Charge and Orbital Ordering and Spin State Transition
Driven by Structural Distortion in YBaCo$_2$O$_5$

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We have investigated electronic structures of antiferromagnetic YBaCo$_2$O$_5$, using the local spin-density approximation (LSDA) + U method. The charge and orbital ordered insulating ground state is correctly obtained with the strong on-site Coulomb interaction. Co$^{2+}$ and Co$^{3+}$ ions are found to be in the high spin (HS) and intermediate spin (IS) state, respectively. It is considered that the tetragonal to orthorhombic structural transition is responsible for the ordering phenomena and the spin states of Co ions. The large contribution of the orbital moment to the total magnetic moment indicates that the spin-orbit coupling is also important in YBaCo$_2$O$_5$.

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Recently, an interesting spin state transition of the Co$^{2+}$ ion in YBaCo$_2$O$_5$ has been reported by Vogt et al. [1] using the neutron powder diffraction (NPD) measurements. The transition is induced by the long-range orbital and charge ordering of Co$^{2+}$/Co$^{3+}$ ions. The ordered oxygen-deficient double perovskite RBaCo$_2$O$_{5+y}$ (R = rare-earths) [2] has attracted much attention as a new spin-charge-orbital coupled system like manganites and also as a new Co-based colossal magnetoresistance (CMR) material. Indeed, giant magnetoresistance are observed for $R$=Gd and Eu, (ρ$_{H}$-$\rho_{\perp}$)/ρ$_{0}$ = 41% and 40% for GdBaCo$_2$O$_{5.4}$ and EuBaCo$_2$O$_{5.4}$, respectively [3].

In the paramagnetic phase, YBaCo$_2$O$_5$ is crystalized in the tetragonal structure of the space group $P4/mnm$. It consists of double CoO$_5$ square base pyramidal backbone layers along the c-axis in which Y and Ba layers intervene alternatively and oxygens are deficient exclusively from the Y layers [4,5]. According to the valency consideration, Co$^{2+}$ and Co$^{3+}$ ions coexist similarly as the Mn$^{3+}$/Mn$^{4+}$ covalency in hole-doped La$_{1-x}$Sr$_x$MnO$_3$. Below $T_N \sim 330$ K, YBaCo$_2$O$_5$ undergoes a G-type antiferromagnetic (AFM) transition and the lattice changes slightly from the tetragonal to orthorhombic structure [6]. At $T_{CO} \sim 220$ K, a pronounced upturn is observed in the resistivity indicating that another transition takes place, i.e., the long-range charge and orbital ordering of Co$^{2+}$/Co$^{3+}$ ions. The stripe type charge ordering is formed in the ab plane. Further, the spin state of the Co$^{2+}$ ion changes from the low to high spin across $T_{CO}$, which is evidenced by the increased magnetic moment per Co ion from $2.10 \mu_B$ at 300 K to $3.45 \mu_B$ at 25 K. More recently, for the isostructural HoBaCo$_2$O$_5$, essentially the same features are observed of $T_N \sim 340$ K and $T_{CO} \sim 210$ K [7].

The phenomenon of the spin state transition is observed usually in cobaltates such as LaCoO$_3$ and La$_{1-x}$Sr$_x$CoO$_3$. In LaCoO$_3$, the magnetic ground state of Co$^{3+}$ ion corresponds to the low spin (LS) state with $t^0_{2g}$ (0). Upon heating, a successive spin state transition to an intermediate spin (IS) state and then to a high spin (HS) state occurs [8]. Note that, distinctly from the case in LaCoO$_3$, the spin state transition in YBaCo$_2$O$_5$ seems to occur for Co$^{2+}$ ion. In fact, this issue is still controversial. Based on the reduction of the magnetic susceptibility below 220K, Akahoshi and Ueda [9] suggested that the AFM transition takes place at $T \sim 220$ K which is associated with a spin state transition of Co$^{3+}$ from the HS to LS state upon cooling. Thus, the nature of the spin state transition and the interplay of the spin state with the charge and orbital ordering are still unclear.

To reveal the mechanism of the spin state transition as well as the charge and orbital ordering, we have explored the electronic structure of the G-type AFM YBaCo$_2$O$_5$ using the local-spin density approximation (LSDA) + $U$ scheme implemented in the linearized muffin-tin orbital band method [10].

We have employed two structural data of nearly tetragonal structure at 300 K (L1) and orthorhombic structure at 25 K (L2) [11]. In the L1 structure, all the Co sites have an equal average bond length of $d$(Co-O) = 1.97 Å. Whereas in the L2 structure, there are two different kinds of Co sites, CoI and CoII. The bond length at CoI sites is extended to $d$(Co-O) = 2.03 Å and that at CoII sites becomes shortened to $d$(CoII-O) = 1.92 Å. The G-type AFM spin order is assumed in all our calculations.

