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Electronic and magnetic properties of the kagome systems $YBaCo_4O_7$ and $YBaCo_3MO_7$ (M=Al, Fe)

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We present a combined experimental and theoretical x-ray absorption spectroscopy study of the class of cobaltates $YBaCo_4O_7$ and $YBaCo_3MO_7$ (M=Al, Fe). The focus is on the local electronic and magnetic properties of the transition metal ions in these geometrically frustrated kagomé compounds. For the mixed valence cobaltate $YBaCo_4O_7$, both the Co^{2+} and Co^{3+} are found to be in the high-spin state. The stability of these high-spin states in tetrahedral coordination is compared with those in the more studied case of octahedral coordination. For the compound $YBaCo_3FeO_7$, we find exclusively Co^{2+} and Fe^{3+} as charge states.

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Cobaltates are currently one of the most investigated classes of transition metal oxides. They show a rich collection of interesting physical phenomena, including superconductivity,[1] giant magneto resistance,[2] strong thermopower,[3] temperature-driven spin-state and metal-insulator transitions,[4] as well as spin-blockade behavior.[5,6] These astonishing physical effects are directly related to the charge, orbital, and spin degrees of freedom of the Co ions.

Some cobaltates also show a high degree of magnetic frustration.[7,8] Recently, a class of cobaltates was introduced[9] with the compound $YBaCo_4O_7$, which contains kagomé layers of tetrahedrally coordinated Co. The strong antiferromagnetic interactions combined with the geometry in the lattice in these compounds lead to magnetic frustration. It is most important to understand the local electronic and magnetic properties of such frustrated systems in order to model their magnetic behavior. Yet, very different values are suggested in the literature concerning the magnetic moments in $YBaCo_4O_7$. The first susceptibility measurements[9] yielded the large number of $5.8\mu_B$ per magnetic ion, but later experiments[10] gave only $2.2\mu_B$. One neutron study estimated $\mu_t=3.49\mu_B$ for the ordered moment in the triangular layer and $\mu_k=2.19\mu_B$ in the kagomé lattice,[10] while another[11] reported $\mu_t=1.66\mu_B$ and $\mu_k=1.68\mu_B$, respectively. It is perhaps *a priori* also not very clear what moments to expect theoretically since it is known, for example, that a Co^{3+} ion has the so-called spin state degree of freedom: it can be low spin (LS, $S=0$, nonmagnetic), intermediate spin (IS, $S=1$) or high spin (HS, $S=2$), depending on the details of the local crystal field.[12,13]

Here, we present a study of the local electronic properties of $YBaCo_4O_7$, and its variants $YBaCo_3AlO_7$ and $YBaCo_3FeO_7$, using soft x-ray absorption spectroscopy (XAS) at the Co and Fe $L_{2,3}$ edges. We critically examine the charge state of the ions as well as their separate orbital and spin contributions to the magnetic moment.

Single crystals of $YBaCo_3FeO_7$ and $YBaCo_3AlO_7$ were prepared by the floating zone technique in an image furnace. For the pure cobaltate $YBaCo_4O_7$, a solid-state reaction was used to obtain polycrystalline samples. All samples have been characterized by x-ray diffraction, magnetic measurements and electrical resistivity which are published elsewhere.[14–18] The materials are insulators and show highly frustrated magnetic properties. The XAS experiments were carried out at the Dragon beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan with an energy resolution of about 0.3 eV. The degree of linear polarization of the incident light was ~99%. Clean sample areas were obtained by cleaving the crystals *in situ* at pressures in the low 10^{-10} mbar range. The absorption of the $L_{2,3}$ edges of Co and Fe was recorded using the total electron yield method. The oxygen K edge XAS was also measured by using both the total electron and fluorescence yield method. The fluorescence detector was manufactured by Quantar Technology and is equipped with a grid and bias voltages to reject ions and electrons. CoO and Fe_2O_3 single crystals were also measured *simultaneously* to serve as energy reference for the Co and Fe $L_{2,3}$ edges, respectively.

