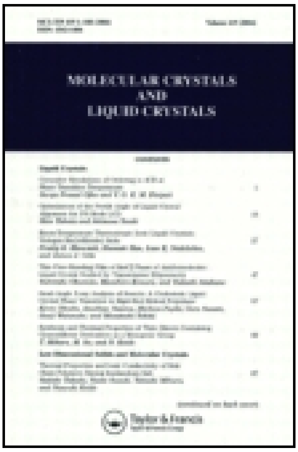

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Theoretical Study of the Charge Transfer Absorption in Cobalt-Iron Cyanide

Tohru Kawamoto [a] , Yoshihiro Asai [a] & Shuji Abe [a]
[a] Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, 305-8568, Japan

To cite this article: Tohru Kawamoto, Yoshihiro Asai & Shuji Abe (2002): Theoretical Study of the Charge Transfer Absorption in Cobalt-Iron Cyanide, Molecular Crystals and Liquid Crystals, 376:1, 423-429

To link to this article: http://dx.doi.org/10.1080/10587250210774

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 423-429
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00

Theoretical Study of the Charge Transfer Absorption in Cobalt-Iron Cyanide

TOHRU KAWAMOTO, YOSHIHIRO ASAI and SHUJI ABE

Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305-8568, Japan

The photo-induced charge transfer followed by the bidirectional phase transition in Fe-Co Prussian blue compounds is theoretically discussed. The result of *ab initio* calculations indicates that both the forward and backward transitions are triggered by photo-induced charge transfer excitations between Co-$d\gamma$ and Fe-$d\varepsilon$ orbitals, although different kinds of Co sites are excited. It is concluded that the charge transfer proceeds by way of the $sp\sigma$-$p\pi$ transition on the nitrogen atom, which can explain such a long range charge transfer between Co and Fe separated by about 5Å.

Keywords: photo-induced phase transition; charge transfer; photo-absorption; *ab initio* calculation.

INTRODUCTION

A reversible photo-induced magnetization was first discovered in a cobalt-iron Prussian blue analogue, $K_{0.4}Co_{1.3}Fe(CN)_6 \cdot 5H_2O$[1, 2, 3]. Illumination of visible light (500 - 700 nm) at low temperature induces a bulk magnetization, which can be diminished by illumination of near-IR light (1319 nm). We proposed that the novel mechanism of the photo-induced phase transition with the *ab initio* band calculations and the cluster calculations in the previous work[4, 5, 6].

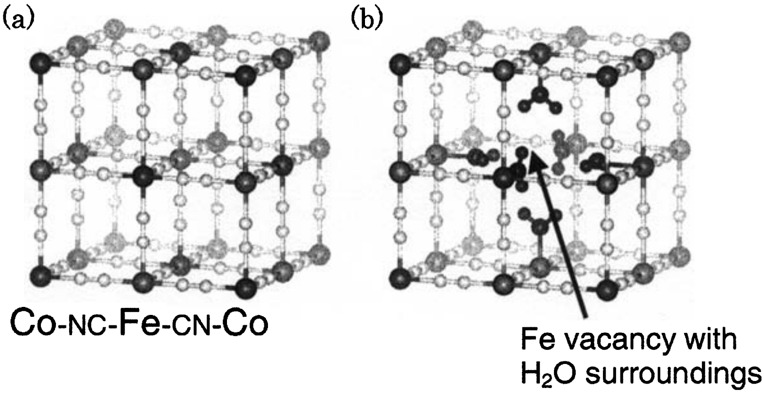

FIGURE 1 Crystal structure of $A_yCo[Fe(CN)_6]_x$ neglecting alkali metals: (a) $x = 1$; (b) $x < 1$. In (b), there is an vacancy at an iron site surrounded by six water molecules substituting cyano anions.

On the basis of our proposal, here we discuss much more details of photo-induced charge transfer triggering such a exotic phenomenon.

PHOTO-INDUCED MAGNETIZATION

The crystal structure of the compound $A_yCo[Fe(CN)_6]_x$ is shown in Fig. 1, where A represents alkali metal. Fe and Co form a lattice of the NaCl structure, while cyano groups are located between Fe and Co. In the case of $x < 1$, there are vacant Fe sites, for which the surrounding six cyano groups are replaced by water molecules (Fig. 1(b)). This implies that the cyano groups octahedrally surrounding a Co atom are partially substituted by water molecules depending on the number of nearest neighbor Fe vacancies.