In Fig. [12] we have compared the LSDA Co 3$d$ partial density of states (PDOS) for the L1 and L2 structures. Most notable is the change of the exchange splitting which becomes larger for CoI site and smaller for CoII in L2 than that for CoI in L1. This indicates that, due to the lattice distortion, 3$d$ electrons in L2 becomes more localized for CoI and less localized for CoII in comparison to those for CoI in L1. The calculated spin magnetic moments are $\mu_S = 1.68 \mu_B$ and $0.95 \mu_B$ for each CoI and CoII site, respectively, in L2 and $\mu_S = 1.13 \mu_B$ for Co in L1. The sizes of the spin moments are consistent with the degree of 3$d$ electron localization. Hence, the LSDA gives a qualitatively good information about the structural transition effects on Co 3$d$ electron states. The LSDA, however, yields an incorrect metallic ground state which pertains even after the structural transition from the L1 to L2 structure. This is different from the experiment which shows unambiguously the semiconducting
The calculated charge occupancies of Co 3d orbitals (electrons) and magnetic moments \((\mu_B)\) of YBaCo\(_2\)O\(_5\) in the LSDA + \(U\) method.

| \(t_{2g}^{\uparrow}\) | \(e_g^{\uparrow}\) | \(t_{2g}^{\downarrow}\) | \(e_g^{\downarrow}\) | \(\mu_S\) | \(\mu_L\) | \(\mu_{tot.}\) | \(\mu_{exp.}\) |
|-----------------|-----------------|-----------------|-----------------|----------|----------|----------|----------|
| 2.98            | 1.99            | 2.02            | 0.37            | 2.61     | 1.04     | 3.65     | 4.2\(^a\) |

\(\mu_{exp.}\) \((\sigma^a)\) \(3.7^b\) \((\mu_B)\) \(2.7^a\) \((\mu_B)\)

\(^{a}\) Reference \(\text{[1]}\).

\(^{b}\) HoBaCo\(_2\)O\(_5\) in Ref. \(\text{[2]}\). The assignment of the magnetic moments to each Co ion is corrected (see text).
method. For Co$^{2+}$ ion, the spin and orbital magnetic moments are $\mu_S = 2.61\mu_B$ and $\mu_L = 1.04\mu_B$, respectively, and for Co$^{3+}$ ion, $\mu_S = 1.84\mu_B$ and $\mu_L = 0.40\mu_B$. The orbital moment of Co$^{2+}$ ion is as much as that of CoO[12,13], and the orbital moment of Co$^{3+}$ is comparable to that of NiO[10,14]. The non-negligible orbital moment, which originates from the localized nature of Co 3d electrons, suggests that YBaCo$_2$O$_5$ should fall in a class of strongly correlated electron system like CoO and NiO. The calculated total magnetic moments of $\mu_{tot} = 3.65\mu_B$ and $2.24\mu_B$ for Co$^{2+}$ and Co$^{3+}$ ion, respectively, are only slightly smaller than the experimental values. Evidently, this interpretation will also be valid for HoBaCo$_2$O$_5$. Suard et al. have improperly assigned the NPD measured $\mu_{exp} = 3.7\mu_B$ and $2.7\mu_B$ in HoBaCo$_2$O$_5$ to Co$^{3+}$ and Co$^{2+}$ ion, respectively. However, their assumptions of spin-only moments and the HS states for both Co$^{2+}$ and Co$^{3+}$ ions are discarded by the present results. To test the calculated results, more experimental works like the x-ray scattering measurement are encouraged, in which separate determination of the spin and orbital moments are possible.

In Fig. 4, we have plotted the geometry of the orbital ordering which is obtained from the orbital dependent occupancy of the 3d minority-spin states at each Co site. At Co$^{2+}$ sites, the orbitals are aligned along $a$-axis, while at Co$^{3+}$ sites, the orbitals are along $b$-axis. This feature is understandable by considering that the bond length of $d$(Co$^{2+}$-O) is larger in $a$-axis than in $b$-axis and vice versa for that of $d$(Co$^{3+}$-O). As for the charge ordering configuration, Co$^{2+}$ and Co$^{3+}$ chains of a stripe type are formed in the $ab$ plane along $b$-axis, which are alternating in the $a$ and $c$ direction. This is in contrast to the charge ordering observed in the isostructural YBaMn$_2$O$_5$. In YBaMn$_2$O$_5$, the Mn$^{2+}$/Mn$^{3+}$ orders in a checkerboard type. This difference gives rise to the different magnetic structures: G-type AFM phase for YBaCo$_2$O$_5$ and G-type ferrimagnetic phase for YBaMn$_2$O$_5$. The theoretical result of the charge and orbital ordering geometry coincides with the experimentally proposed one. Thus, it can be inferred that the deformed bond lengths of $d$(Co-O) determine the charge and orbital ordering geometry.

The G-type AFM ordering in YBaCo$_2$O$_5$ is consistent with...
The electron-phonon interaction effects in YBaCo$_2$O$_5$ is urgently demanded.

In conclusion, we have performed the LSDA + U calculations for a new spin-charge-orbital-lattice coupled system YBaCo$_2$O$_5$. It is found that the Co$^{2+}$/Co$^{3+}$ charge and orbital ordering and the Co$^{2+}$ HS state transition are closely correlated with the lattice distortion from the tetragonal to orthorhombic structure. The orbital moment has a substantially large contribution to the total magnetic moment. All of the effects of the Coulomb correlation, the spin-orbit coupling, and the electron-phonon interaction should be properly taken into account to understand physical properties of YBaCo$_2$O$_5$.

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FIG. 4. The orbital ordering geometry of the occupied minority-spin states at each Co site. At Co$^{2+}$ sites, 3$d$ orbitals are aligned along the $a$-axis while at Co$^{3+}$ sites, along the $b$-axis.