Figure 1 contains the Co $L_{2,3}$ XAS spectra of $YBaCo_3AlO_7$, $YBaCo_3FeO_7$, and $YBaCo_4O_7$. The spectra are the result of the dipole-allowed Co $2p^63d^n \rightarrow 2p^53d^{n+1}$ absorption process. The spin-orbit coupling of the $2p$ core hole causes the largest splitting in the spectra: the appearance of the distinct L_3(≈780 eV) and L_2(≈795 eV) white lines can be associated with the $2p_{3/2}$ and $2p_{1/2}$ core hole final states, respectively. The intense peaks at about 5 eV above the Co white lines represent the $M_{4,5}$ absorption lines of barium, i.e., the Ba $3d^{10}4f^0 \rightarrow 3d^94f^1$ transitions. As the cobalt is of interest, we need to subtract the Ba signal using a reference material. For this the isostructural compound $YBaZn_3AlO_7$ was synthesized. Its Ba $M_{4,5}$ spectrum is shown at the bottom of Fig. 1. The inset displays the oxygen K XAS spectrum of $YBaCo_4O_7$ measured in total electron yield and fluorescence yield mode. The close similarity of the spectra collected by these two methods confirms that our measurements are indeed representative for the bulk material and are not plagued by possible surface effects.

Figure 2 shows the Co $L_{2,3}$ edge spectra with the Ba $M_{4,5}$ signal subtracted. Remnants of the subtraction produce small glitches at around 785 and 799 eV and are omitted from the

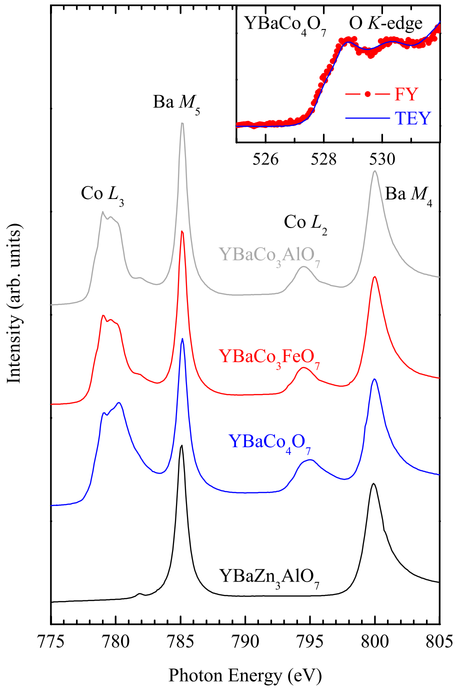

FIG. 1. (Color online) Experimental Co $L_{2,3}$ XAS spectra of $YBaCo_3AlO_7$, $YBaCo_3FeO_7$, and $YBaCo_4O_7$. The $YBaZn_3AlO_7$ spectrum shown at the bottom serves as a reference for the Ba $M_{4,5}$ edges. The inset depicts the oxygen K XAS spectrum of $YBaCo_4O_7$ collected by the total electron yield (TEY) and fluorescence yield (FY) methods.

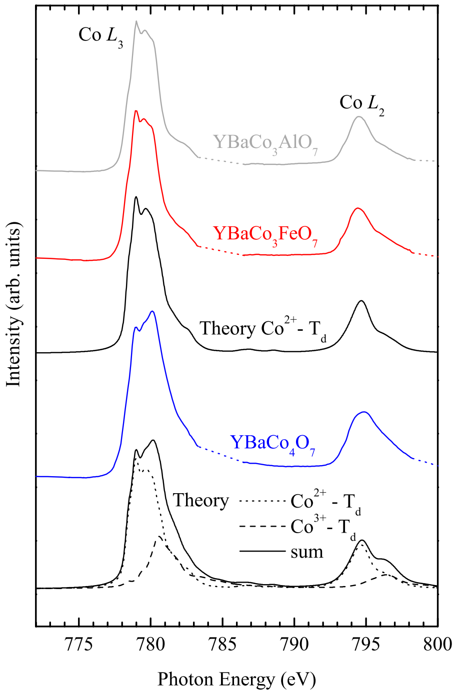

FIG. 2. (Color online) Experimental Co $L_{2,3}$ XAS spectra of $YBaCo_3FeO_7$, $YBaCo_3AlO_7$, and $YBaCo_4O_7$ after subtraction of the Ba $M_{4,5}$ white lines. The theoretical calculation for Co^{2+} in tetrahedral symmetry is to be compared with the experimental spectra of $YBaCo_3FeO_7$ and $YBaCo_3AlO_7$. The bottom curve depicts the weighted sum of a calculation for Co^{2+} and Co^{3+} as a simulation for $YBaCo_4O_7$.

