 eV) and $L_2$ (at 795 eV) white line regions. The strong absorption at 5 eV above the Co-$L_{2,3}$ white lines is due to the Ba-$M_{4,5}$ signal (shaded area) as shown by the BaFeO$_3$ spectrum in figure 2(b). We now use this BaFeO$_3$ spectrum to remove the Ba-$M_{4,5}$ signal from the GdBaCo$_2$O$_{5.5}$ Co-$L_{2,3}$ spectra. The result is given in figure 3(a), which displays the net Co-$L_{2,3}$ spectra of GdBaCo$_2$O$_{5.5}$ taken at 78, 285 and 400 K. The set is at first sight similar to those reported earlier [23, 24], but it is in fact essentially different in detail. Firstly, our spectra do not show a shoulder at 3 eV below the main peak at the Co-$L_3$ edge, which would represent a significant amount of Co$^{2+}$ in the sample. This indicates that our spectra are free from Co$^{2+}$ impurity signal [30]. Secondly, our set includes the very important low-temperature (78 K) spectrum.

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Figure 2. Measured Co-$L_{2,3}$ XAS spectrum of GdBaCo$_2$O$_{5.5}$ at 78 K (a) and Ba-$M_{4,5}$ spectrum of BaFeO$_3$ (b).

To analyse the Co-$L_{2,3}$ spectra, we have performed theoretical simulations based on the multiplet cluster method [34, 35] using the XTLS 8.3 code [36], taking into account the real local environment of the Co$^{3+}$ ions in GdBaCo$_2$O$_{5.5}$, which we assume to be the same as in TbBaCo$_2$O$_{5.5}$ [18]. The simulations for the octahedral HS (orange), octahedral LS (black) and pyramidal HS (light blue) Co$^{3+}$ clusters are shown in figure 3(e). We first make a sum of these contributions in a 1:1:2 ratio and we also add a standard edge jump (dashed curve) to take into account transitions to continuum states$^{12}$. Figure 3(b) clearly shows that this sum agrees excellently with the experimental 78 K spectrum. This confirms our O-$K$ XAS finding, namely that the low-temperature phase of GdBaCo$_2$O$_{5.5}$ consists of 50% LS–50% HS Co$_{\text{oct}}$. To double check, we also make a sum in a 0:2:2 ratio to mimic the commonly accepted scenario for the low-temperature phase in which all Co$_{\text{oct}}$ are believed to be in the LS state. Figure 3(c) reveals unambiguously significant discrepancies from the experiment as marked by ellipses. We can therefore safely reject this scenario.

Figure 3(a) shows also that there is only a very small temperature dependence in the Co-$L_{2,3}$ spectra of GdBaCo$_2$O$_{5.5}$, in strong contrast to, for example, LaCoO$_3$ [35]. This observation indicates again a very modest and only partial spin-state transition of the Co$_{\text{oct}}$ ions in GdBaCo$_2$O$_{5.5}$ across the MIT, fully in agreement with the findings of the O-$K$ XAS study above. Our data therefore also rule out the commonly accepted scenario of a sharp and massive LS–HS transition across $T_{\text{MI}}$. For completeness, we have investigated what the spectral lineshape of an all HS Co$_{\text{oct}}$ high-temperature phase could look like, and we can see from figure 3(d) that the 2:0:2 sum strongly disagrees with the experimental 400 K spectrum.

Recent diffraction data showed that in going from high to low temperature, the MIT is accompanied by a structural transition towards a distorted structure with two inequivalent Co$^{3+}_{\text{oct}}$ sites, one with the average Co–O bond length of 1.928 Å, called Co$^{3+}_{\text{oct1}}$, and the other with $^{12}$See the appendix for details of the cluster calculations.

$^{13}$Earlier work proposed the 100% LS Co$^{3+}_{\text{oct}}$ scenario, claiming that this is necessary to reproduce the weak feature C (see figure 2) [23]. We find that feature C stems from the $^3\text{P}_1$ final state in the Ba-$M_{4,5}$ spectrum and not from the Co $L_{2,3}$ signal, see the BaFeO$_3$ spectrum in figure 2.
1.978 Å, called Co$^{3+}_{\text{oct2}}$ [18, 22]. This transition was interpreted as the effect of an orbital [17, 23] or a spin-state order transition [22]. Our results showing a 50:50 mixture of LS/HS Co$^{3+}_{\text{oct}}$ ions provide direct evidence that these low temperature distortion and superstructure are caused by LS/HS spin-state ordering of the Co$^{3+}$ ions at the octahedral sublattice. Also a direct link can then be made between the differences in Co–O bond lengths with differences in the spin state [35]. In LaCoO$_3$, for example, the bond length is 1.925, 1.949 and 1.962 Å at 5, 650 and 1000 K, respectively [39]. The Co$^{3+}_{\text{oct1}}$ ion in GdBaCo$_2$O$_5.5$ has a bond length close to LaCoO$_3$ at 5 K, i.e. LS. The Co$^{3+}_{\text{oct2}}$ ion has a bond length even larger than LaCoO$_3$ at 1000 K, i.e. HS, again fully consistent with the above finding.

