

## Intra-atomic exchange and ferromagnetic interaction in metallocene-based donor-acceptor stacked crystals

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A model explaining the nature of ferromagnetic exchange in organometallic charge-transfer molecular stacks is presented. It arises because of both the weak delocalization of unpaired electrons occupying the acceptor sites and the ferromagnetic exchange interaction between slightly delocalized acceptor electrons and perfectly localized ones in the  $d$  orbitals of the donor sites. It is shown that both the ground state of the system and the low-energy excitations can be described (in line with Anderson's theory of exchange in insulators) with use of a one-dimensional Heisenberg spin Hamiltonian with ferromagnetic nearest-neighbor interactions. Theoretical estimates of the effective exchange parameter of the Heisenberg Hamiltonian agree with those obtained from experimental data on magnetic susceptibility and specific heat.

### I. INTRODUCTION

The discovery of organometallic ferromagnets based on the charge-transfer salt of decamethylferrocene (DMeFc) and tetracyanethylene (TCNE) by Miller, Epstein, and Reiff<sup>1</sup> and recent achievements in this area due to Hoffman with co-workers<sup>2</sup> made remarkable breakthroughs toward the understanding of molecular magnets. Below the Curie temperature ( $T_C$ ) of about 5 K the DMeFc-TCNE salt is a bulk ferromagnet. Above  $T_C$  its magnetic susceptibility<sup>1</sup> as well as specific heat<sup>3</sup> can be nicely fit to the spin- $\frac{1}{2}$  Heisenberg ferromagnetic model with two types of spins differing by their  $g$  factors and effective exchange parameter of about 30 K. However, the specific features of electronic structure of materials of this class that are responsible for the very origin of the effective ferromagnetic interactions remain unclear. Moreover, the Heisenberg Hamiltonian is itself semi-empirical and its applicability must be substantiated. The purposes of this paper are to reveal the interactions which are responsible for the ferromagnetic interaction, to derive the Heisenberg Hamiltonian for the stack, and to estimate its parameters.

The paper is organized as follows. In Sec. II we outline the current state of the problem, present basic ideas, and describe electronic structure of the ions forming the stack. In Sec. III we describe the model of the stack. In Sec. IV we reduce the description of the separate DMeFc-TCNE stack to the Heisenberg model, and make numerical estimations for its parameters. Some discussions and remarks are given in Sec. V.

### II. STATE OF THE PROBLEM AND BASIC IDEAS

#### A. Review of the problem

The DMeFc-TCNE crystals consist of one-dimensional stacks of the type  $\cdots D A D A D A \cdots$  formed by the alternating donors  $D$  (DMeFc) and acceptors  $A$  (TCNE)<sup>1</sup>

(see Fig. 1). According to Ref. 1 electrons in the crystal are localized and their distribution may be depicted as  $\cdots D^+ A^- D^+ A^- D^+ A^- \cdots$ , where  $D^+$  stands for the cation (DMeFc)<sup>+</sup> with a single unpaired electron in its  $d$  shell and  $A^-$  stands for the radical-anion (TCNE)<sup>-</sup>. In the ferromagnetic phase the spins of unpaired electrons placed on DMeFc and TCNE sites are aligned in the same direction.

According to Miller, Epstein, and Reiff<sup>1</sup> and Miller and Epstein<sup>4</sup> (ME) the effective ferromagnetic exchange arises due to electron hopping (resonance interaction) between one of the orbitals of the triply occupied doubly degenerate manifold on (DMeFc)<sup>+</sup> and the singly occupied orbital on (TCNE)<sup>-</sup>. An estimate for the effective exchange parameter according to Refs. 1 and 4 is  $t^2/U$  where  $U$  is the energy of intramolecular electron-electron repulsion of the order of  $10^4$  K. If one assumes that the doubly degenerate orbital is confined only to the Fe<sup>3+</sup> ion, both the *intrastack* and *interstack* distances between Fe atoms and TCNE molecules are too large (5.2 Å) for any direct interaction to take place. Indeed, the overlap integrals  $S_{dA}$  between the singly occupied  $d$  orbital of the Fe atom and the  $2p_z$  orbitals of carbon or nitrogen atoms of TCNE molecule do not exceed  $10^{-3}$  at the given inter-