curves. It can be seen that the spectra of $YBaCo_3AlO_7$ and $YBaCo_3FeO_7$ are practically identical, and that they are different from that of $YBaCo_4O_7$. We have also investigated the possible dependence of the spectra on the polarization of the light, but we found no indications for linear dichroism in these $YBaCo_3AlO_7$ and $YBaCo_3FeO_7$ compounds. It is interesting to note that all these spectra are very different from the ones reported for the more known Co compounds with CoO_6 coordination such as CoO,[19,20] $LaCoO_3$,[12] $LaMn_{0.5}Co_{0.5}O_3$,[21] $Ca_3Co_2O_6$,[22] Ca_3CoRhO_6,[22] and $La_{1.5}Sr_{0.5}CoO_4$.[6]

We first focus on the Co spectrum of $YBaCo_3AlO_7$. From the chemical formula, for which Al is known to be very stable as a nonmagnetic trivalent ion, one is expecting the Co to be in the divalent state. The fact that its spectrum is quite different from that of the divalent Co in CoO, must be sought in the very different local coordination: tetrahedral in $YBaCo_3AlO_7$ and octahedral in CoO. To prove this conjecture, we have carried out a simulation based on the successful configuration interaction cluster model that includes the full atomic multiplet theory and the local effects of the solid.[19,20] It accounts for the intra-atomic Co $3d$-$3d$ and $2p$-$3d$ Coulomb and exchange interactions, the atomic $2p$ and $3d$ spin-orbit couplings, the O $2p$-Co $3d$ hybridization, and the local crystal field. Here, we set up a CoO_4 cluster in T_d symmetry and used a negative value for the crystal field parameter $10Dq$ to represent the splitting between the low twofold e and the high-threefold t_2 orbitals. The cluster model calculations were done using XTLS 8.3.[20] The parameter values[23] are based on those already[24] known for bulk CoO.[19,20] The strength of the O $2p$-Co $3d$ hybridization was estimated using Harrison's description[25] for the experimental value of the Co-O bond length. The $10Dq$ value was tuned to fit the experimental spectrum. The simulation result is shown as the middle curve in Fig. 2. The model excellently matches the experimental spectrum. The negative value of $10Dq = -0.15$ eV, needed in the simulation, confirms the T_d symmetry of the local coordination of Co^{2+} in $YBaCo_3AlO_7$. The lack of any polarization dependence in the experiment is also fully consistent with the completely filled e and half-filled t_2 shell for a Co^{2+} in perfect T_d.

The striking similarity between the $YBaCo_3FeO_7$ spectrum with that of $YBaCo_3AlO_7$ suggests that all the Co ions are also divalent in $YBaCo_3FeO_7$. To fulfill the charge balance, the Fe ions must be trivalent. To confirm this, we have carried out XAS measurements on the Fe $L_{2,3}$ edges. The results are shown in Fig. 3, along with a reference for Fe^{2+} measured on FeO,[26] and Fe^{3+} taken from the Fe_2O_3 single crystal. The Fe spectrum of $YBaCo_3FeO_7$ is quite different from that of FeO. It is also appreciably dissimilar from that of Fe_2O_3, although the energy positions match quite well, strongly suggesting that Fe in $YBaCo_3FeO_7$ could indeed be trivalent. Similar to the case with Co, these deviations are caused by the fact that the local coordination is different: T_d in $YBaCo_3FeO_7$ vs O_h in Fe_2O_3. To clarify this point, we have carried out simulations for an Fe^{3+} ion in T_d symmetry, and the result is shown at the bottom of Fig. 3. The experi-

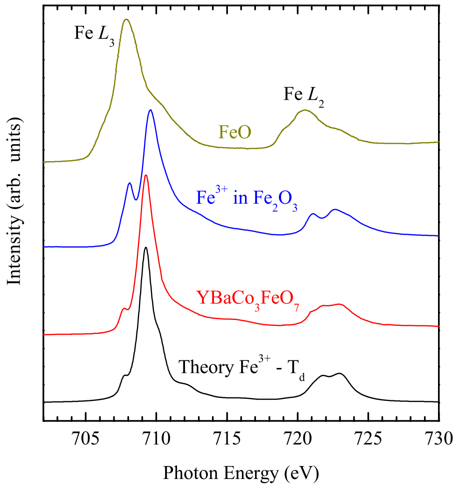

FIG. 3. (Color online) XAS spectrum on the Fe $L_{2,3}$ edges of $YBaCo_3FeO_7$. Reference spectra of Fe^{2+} in FeO(O_h) and Fe^{3+} in Fe_2O_3(O_h) are also given. The spectrum at the bottom is a simulation for Fe^{3+} in T_d symmetry.