Figure 3. Co-$L_{2,3}$ XAS spectra: (a) GdBaCo$_2$O$_{5.5}$ at 78 K (black), 285 K (blue) and 400 K (red) after subtracting the Ba-$M_{4,5}$ spectrum of BaFeO$_3$, and (e) theoretical simulations for the oct-HS (orange), oct-LS (black) and pyr-HS (light blue) Co$^{3+}$ ions. The experimental GdBaCo$_2$O$_{5.5}$ spectrum at 78 K (black) is compared with the sum of the simulations (green) in a 1:1:2 ratio (b) and a 0:2:2 ratio (c), respectively. (d) Comparison of the experimental GdBaCo$_2$O$_{5.5}$ spectrum at 400 K (red) to the 2:0:2 sum of the simulations (green). The dashed curve represents the edge jump.

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We now investigate the effect of the spin-state configurations on the band width and band gap of GdBaCo$_2$O$_{5.5}$. Figure 4 shows the valence band PES at temperatures below and above $T_{MI}$. Surprisingly, and in contradiction with a previous report, the valence band PES of GdBaCo$_2$O$_{5.5}$ reveals that the spectral weight at the Fermi level is negligible at 78 K (black) and 285 K (blue), and still very weak at 400 K (red), so that we have to conclude that actually the material is an insulator or semiconductor even above $T_{MI}$. What we found is that the band gap is indeed reduced when the temperature is increased: the top of the valence band (figure 4, left panel) moves up by about 60 meV in going from 285 to 400 K, while the bottom of the conduction band (figure 4, right panel) shifts downwards by 70 meV from 285 to 400 K. So, in total, the band gap is reduced by about 130 meV across $T_{MI}$. Using $\rho \propto E_g/k_B T_{MI}$ with $k_B T_{MI} \sim 30$ meV, this gap narrowing accounts well for the observed reduction of resistivity by two orders of magnitude at $T_{MI}$ [5, 9, 11, 14, 16]. From figure 4 one can see that there is no pronounced LS peak at 0.8 eV as found in the spectrum (magenta) of LaCoO$_3$ at 65 K, where the Co$^{3+}$ ions are basically in the LS state [35]. However, we see that the weak feature at 0.6 eV in GdBaCo$_2$O$_{5.5}$ corresponding to 50% LS Co$^{3+}$ 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, the superstructure associated with the 50% LS–50% HS spin-state ordering of Co$^{3+}$ oct ions stabilizes the insulating state of the GdBaCo$_2$O$_{5.5}$ system. On increasing the temperature across $T_{MI}$, part of the LS Co$^{3+}$ oct ions undergo a transition to the HS state, thereby breaking down the superstructure as is shown by x-ray diffraction [17]. This loss of order causes a reduction of the band gap. In converting an HS–LS neighbouring 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 HS to LS, thereby increasing the amount of charge.

The spectral weight at the Fermi level found in the previous work might be due to the very poor experimental resolution of 600 meV [21] as compared with 110 meV in this work.
fluctuations. However, the band gap does not vanish since the hopping of an extra hole or electron is energetically quite difficult in such an antiferromagnetic situation. Reversely, the observation that the changes in widths of the valence (PES) and conduction (O-K XAS) bands are very modest reaffirms that the IS state scenario does not become active, since otherwise the presence of IS Co$^{3+}_{\text{oct}}$ ions would allow for free propagation of an extra hole or electron in a ferromagnetically aligned e$_{g}$ band.

To summarize, we have utilized O-K and Co-L$_{2,3}$ XAS spectroscopy to reveal that the low-temperature insulating phase of GdBaCo$_2$O$_{5.5}$ is characterized by a LS–HS spin-state ordering in the Co$^{3+}_{\text{oct}}$ sublattice. We found a very modest spin-state transition in the Co$^{3+}_{\text{oct}}$ with increasing temperature across the insulator–metal transition. Our photoemission experiments show that the band gap is reduced but does not close, in quantitative agreement with the change in resistivity. The MIT should be modelled in terms of a spin-state order–disorder transition with a modest gain in band width.

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Appendix

Here we describe the procedure for data analysis and the model calculation of the XAS spectra.

