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Theoretical Study on Necessary Conditions for Reversible Photoinduced Magnetization: Cobalt-Iron Cyanide System

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We study metastability of the Cobalt-Iron Prussian blue compound. DFT calculations are performed for model clusters (a) $(NC)_5$-Fe-CN-Co-$(NC)_5$ and (b) $(NC)_5$-Fe-CN-Co-$(NC)_3$ $(H_2O)_2$ and the energy difference between the low spin state ($S = 0$) and the high spin state ($S = 1$) is estimated. Correction due to impurity effect is evaluated and screening effect in a solid state is also discussed.

Keywords: photoinduced magnetization; cobalt-iron cyanide; DFT calculation; Prussian blue compound

INTRODUCTION

Active controls of spin properties by chemical and physical techniques have been investigated extensively. Prussian blue type magnetic materials $A_lM'_m[M(CN)_6]_n(H_2O)_y$ [1-5] are very interesting because of several reasons: high transition temperature (T_c), varieties of transition metal combinations (M, M'), tunable magnetism, etc. Especially, reversible photoinduced magnetization observed in cobalt-iron cyanide (the formula is $K_{0.2}Co_{1.4}[Fe(CN)_6] \cdot 6.9H_2O$ or $K_{0.4}Co_{1.3}[Fe(CN)_6] \cdot 5H_2O$) by O. Sato et al [6, 7] has received much attention.

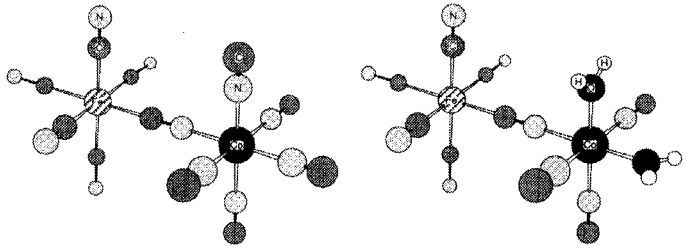
In our previous study [8-10], UHF and DFT calculations using the triple-

zeta basis sets were performed in order to elucidate the signs and magnitudes of the effective exchange integrals $J_{MM'}$ of cluster models of Prussian blue analogs. We showed that the signs of effective exchange integrals $J_{MM'}$ predicted from the symmetry rules and the ab initio calculations are consistent with the experimental values. We also revealed that having cyano groups surrounding the transition metal ions is essential for the $J_{MM'}$ integrals between the transition metal ions and magnetic phase transition temperatures T_c and $J_{MM'}$ values by DFT are reasonably close to those of experiments.

As a continuation of previous work, we here focus on the Cobalt Iron Prussian blue compound and study the metastability of this system. It is found from the experiments that the electronic states of Fe and Co change from Fe (t_{2g}^6, $S = 0$) and Co (t_{2g}^6, $S = 0$) (stable state, referred to LS) to Fe (t_{2g}^5, $S = 1/2$) and Co ($t_{2g}^5 e_g^2$, $S = 3/2$) (metastable state, referred to HS) by irradiation and reversible magnetization is possible. It is indicated that impurity H_2O ligands play the important role of this phenomenon [11]. The average coordination number of NC to a cobalt ion is less than 6, i.e., 4.3 or 4.6 and residual 1.7 or 1.4 sites can be occupied by H_2O ligands. Here the following scenario can be considered. This reduction allows the high spin state to get close to the low spin ground state because H_2O gives weaker crystal field than NC and makes the high spin state more stable. Consequently, the ideal relation of the energies are realized. We examine the difference of energies between LS and HS. In addition, correction by H_2O ligands is estimated and screening effect in a solid state is also investigated.

Method

We treated two types of cluster models shown in Fig. 1. In model (a) Fe and Co are surrounded by only CN or NC ligands, while in model (b) two impurity ligands H_2Os are included. We perform DFT(mUS2VWN) calculations by the use of triple-zeta (TZ) basis sets. Calculations are carried out using GAUSSIAN 94 [12] program package. We estimate occupation numbers of t_{2g} and e_g orbitals, spin densities and energy gaps between HS and LS for models (a) and (b).



(a) (b)

Figure 1. Cluster models of Co-Fe Cyanide. Model (a) includes no impurity ligands while model (b) includes impurity ligands.