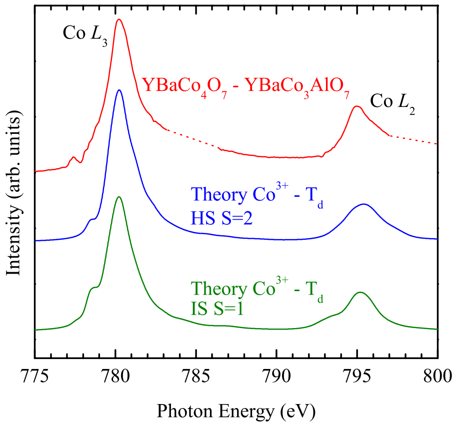

FIG. 4. (Color online) Experimental Co $L_{2,3}$ XAS spectrum of the Co^{3+} ion in $YBaCo_4O_7$ as extracted from the subtraction of the $YBaCo_4O_7$ spectrum with the $YBaCo_3AlO_7$ one in a 4:3 weight ratio. Theoretical simulations for the Co^{3+} ion in T_d symmetry are also included for the high-spin ($S=2$) and intermediate-spin ($S=1$) state cases.

mental spectrum can be excellently reproduced. This thus confirms that the Fe is trivalent. The parameter values[27] used are reasonable with a negative $10Dq(-0.35\text{ eV})$ for a T_d local coordination.

We now return to the Co spectrum of $YBaCo_4O_7$, which is a mixed valent compound, with a relation of 3:1 for $Co^{2+}:Co^{3+}$ as expected from the chemical formula. Here, the spectrum is constructed as an incoherent sum of the Co^{2+} and Co^{3+} simulations in T_d symmetry, weighted in a 3:1 ratio. We note that taking the sum incoherently is a reasonable approximation because the $YBaCo_4O_7$ compound is an insulator.[15,16] The final result is shown at the bottom of Fig. 2. The match between simulated and experimental spectra is very good. For this simulation we used the Co^{2+} parameters found for the $YBaCo_3AlO_7$ compound, and we set the Co^{3+} parameters[28] such that the $3d^6$ ion is in the high-spin state (HS, $S=2$).

As already explained above, a Co^{3+} ion can be HS, IS, or LS depending on the details of the local crystal field.[12,13] To study this aspect more in detail for the Co^{3+} ion in $YBaCo_4O_7$, we first made a subtraction of the $YBaCo_4O_7$ spectrum with the $YBaCo_3AlO_7$ spectrum weighted in a 4:3 ratio. The resulting difference spectrum is plotted in Fig. 4 and is meant to represent the Co $L_{2,3}$ XAS spectrum of the Co^{3+} ion in $YBaCo_4O_7$. We have carried out simulations for this Co^{3+} ion in T_d symmetry, and we have done so for the HS ($e^3t_2^3$, $S=2$) and IS ($e^4t_2^2$, $S=1$) cases, see Fig. 4. For the HS state, we have used $10Dq=-0.34$ eV, a modest and realistic value close to the -0.15 eV value found for the Co^{2+} ion in the $YBaCo_3AlO_7$ compound. The simulation is almost equal to the experimental spectrum. To reach the IS situation, we have to increase in absolute sense the $10Dq$ value. As will be explained later, the crossing between the HS and IS cases is at about $10Dq=-1.65$ eV, a very large and rather unphysical number since it is larger than what one could encounter in an O_h coordination.[12,29] For this particular IS simulation we have used -1.9 eV. The agreement with the experimental spectrum is reasonable, but there are distinct features in the simulation, such as the shoulder at 793 eV, which is not present in the experiment. We have not shown simulations for the LS ($e^4t_2^2$, $S=0$) state, since in T_d symmetry it is not possible to have the two spins of the t_2 electrons to be antiparallel. For the LS state to be stabilized, one would need a very strong local distortion such that the xy orbital in the t_2 shell is lowered by at least 0.7 eV with respect to the xz/yz to overcome the local Hund's exchange interaction. There is no experimental evidence for such strong distortions. We therefore can conclude that the Co^{3+} ion in $YBaCo_4O_7$ is most likely in the HS state.

