A Theoretical Study on Superexchange Interaction in KCoF₃ and Cs₁₋ₓNaₓMn⁡⁺(CN)₃ by Chemical Bonding Rule

Taku ONISHI

Department of Chemistry for Materials, and The Center of Ultimate Technology on nano-Electronics, Mie University
1577 Kurimamachiya-cho, Tsu, Mie 517-8507, Japan
e-mail: taku@chem.mie-u.ac.jp

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Previously, we demonstrated that Cs₁₋ₓNaₓMn⁡⁺(CN)₃ prussian blue analog exhibits high-efficient cesium adsorption, through the ion-exchange between cesium and sodium ions under applied voltage. In this study, we investigated the superexchange interaction between manganese atoms via cyano-ligand, by the use of chemical bonding rule.

Keywords: Cesium adsorbent, Prussian blue analog, Chemical bonding rule, Hybrid Kohn-Sham DFT, Superexchange interaction

1 Introduction

We already reported that Cs₁₋ₓNaₓMn⁡⁺(CN)₃ prussian blue analog exhibits the high-efficient cesium adsorption, through the ion-exchange between cesium and sodium ions under applied voltage [1–3]. Chemical bonding analysis was performed for molecular orbitals related to cesium and sodium ions, by the use of chemical bonding rule [4,5]. It was concluded that sodium ion-conduction is responsible for ionic bonding between sodium ion and others. In this study, we investigate the superexchange interaction between manganese atoms via cyano-ligand, by the use of chemical bonding rule. As the simple case, we first investigated KCoF₃ perovskite [6].

2 Calculation

The calculations presented here were performed using the BHHLYP hybrid Kohn–Sham density functional theory (DFT) method [7], which properly reproduces electronic structures of transition metal compounds [4,5]. All calculations were performed with the GAMESS program [8]. The molecular orbitals were plotted using MOLEKEL 4.3 [9]. We constructed Co₄F₄ model for KCoF₃ perovskite and MnNCMn model for Cs₁₋ₓNaₓMn⁡⁺(CN)₃ (see Figure 1).

3 Chemical bonding rule

Molecular orbital analysis is very useful to examine chemical bonding formation. Chemical bonding rule can be applicable to judge chemical bonding character (covalency or ionicity).

1. In molecular orbitals including outer shell electrons, check whether the orbital overlap exists or not.
2. With orbital overlap, the bonding character is covalent. Without orbital overlap, it is ionic.
Results and Conclusions

The superexchange interaction in KCoF$_3$

Figure 2 shows the schematic drawing of the antiferromagnetic interaction between cobalt atoms via fluorine atom. The cobalt spin configuration is $t_{2g}^5e_g^2$ ($S = 3/2$). It was found that cobalt $3d_{x^2-y^2}$ alpha (beta) orbital forms covalent bonding with fluorine 2p alpha (beta) orbital in Co$_4$F$_4$ model, from chemical bonding rule (see Figure 2). As the result, cobalt up-spin and down-spin alternately exist in cobalt atoms of Co$_4$F$_4$ model. Hence, the antiferromagnetic interaction between cobalt $3d_{x^2-y^2}$ orbitals via fluorine 2p orbital is caused.

The superexchange interaction in Cs$_{1-x}$Na$_x$Mn$^{II}$(CN)$_3$

In the case of Cs$_{1-x}$Na$_x$Mn$^{II}$(CN)$_3$, as the bridge-cyano ligand consists of two atoms, the chemical bonding formation between carbon and nitrogen should be also considered. The manganese spin configuration is $t_{2g}^3e_g^2$ ($S = 5/2$). It was found that manganese $3d_{x^2-y^2}$ alpha (beta) orbital forms covalent bonding with carbon 2p orbital (nitrogen 2p orbital), and covalent bonding is formed between carbon 2p orbital and nitrogen 2p orbital in MnNCN model, from chemical bonding rule (see Figure 3). As the result, manganese up-spin and down-spin alternately exist in MnNCN model. Hence, the antiferromagnetic interaction between $3d_{x^2-y^2}$ orbitals via cyano-ligand is caused.

References

[9] Ugo Varetto, <MOLEKEL 4. 3. >; Swiss National Supercomputing Centre: Manno (Switzerland)