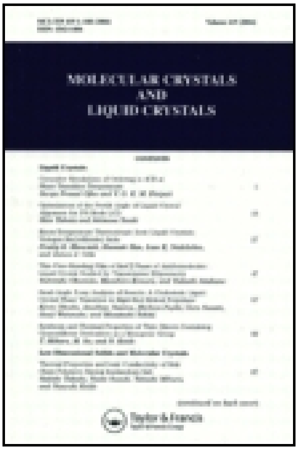

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Akiomi Mishima (1992): Electronic and Optical Properties in the One-Dimensional Molecular Conductor Cobalt-Rich Nickel Phthalocyanine Iodide, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 216:1, 189-193

To link to this article: http://dx.doi.org/10.1080/10587259208028771

Mol. Cryst. Liq. Cryst. 1992, Vol. 216, pp. 189–193
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Printed in the United States of America

ELECTRONIC AND OPTICAL PROPERTIES IN THE ONE-DIMENSIONAL MOLECULAR CONDUCTOR COBALT-RICH NICKEL PHTHALOCYANINE IODIDE

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Abstract An one-dimensional two-channel model in the molecular conductor cobalt-rich nickel phthalocyanine iodide is presented. In the model, the localized-d-electron spins on the metal spine couple ferromagnetically the itinerant-π-electron spins on the macrocycle. The energy bands, the charge and spin densities, and the optical-absoption spectrum of the one-dimensional dπ-coupled system are computed with aid of the periodic-boundary condition in the mean-field approximation. The optical-absorption spectrum shows the peaks of the π and d electrons. It turns out that the origin of the π-band gap is the dπ-ferromagnetic-exchange coupling in the cobalt-rich nickel phthalocyanine iodide.

INTRODUCTION

Many studies have been done on the electric and magnetic properties of alloys between the two isostructural porphyrinic molecular conductors phthalocyaninatonickel iodide, NiPcI, and phthalocyaninatocobalt iodide, CoPcI of composition $Co_xNi_{1-x}PcI$.[1] MPcI consists of metal-over-metal stacks of MPc units surrounded by chains of iodine. Iodine chains provide the partial oxidation and weaken the interstack interaction to make the one-dimensional (1D) character of these molecular conductors. In NiPcI,[2] the itinerant-charge carriers are the π electrons on the Pc ring. This compound is metallic down to 10 K with no phase transition. The Ni^{2+} (d^8) ions of NiPcI are diamagnetic and play no role in the electric or magnetic properties of NiPcI. However, the Co^{2+} (d^7) ions of CoPcI[3] are paramagnetic. The triplet-ground state has been found in $CoTPP(SbF_6)_{1.0}$ (TPP=tetraphenylporphyrinato).[4] The electronic structure of phthalocyanine is similar to that of porphyrin. The d_{z^2} orbital is orthogonal to the π orbital in CoPc. These lead to the physical picture of the dπ-ferromagnetic-exchange coupling in the cobalt-rich nickel phthalocyanine iodide.[5]

Here, we clarify the electronic states and the optical properties of the 1D-dπ-coupled system for the cobalt-rich nickel phthalocyanine iodide. We compute the total energy of the system, the energy bands of d and π electrons, the charge and spin densities of d and π electrons, and the optical-absorption spectrum by using the periodic boundary condition in the mean-field approximation.

MODEL

We start with the following hamiltonian:

$$\begin{aligned} H = &-T_d \sum_{l,\sigma} \Big(\sum_{m=1}^{5} d^{\dagger}_{l,m+1,\sigma} d_{lm\sigma} + d^{\dagger}_{l+1,1,\sigma} d_{l6\sigma} + \mathrm{H.c.}\Big) \\ &+ U_d \sum_{l} \sum_{m=1}^{6} n^{d}_{lm\alpha} n^{d}_{lm\beta} - T_p \sum_{l,\sigma} \Big(\sum_{m=1}^{5} p^{\dagger}_{l,m+1,\sigma} p_{lm\sigma} + p^{\dagger}_{l+1,1,\sigma} p_{l6\sigma} \\ &+ \mathrm{H.c.}\Big) - 4J \sum_{l} \sum_{m=1}^{6} \underline{S}^{p}_{lm} \cdot \underline{S}^{d}_{lm}, \end{aligned} \tag{1}$$

where $d_{lm\sigma}$ ($p_{lm\sigma}$) and $d^{\dagger}_{lm\sigma}$ ($p^{\dagger}_{lm\sigma}$) are the annihilation and creation operators of d (π) electrons with spin σ (α and β are up and down spins, respectively) at the m-th site in the l-th unit cell, $n^{d}_{lm\sigma} = d^{\dagger}_{lm\sigma} d_{lm\sigma}$ ($n^{p}_{lm\sigma} = p^{\dagger}_{lm\sigma} p_{lm\sigma}$) the number operator of d (π) electrons, T_d (T_p) the transfer energy of the d (π) electron between neighboring sites, U_d the on-site Coulomb repulsion between d electrons, J the ferromagnetic-exchange coupling between nearest-neighbor d and π electrons, $\underline{S}^{d}_{lm}$ ($\underline{S}^{p}_{lm}$) the spin-1/2 operator of the d (π) electron. We set T_d=0.15 eV, T_p=-0.3 eV, U_d=1.5 eV and J=0.027 eV at x=2/3 in $\mathrm{Co_xNi_{1-x}PcI}$.[5] The normalized spectral intensity is computed by using