The ligand substitution changes the relative stability between the low spin (LS) state and the high spin (HS) state[4, 5]. The depen-

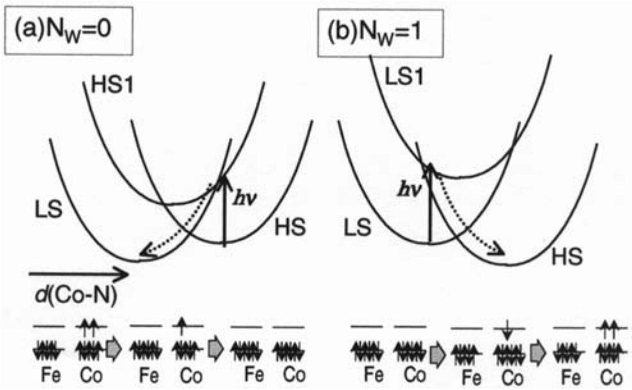

FIGURE 2 Schematic potentials of the cobalt-centered clusters with (a) N_W=0 and (b) N_W=1. Possible primary relaxation paths for the LS→HS and HS→LS transitions are indicated by arrows in (b) and (a), respectively. LS1 and HS1 represent the intermediate state in each transition. Solid and dotted arrows represent photo-excitation and relaxation with intersystem crossing.

dence of the stability of each spin state on the number of cyano groups can be represented by 'cluster potentials'[6] derived for a model cluster consisting of a cobalt ion and its six ligand cyano groups. To take into account the partial substitution of ligands by water molecules, we consider various numbers N_W of H_2O substitutions. The energies are calculated for each value of Co-N bond length, d(Co-N), common to all the Co-N bonds.

Figure 2 schematically shows calculated cluster potentials as functions of d(Co-N) for $N_W = 0$ and 1[6]. The lower part of Fig. 2 indicates the transition process on the d-orbitals of both Co and Fe. The LS and HS states are converted to the intermediate states by photo-induced charge transfer (CT) between iron and cobalt atoms, and then to the final states HS and LS by intersystem crossing due to spin-orbit coupling at cobalt sites. We find in the obtained potential that the structural difference between the LS and HS states lies in the d(Co-N), which is longer by about 0.2Å in HS than in LS. This implies that the transition between LS and HS states requires a volume change, which may be a major origin of a large energy barrier between the two states.

We also obtained the Frank-Condon excitation energies of the CT excitations. The calculated excitation energy $\sim$ 2.3 eV of LS→LH1 in Co(N_W=1) reasonably corresponds to the observed absorption energy 2.4 eV inducing the magnetization. This implies that the photo-induced LS→HS transition is triggered by CT excitation mainly between a Co atom with N_W=1 and a nearby Fe atom. The reverse (HS→LS) transition experimentally required near-IR irradiation($h\nu$ $\sim$ 0.9eV). We assign it to the excitation energy of Co(N_W=0) at $\sim$0.8 eV. This implies that the HS→LS transition is triggered mainly by the excitation of Co atoms with N_W=0, in contrast to the forward transition.

CT-ABSORPTION THROUGH NITROGEN ATOMS

We have concluded that both the forward and the backward transition are triggered by the photo-induced charge transfer between the Co-$d\gamma$ and the Fe-$d\varepsilon$ orbitals. Hereafter we discuss the process of the charge transfer. The direct transition probability seems to be small because Co and Fe atoms are about 5Å away due to the insertion of the cyano group. However, we can obtain helpful information from our *ab initio* band structure calculations with full potential augmented plane wave method[4].

Figure 3 represents the partial density of states in muffin tin sphere around each atom in the LS state without vacancies. It is found that the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) respectively consist of Co-$d\gamma$ orbital and Fe-$d\varepsilon$ one, with hybridization with the nitrogen-p