Results and Discussion

A few electrons flow into vacant d orbitals from lone pairs of ligands (Figs 2 and 3). Charge densities of Fe(II) and Co(III) in LS are reduced to 0.94 and 1.57, respectively and those of Fe(III) and Co(II) in HS are reduced to 1.48 and 1.44 in the same way, while spin densities of Fe(II) and Co(III) in LS are 0.0 and 0.0 and those of Fe(III) and Co(II) in HS are –1.1 and 2.8, where the expected configurations are obtained. Figure 4 shows energies versus unit cell parameters (d(M-M)Å). Optimal unit cell parameters d(M-M) in LS and HS by calculations are a little larger than those by experiments but the difference of them is reasonably reproduced. The lowest energy of HS in the model (a) is found to be lower than that of LS by 1.64 eV contrary to our expectation. Furthermore for the model (b) the difference grows into 3.3 eV and this result apparently seems to be inconsistent with the experimental results. Here another dominant factor should be considered. Correction of on-site coulomb energy (U) is necessary. U in a crystal is generally smaller than that in an isolated molecule because of screening effect. In this case overestimated Ut_{2g}(Fe) and Ut_{2g}(Co) contribute to the instability of LS. We define following quantities to correct the energy difference. Δ_1 = 1.64 eV: energy difference between LS and HS of the model Co (a), Δ_2 = 3.3-1.64 = 1.66 eV: ligand effect, ΔUt_{2g}(Fe): correction of Ut_{2g}(Fe), ΔUt_{2g}(Co): correction of Ut_{2g}(Co), $\Delta \equiv -\Delta_1 - \Delta_2 + \Delta Ut_{2g}(\mathrm{Fe}) + \Delta Ut_{2g}(\mathrm{Co}) = -3.3 + \Delta Ut_{2g}(\mathrm{Fe}) + \Delta Ut_{2g}(\mathrm{Co})$: the

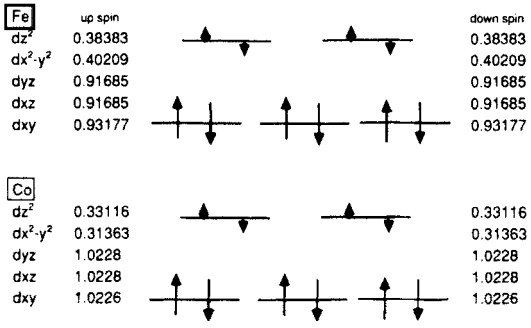


Figure 2. Occupation number of each d orbital for LS in the optimal d(M-M).

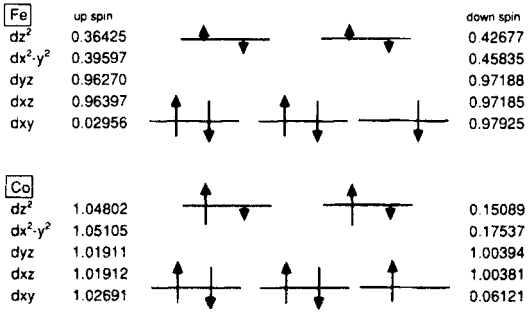


Figure 3. Occupation number of each d orbital for HS in the optimal d(M-M).

corrected energy difference. ΔU(M) is estimated at about 10 eV using LSDA between a isolated atom and a solid in transition metal oxides [13]. In this case between a small cluster and a solid ΔU(M) should be less than 10 eV but is still large value and the sign of the energy difference can be reversed. Probably Δ_1 and Δ_2 are comparable to $\Delta U t_{2g}$(Fe) + $\Delta U t_{2g}$(Co) for the Cobalt-Iron Prussian blue compound and an ideal relation ($0 < \Delta < 1$ eV) is realized. Figure5 illustrates a modified potential curve by consideration of the ΔU and other ligand effects. Of course this is only a necessary condition but not a sufficient condition for the reversible switching [14]. Estimation of ΔU(M) is difficult in this stage but it will become

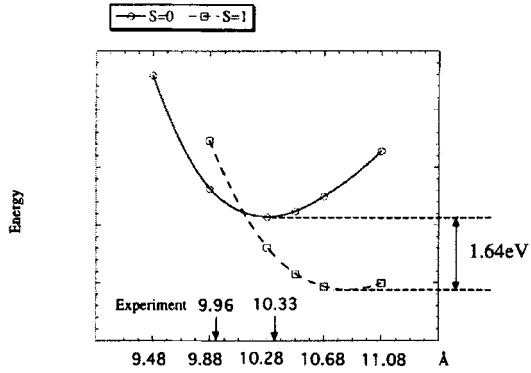


Figure 4. Energy curves of LS and HS of the model (a).

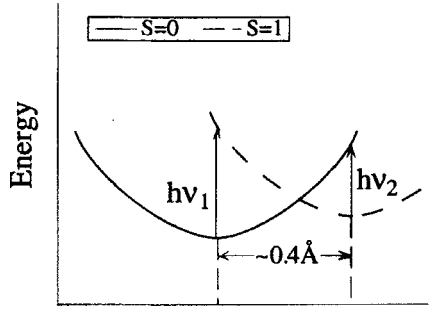


Figure 5. Modified curves of LS and HS of the model (a)

possible to estimate approximately in the near future by calculating energies and *U*s of larger clusters changing the size of them.

Concluding Remarks

We estimated the energy difference of the low spin state and the high spin state of cluster models (a) and (b) of the Cobalt-Iron Prussian blue compound. It was found that the effect of impurity ligand H_2O is not negligible and makes the high spin state more stable. It is necessary to estimate the other main factor of screening effect in order to determine the subtle

difference precisely. This factor makes the low spin state more stable. From a microscopic viewpoint, these two competing factors are essential to the stubborn metastable structure.

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