Having established the local electronic structure and having obtained reasonable estimates for the size of the crystal fields, we now will look at the consequences for the local magnetic properties of Co^{2+} and Co^{3+} in T_d symmetry with the aid of full multiplet theory. The ground state of Co^{2+} in a tetrahedral crystal field is fourfold spin degenerate, as in first order the e subshell is completely filled and the t_2 subshell half-filled giving $S=3/2$, leaving no orbital degeneracy. This would also completely quench the orbital momentum. In second order, however, the on-site Coulomb and exchange interactions (multiplet effects) mix a certain amount of e electrons into the t_2 shell and restore the orbital momentum partially. This mixing depends on the relative size of the ligand field splitting and the spin-orbit coupling and does not *split* the ground state. But its energy is lowered and the total magnetic moment is enhanced by the orbital momentum. While in octahedral complexes the ligand field is often strong enough to suppress such second order effects, they play a role in tetrahedral coordination. In the calculation for Co^{2+}, the amount of orbital momentum is $0.5\mu_B$, increasing of the total magnetic moment to $3.5\mu_B$. In a magnetic susceptibility measurement, the effective moment at room temperature extracted from the Curie-Weiss law would be $\mu_{eff}=4.6\mu_B$ (the spin-only value is $3.9\mu_B$). Figure 5(a) shows that in T_d the lowest quartet $S=3/2$ state is stable over a wide range of negative $10Dq$ values. This is to be contrasted to the O_h case, in which for large enough positive $10Dq$ the

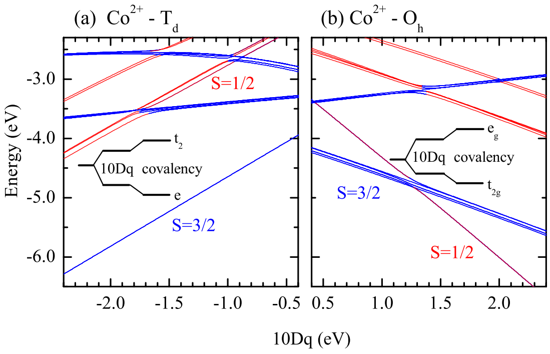

FIG. 5. (Color online) Energy level diagrams for Co^{2+} in a tetrahedral crystal field (panel (a), T_d, negative $10Dq$) and octahedral crystal field [panel (b), O_h, positive $10Dq$]. The full-multiplet calculations include covalency due to O $2p$-Co $3d$ hybridization.

ion converts from a $S=3/2$ into a $S=1/2$ system, see Fig. 5(b). Moreover, the $S=3/2$ state in O_h is not a simple quartet: it is consists of several closely lying sub-levels split by the spin-orbit interaction giving rise to a non-Curie-Weiss temperature dependence of the magnetic susceptibility.

The spin state of Co^{3+} has been intensively studied for the cubic and tetragonal local symmetries, but much less so for the tetrahedral case. Figure 6(a) shows the energy level diagram with the energy of the spin states depending on the ionic T_d crystal field splitting, including hybridization and spin-orbit coupling. For comparison, a diagram for the O_h coordination is shown on the right panel of Fig. 6(b). Both panels use the same value for $pd\sigma=-1.53$ eV. A crossing of the HS state ($t_{2g}^4 e_g^2$, $S=2$) to the LS state (t_{2g}^6, $S=0$) can be seen at $10Dq \approx 0.65$ eV for O_h symmetry. Such a crossing is also found in T_d symmetry, but at a significantly higher crystal field energy $10Dq \approx 1.65$ eV, and the ground state turns from a HS state ($e^3 t_2^3$, $S=2$) into a IS state ($e^4 t_2^2$, $S=1$). The LS ($S=0$) state is never the ground state in T_d as already explained above. The spin state found for $YBaCo_4O_7$ is HS, far away from the HS-IS crossing. A realization of the IS as a ground state for Co^{3+} in T_d is indeed very unlikely for two reasons. The first is that the crossing of the spin states occurs at much higher crystal field values than found for compounds with Co^{3+} in O_h coordination. The second reason is that it is difficult to generate such large crystal field values in T_d since the magnitude of the splitting in T_d is generally smaller than in O_h for identical bonding lengths between metal and ligand ions, as it can be seen from point charge calculations that $Dq(T_d)=-\frac{4}{9}Dq(O_h)$.[29]