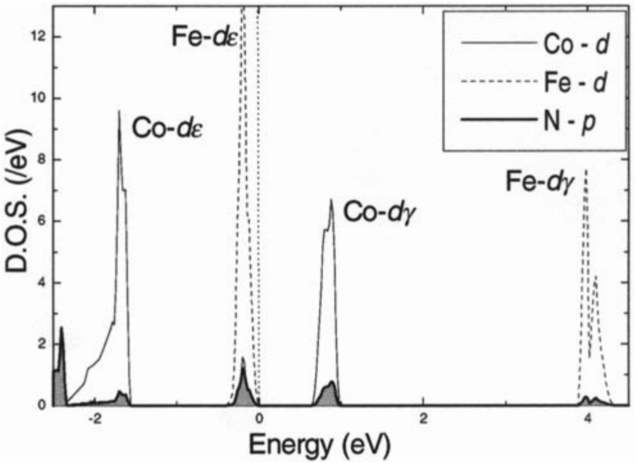

FIGURE 3 Partial densities of states in Co-Fe cyanide around the Fermi energy, $E_F=0$. The component of p-orbital on nitrogen atoms is shaded.

component. The hybridization pattern is shown in Fig. 4 more apparently. It is found that the Fe-$d\varepsilon$ and Co-$d\gamma$ orbitals are strongly connected with the N-$p\pi$ and N-$sp\sigma$ orbitals, respectively. The distinction is caused by the symmetry difference of the main component of each orbitals on the transition metals. The dotted line in Fig. 4 shows the four-fold axis, for which the $d\varepsilon$ and $p\pi$ orbital are anti-symmetric. On the other hand, $d\gamma$ and $sp\sigma$ orbitals are symmetric. A large probability of the optical dipole transition between HOMO and LUMO is expected due to the component on the nitrogen atoms because the transition between N-$p\pi$ and N-s orbitals satisfies the selection rule. As a result, optical absorption accompanied by the charge transfer between Co and Fe is observed.

It was reported that the photo-induced phase transition efficiently proceeded with the higher photon densities[7, 8]. The absorp-

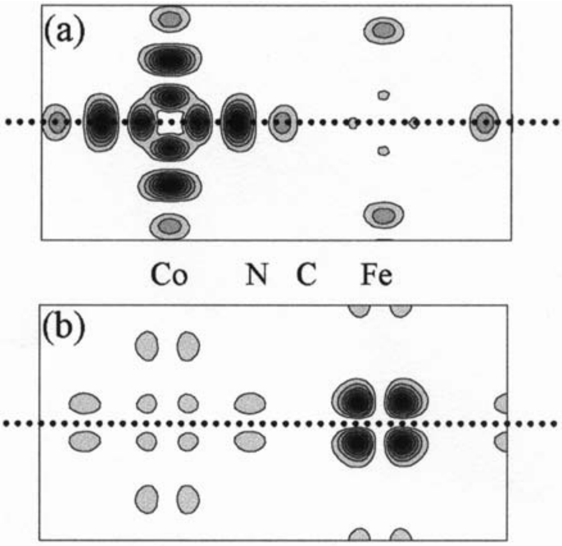

FIGURE 4 Partial charge distribution of each orbitals. (a) lowest unoccupied molecular orbital, and (b) highest occupied molecular orbital. The dotted lines in each figure represents the four-fold axis of the crystal.

tion of photons through the nitrogen orbitals is an initial process of such a exotic phenomenon in the Co-Fe cyanide.

Acknowledgments

The authors would like to acknowledge Professor K. Hashimoto and Dr. O. Sato for useful discussions. They also thank Professor A. Yanase and Professor H. Harima for kindly providing a source code of the FLAPW band calculation. Computations have been done partly using the facilities of Tsukuba Advanced Computing Center, Agency of Industrial Science and Technology.

References

[1] O. Sato, Y. Einaga, T. Iyoda, A. Fujishima, and K. Hashimoto, J. Electrochem. Soc. **144**, L11 (1997).

[2] O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, Science **272**, 704 (1996).

[3] M. Verdaguer, Science **272**, 698 (1996).

[4] T. Kawamoto, Y. Asai, and S. Abe, Phys. Rev. B **60**, 12990 (1999).

[5] T. Kawamoto, Y. Asai, and S. Abe, J. Lumin. **87-89**, 658 (2000).

[6] T. Kawamoto, Y. Asai, and S. Abe, Phys. Rev. Lett. *in press.*

[7] Y. Ogawa, S. Koshihara, Koshino. K., T. Ogawa, C. Urano, and H. Takagi, Phys. Rev. Lett. **84**, 3181 (2000).

[8] H. Mizouchi and K. Nasu, J. Phys. Soc. Jpn. **69** 1543 (2000)