A.1. Oxygen K-edge data analysis (figure 1)

For each temperature and polarization, several total fluorescence yield spectra (measured under the same conditions) were summed and a (constant) pre-edge background was subtracted. For normalization we divided each background-subtracted spectrum by the average of its spectral intensity in the energy range 550–600 eV. The GdBaCo$_2$O$_{5.5}$ spectra were renormalized by a factor of 1.9 (in order to compare with the sum of LaCoO$_3$ and Sr$_2$CoO$_3$Cl).

For GdBaCo$_2$O$_{5.5}$ the energy of each spectrum was calibrated using a (simultaneously recorded) CoO spectrum. The CoO reference spectrum was compared with a NiO spectrum taken under the same conditions. The NiO spectrum was calibrated by comparing it with an electron energy loss spectrum published in [40]; the first NiO pre-edge peak was identified to be at 531.9 eV. For each temperature the $E_{\parallel ab}$ and $E_{\parallel c}$ spectra were averaged with a weighting ratio 2:1 in order to obtain the isotropic spectrum.

The energy in the LaCoO$_3$ spectra was calibrated by a NiO reference sample spectrum. For Sr$_2$CoO$_3$Cl we used the same data as published in [41]. The energy of this spectrum was re-calibrated using more recent Sr$_2$CoO$_3$Cl data recorded together with a CoO reference spectrum.
A.2. Cobalt L-edge data analysis and model calculation (figures 2 and 3)

The total electron yield was divided by $I_0$ (the intensity of the incoming beam). Then a (constant) pre-edge background was subtracted. As normalization we divided each background-subtracted spectrum by the average of its spectral intensity in the energy range 807–815 eV.

The energy of each GdBaCo$_2$O$_{5.5}$ spectrum was calibrated using a (simultaneously recorded) reference CoO spectrum identifying the first peak of CoO to be at 778.1 eV [40]. For each temperature we averaged the $E \parallel ab$ and $E \parallel c$ spectra with a weighting ratio 2:1 in order to obtain the isotropic spectrum. In order to subtract the Ba $M$-edge signal we measured a polycrystalline BaFeO$_3$ spectrum. This BaFeO$_3$ spectrum has a background with a slope; the pre-edge background was fitted using a linear function (for the fit we considered the first 40 points) and we subtracted this linear background from the spectrum. Then the BaFeO$_3$ spectrum was subtracted from the GdBaCo$_2$O$_{5.5}$ spectra—the scaling factor and energy position of the BaFeO$_3$ spectrum were adjusted such that the irregularities in the difference spectrum were minimized.

A theoretical calculation of the x-ray absorption spectra was performed with the program XTLS 8.3 [42]. The following parameters have been used (HF refers to Hartree–Fock calculations for a single Co ion):

- Slater integrals were reduced to 80% of the HF values.$^{15}$
- For the 3d spin–orbit coupling HF values were used.
- Electron–electron Coulomb repulsion: $U_{3d3d} = 5.5$ eV, $U_{3d2p} = 7.0$ eV [41, 43].
- Charge transfer energy (from the oxygen ligand to Co 3d): $\Delta = +2.0$ eV [43].
- Energy splitting of ligand orbitals due to ligand–ligand hybridization: $2T_{pp} = +1.0$ eV [41].
- Hybridization parameters of Co d-electrons and oxygen ligand p-electrons were estimated according to the distance to the power of 7/2 law by Harrison [44], starting from $V_{pd\sigma} = -1.7$ eV for a Co–O distance of 1.925 Å [43].
- The ionic crystal field was taken into account by a purely octahedral splitting parameter $10Dq$.
- For the final state we used the same values of the hybridization parameters and reduced the ionic crystal field parameter $10Dq$ by 30% with respect to the initial state value.

(i) Octahedral sites HS.

- Energy difference between $2p^63d^6$ and $2p^53d^7$ configuration: 784.9 eV.
- Ionic CF parameter of the initial state: $10Dq = 0.5$ eV.
- Ligand positions [45] and the corresponding hybridization parameters $V_{pd\sigma}$, $V_{pd\pi}$:

| $x$ (Å) | $y$ (Å) | $z$ (Å) | $V_{pd\sigma}$ (eV) | $V_{pd\pi}$ (eV) |
|--------|--------|--------|----------------|-----------------|
| 0.000  | 0.000  | 1.890  | −1.813          | 0.836           |
| 0.000  | 0.000  | −1.880 | −1.847          | 0.851           |
| 1.920  | 0.000  | −0.120 | −1.705          | 0.785           |
| −1.920 | 0.000  | −0.120 | −1.705          | 0.785           |
| 0.000  | 2.100  | −0.390 | −1.182          | 0.545           |
| 0.000  | −2.100 | −0.390 | −1.182          | 0.545           |

$^{15}$ Slater integrals and spin–orbit coupling were obtained with the R D Cowans program RCN36K [46].
(ii) Octahedral sites LS.