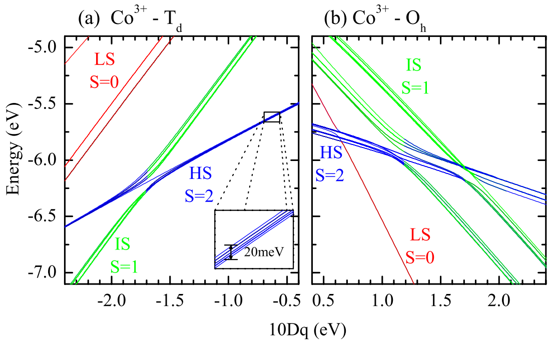

FIG. 6. (Color online) Energy level diagrams for Co^{3+} in a tetrahedral crystal field [panel (a), T_d, negative $10Dq$] and octahedral crystal field [panel (b), O_h, positive $10Dq$]. The full-multiplet calculations include covalency due to O $2p$-Co $3d$ hybridization.

The influence of the spin-orbit coupling on the Co^{3+} spin-state has been studied in detail for the octahedral case.[12] It was found that it plays a decisive role for the magnetic properties of $LaCoO_3$: the HS state with $S=2$ is split in three sublevels with $\tilde{J}=1,2,3$, the lowest of which is threefold degenerate and not fivefold as expected for a $S=2$. By contrast, the IS state with $S=1$ is split into $\tilde{J}=2$, 1, and 0, resulting in a lowest state, which is fivefold degenerate and not threefold as expected for a $S=1$. Recognizing these true degeneracies resolved much of the confusion concerning the interpretation of the magnetic susceptibility data.[12] The situation for a Co^{3+} ion in T_d is rather different. The stable HS with $S=2$ state is a ten-fold degenerate ^5E state if the spin-orbit coupling effects were absent. The presence of spin-orbit interactions will split this state into 4 singlets and 3 doublets. The energy splitting however, is rather small, not much larger than 15–20 meV in total, see inset in Fig. 6. For temperatures lower than about 20 K, the magnetic susceptibility will be quite complicated and will depend strongly on the magnitude of the applied field or effective molecular field in the solid. In the high-temperature regime, the magnetic susceptibility will be Curie-Weiss like corresponding to a ^5E ion. The effective moment at 300 K is then estimated to be $\mu_{eff}=5.1\mu_B$, close to the spin-only value of $4.9\mu_B$. The total effective moment estimated for $YBaCo_4O_7$ is $(\frac{3}{4}(4.6\mu_B)^2 + \frac{1}{4}(5.1\mu_B)^2)^{1/2}=4.7\mu_B$ per Co ion. If these moments would be ferromagnetically ordered without frustration, the ordered moment is $\frac{3}{4}3.5\mu_B+\frac{1}{4}4\mu_B=3.6\mu_B$.

To summarize, we have investigated the electronic properties of $YBaCo_3AlO_7$, $YBaCo_3FeO_7$, and $YBaCo_4O_7$ in detail. This was done by the use of XAS spectroscopy and the comparison to configuration interaction calculations. We have obtained estimates for the crystal fields and have determined the charge and spin states of the relevant ions. These findings allowed us to analyze reliably the local magnetic properties: in T_d symmetry the Co^{2+} ions have essentially the $S=3/2$ configuration, while the Co^{3+} are in the high-spin $S=2$ state. The reduced ordered moment of Co in $YBaCo_4O_7$ as seen from neutron scattering must therefore be related to magnetic frustration. Spin-orbit effects do induce an orbital moment in the magnetism of Co^{2+} in all three compounds, but will not lead to a large magnetic anisotropy as the tetrahedral structure is almost regular. For Co^{3+}, the spin-orbit induced splitting of the $S=2$ manifold could lead to an intriguing low-temperature magnetic behavior. For the $YBaCo_3FeO_7$ compound, we have determined the Fe charge state to be Fe^{3+}, meaning that Fe will act as a magnetic ion with spin-only moment in the compound. Evidently, this family of cobaltates is a good basis to study strongly interacting moments on a kagomé lattice.

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[27] FeO_4 cluster parameters [eV]: $\Delta=3.5$, $pd\sigma=-1.65$, $U_{dd}=5.0$, $U_{pd}=6.0$, $10Dq=-0.35$, Slater integrals 70% of Hartree-Fock values.

[28] CoO_4 cluster parameters for Co^{3+} [eV]: $\Delta=3.0$, $pd\sigma=-1.53$, $U_{dd}=5.5$, $U_{pd}=7.0$, $10Dq=-0.36$, Slater integrals 65% of Hartree-Fock values.

[29] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, 1962), p. 110.