$$\begin{aligned} I(E) = \sum_{i,j} \Big| \langle j \,|\, \sum_{l,\sigma} \Big(\sum_{m=1}^{5} c^{\dagger}_{l,m+1,\sigma} c_{lm\sigma} + c^{\dagger}_{l+1,1,\sigma} c_{l6\sigma} \\ - \mathrm{H.c.}\Big) | i \rangle \Big|^2 \delta(E_j - E_i - E), \end{aligned} \tag{2}$$

where $|i\rangle$ ($|j\rangle$) is the eigenstate with energy E_i (E_j) occupied (unoccupied) by electrons, $c_{lm\sigma}$ is $d_{lm\sigma}$ ($p_{lm\sigma}$) for a d (π) electron. We consider a single-electron excitation within the mean-field theory.

RESULTS AND DISCUSSION

Figure 1 shows the gap energy of the π band vs. the dπ-exchange coupling J at x=2/3 in $Co_xNi_{1-x}PcI$. The gap energy of the π band increases monotonically as J increases. Thus the π-band gap occurs due to the dπ-ferromagnetic-exchange coupling.

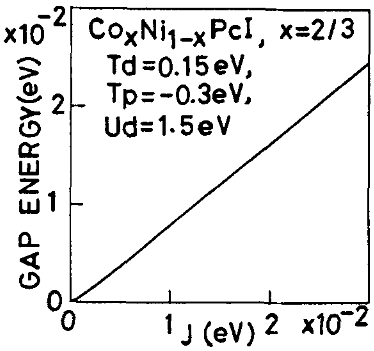

FIGURE 1 Gap energy of the π band vs. dπ-exchange coupling J.

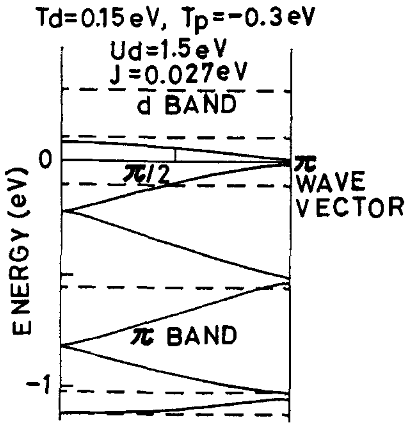

FIGURE 2 Energy vs. wave vector of d and π bands.

The d and π bands are shown for T_d=0.15 eV, T_p=−0.3 eV, U_d=1.5 eV and J=0.027 eV in Fig. 2. The dashed and solid lines denote the d and π bands, respectively. The energy gap of about 0.022 eV opens at the Fermi point of the π band. Figure 3 depicts the spin, S_d (S_p), and charge, C_d (C_p), densities of the d (π) electron vs. site number. The localized-d and itinerant-π spins form the state of a spin-density wave with a six-times period.

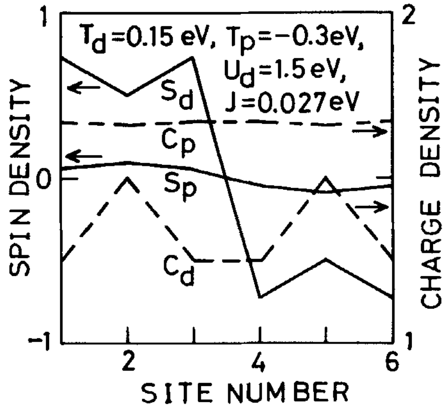

FIGURE 3 Spin and charge densities vs. site number.

The optical-absorption-spectral intensity vs. the absorption

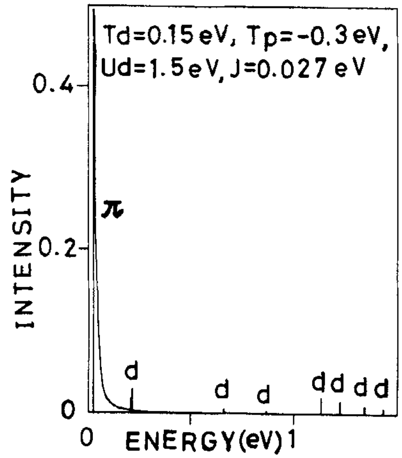

FIGURE 4 Spectral intensity vs. absorption energy.

energy is shown in Figure 4. The spectrum shows the asymmetric band of the π electron with a peak at 0.02 eV and with a tail to 0.5 eV, and the seven-discrete peaks of the d electron.

As the carriers are the π holes at x=2/3 in this model, the result is consistent with the experiment of the thermoelectric power for $0.5 \leq x \leq 0.75$ in $Co_xNi_{1-x}PcI$. It turns out that the π holes contribute to the electric transport and the origin of the π-band gap is the dπ-ferromagnetic-exchange coupling at x=2/3 in the cobalt-rich nickel phthalocyanine iodide.

In future, the randomness and the site energy difference of d_{z^2} electrons on the Ni^{2+} and Co^{2+} will be taken into consideration.

The author acknowledges fruitful discussions with Professor Kyuya Yakushi.

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