- Energy difference between $2p^63d^6$ and $2p^53d^7$ configuration: 784.6 eV.
- Ionic CF parameter of the initial state: $10Dq = 0.8$ eV.
- Ligand positions [45] and the corresponding hybridization parameters $V_{pd\sigma}, V_{pd\pi}$:

| $x$ (Å) | $y$ (Å) | $z$ (Å) | $V_{pd\sigma}$ (eV) | $V_{pd\pi}$ (eV) |
|---------|---------|---------|---------------------|-------------------|
| 0.000   | 0.000   | 1.840   | −1.992              | 0.918             |
| 1.950   | 0.000   | −1.920  | −1.716              | 0.791             |
| −1.950  | 0.000   | 0.130   | −1.613              | 0.743             |
| 0.000   | 1.930   | 0.280   | −1.625              | 0.749             |
| 0.000   | −1.930  | 0.280   | −1.625              | 0.749             |

(iii) Pyramidal sites HS.

- Energy difference between $2p^63d^6$ and $2p^53d^7$ configuration: 784.7 eV.
- Ionic CF parameter of the initial state: $10Dq = 0.7$ eV.
- Ligand positions [45] and the corresponding hybridization parameters $V_{pd\sigma}, V_{pd\pi}$ for pyramidal site 1:

| $x$ (Å) | $y$ (Å) | $z$ (Å) | $V_{pd\sigma}$ (eV) | $V_{pd\pi}$ (eV) |
|---------|---------|---------|---------------------|-------------------|
| 0.000   | 0.000   | −1.850  | −1.954              | 0.901             |
| 1.910   | 0.000   | 0.420   | −1.609              | 0.742             |
| −1.910  | 0.000   | 0.420   | −1.609              | 0.742             |
| 0.000   | 1.970   | 0.310   | −1.503              | 0.693             |
| 0.000   | −1.970  | 0.310   | −1.503              | 0.693             |

- Ligand positions [45] and the corresponding hybridization parameters $V_{pd\sigma}, V_{pd\pi}$ for pyramidal site 2:

| $x$ (Å) | $y$ (Å) | $z$ (Å) | $V_{pd\sigma}$ (eV) | $V_{pd\pi}$ (eV) |
|---------|---------|---------|---------------------|-------------------|
| 0.000   | 0.000   | 1.990   | −1.514              | 0.698             |
| 1.960   | 0.000   | −0.290  | −1.537              | 0.708             |
| −1.960  | 0.000   | −0.290  | −1.537              | 0.708             |
| 0.000   | 1.810   | −0.310  | −2.006              | 0.924             |
| 0.000   | −1.810  | −0.310  | −2.006              | 0.924             |

XAS spectra are calculated using the finite imaginary constant $i\Gamma$ in the denominator of Green’s function with $\Gamma = 0.1$ eV (much larger than the step size of 0.02 eV). In order to take into account experimental resolution and lifetime effects, we applied additional line broadening to the spectra: (i) a Gaussian broadening with 0.45 eV FWHM, and (ii) an energy-dependent Lorentzian broadening.

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An edge jump was added to the results of the calculation. The edge jump \( I_{\text{edge}}(E) \) is modelled by the formula

\[
I_{\text{edge}}(E) = 0.0164 \left[ \frac{\pi}{2} + \arctan \left( 1.5 \left( \frac{E}{\text{eV}} - 783.2 \right) \right) \right] \\
+ 0.0134 \left[ \frac{\pi}{2} + \arctan \left( 1.5 \left( \frac{E}{\text{eV}} - 795.0 \right) \right) \right].
\]

The results of the model calculation are compared with the experimental data in figure 3 of the main text. The sum of oct-HS, oct-LS and pyr-HS contributions with the 1:1:2 spectral weight agrees best with the experimental data and supports our conclusion about the presence of a LS–HS spin-state ordering in the \( \text{Co}^{3+}_{\text{oct}} \) sublattice of GdBaCo\( _{2} \)O\( _{5.5} \).

A.3. PES data analysis (figure 4)

The valence band PES spectra of GdBaCo\( _{2} \)O\( _{5.5} \) were calibrated in energy by fitting a Gaussian broadened Fermi function to Ag reference spectra taken under the same conditions immediately after and before. The Fermi energy is shown by a vertical line in figure 4. A constant background has been subtracted from each spectrum. For normalization, we divided each background-subtracted spectrum by the average of its spectral intensity in the energy range 2–3 eV.

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