

Metal-insulator transition induced by a spin-state transition in TbBaCo₂O_{5.5} from first-principles

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Abstract – First principles calculations using the APW+lo method, as implemented in the WIEN2k code, has been used to investigate the structural, electronic and magnetic properties of TbBaCo₂O_{5.5} with the temperature variation, especially as regards the spin-state (SS) transition. The oxygen-deficient perovskite structure of the compound has alternating CoO₆ octohedral and CoO₅ pyramidal chains along the y-axis. Both the pyramidal and octahedral parts are significantly distorted in the insulating phase below T_{MI}. Furthermore, the relationship between metal-insulator transition and the SS transition is also discussed. The SS of Co³⁺ ions with octahedral coordination are from diamagnetic ($t_{2g}^6 e_g^0$, S=0) to paramagnetic ($t_{2g}^4 e_g^2$, S=2) as the temperature increase, while ones with pyramidal coordination still keep the intermediate SS (IS, $t_{2g}^5 e_g^1$, S=1) independent of the temperature. Magnetic structure in the high-temperature magnetic phase consists of ferromagnetic and G-type antiferromagnetic components, while in the low-temperature phase only the G-type component exists with a $d_{3x^2-r^2}/d_{3y^2-r^2}$ -type orbital ordering pattern.

In recent years there has been an upsurge of interest in perovskite-like transition metal oxides as their wide physical properties such as electronic transport and magnetism [1]. It has been recognized that the charge, spin, and orbital degrees of freedom play important roles in the electronic and magnetic properties of these compounds. Especially, cobalt-containing oxide compounds shows many interesting phenomena such as metal-insulator transition, giant magnetoresistance, complicated charge and spin ordering, which coupled with the orbital ordering (OO) on the background of Co³⁺ SS transitions [2].

One of the classical examples of the oxygen-deficient structure is TbBaCo₂O_{5.5} [3], which contain double layers of the CoO₆ octahedral and the CoO₅ pyramids separated by Tb³⁺ (Fig.1). The crystal structure, especially distortion of the CoO₆ octahedral, has significant effects on the orbital as well as spin ordering. The compound shows a prominent MI transition at T_{MI} ≈ 340K [4] and a $d_{3x^2-r^2}/d_{3y^2-r^2}$ -type OO (if the Co³⁺ ions take the IS) in insulating phase was concluded by the neutron and synchrotron radiation (SR) x-ray powder diffraction measurement. This OO was ascribed to an alternation of the Co-O bond length $d_{Co-O(b)}$ along the b axis. However, despite intensive experimental investigations for SS and charge-orbital ordering phenomena, the detailed pattern or even the existence of the charge ordering in TbBaCo₂O_{5.5}, or in general the relationship between charge-orbital ordering and spin ordering is still not fully resolved.

We have preformed systematic GGA and GGA+U calculations for the oxygen defect double perovskite transition-metal oxide TbBaCo₂O_{5.5}. We conclude that TbBaCo₂O_{5.5} is an insulator at T<340K. While the screening of the e_g orbitals is so effective that the total charge disproportion and the derivation of magnetic moments is rather small. The analysis of spin density plot and density of states inevitably demonstrates the $d_{3x^2-r^2}^2 / d_{3y^2-r^2}^2$ OO of Co³⁺ cations. The OO corresponds to the local distortions toward the apical oxygens coordination. In addition, the $d_{3x^2-r^2}^2 / d_{3y^2-r^2}^2$ OO is responsible for the stability of the G-type antiferromagnetic spin ordering pattern.

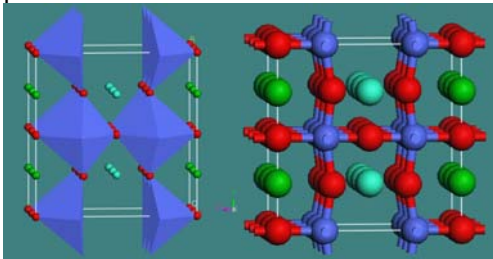


Fig.1. Crystal structure for TbBaCo₂O_{5.5}.

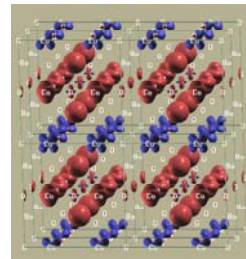


Fig.2. Spin density plot.(isosurface at 0.15 e/Å³ produced using XCRYSDEN)

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