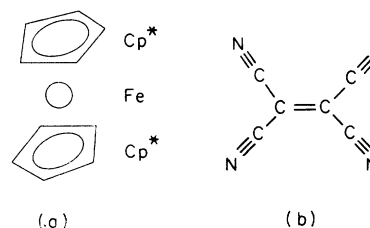


FIG. 1. Constituent molecules. (a) Decamethylferrocene (methyl groups to be attached to the rings are not shown) Cp\* stands for the permethylated cyclopentadienyl rings. (b) Tetracyanethylene (TCNE).

molecular distance. The resonance (hopping) parameter  $t \propto S_{dA}$  does not exceed  $10^2$  K. Thus an upper estimate for the magnitude of the effective exchange in the framework of the ME mechanism does not exceed 1 K and does not explain the observed value of the exchange constant.

The admixture of the orbitals of the ligands (the five-membered pentamethylcyclopentadienyl rings  $Cp^*$ ) to the singly occupied  $d$  orbital of the Fe atom does not improve the overall situation because of the symmetry constraints.<sup>5</sup> For the model geometry proposed in Ref. 5 the triply occupied degenerate orbitals of DMeFe, even being extended to the rings, differ by symmetry from the singly occupied orbital of TCNE and do not overlap with it. Thus no effective exchange of the kinetic origin between DMeFc and TCNE orbitals appears at all (see below).

For the direct Heisenberg exchange between singly occupied orbitals on DMeFc and TCNE, which was proposed as a possible origin for the effective ferromagnetic interaction by Soos and McWilliams,<sup>5</sup> the exchange integral can be estimated (according to Mulliken) as  $\gamma_{dA} S_{dA}^2$  where  $\gamma_{dA} \approx 1/R$  is the Coulomb two-electron integral ( $R$  is interatomic distance). The Heisenberg exchange parameter is thus about  $10^{-2}$  K (see also Ref. 5).

One can see that the above estimates are incompatible with the known value of effective exchange integral in these compounds (30 K). To avoid this contradiction it was suggested in Ref. 5, that some charge-transfer process (alternative to those by ME) involving the ligands should exist to make the effective interaction be ferromagnetic.

Two problems arise in the scope of this promising approach. The first one is to find the particular molecular orbitals (MO) of both DMeFc and TCNE responsible for the desired intermolecular charge-transfer process. The second one is to describe the *intramolecular* interaction [inside the  $(DMeFc)^+$  cation] which couples the unpaired electron in the  $d$  shell of  $Fe^{3+}$  ion with electrons in the ligands to produce the total ferromagnetic interaction. Both the problems were outlined in Ref. 5, but unfortunately the authors did not give any definite solution for them.

In our recent paper<sup>6</sup> a model Hamiltonian was proposed in order to describe a separate stack. This Hamiltonian involves (in line with Ref. 5) both the TCNE-ligand electron hopping and the intramolecular charge transfer between the  $d$  shell and the ligands. The latter was accounted by the intramolecular *antiferromagnetic* kinetic exchange interaction which couples unpaired electrons in the  $d$  shell of  $Fe^{3+}$  ions with those in ligands. In the unrestricted Hartree-Fock (UHF) approximation the wave function for the ferromagnetic (high spin) state of the stack has been found in Ref. 6. However, the total spin of the electronic state described by the wave function from Ref. 6 is incorrect. The wave function found in Ref. 6 contains only one unpaired electron per formula unit whereas the experiment<sup>1</sup> shows two unpaired electrons to present per formula unit. One can see that on the one hand the ME model of the ground state describes the total spin (and thus the saturation magnetization) correctly but it fails to explain the origin of the ferromag-

netic interaction quantitatively. On the other hand the model<sup>6</sup> gives the ferromagnetic ground state but its total spin is incorrect.

### B. Basic ideas and assumptions

Any satisfactory theory should organize into a single picture the following facts reviewed in Ref. 1.

(i) One-electron states are perfectly localized.

(ii) Spins of the localized electrons are aligned in the same direction in the ground state.

The above facts are in certain contradiction with theoretical concepts existing in this area. The origin of ferromagnetism in the considered system is generally attributed to charge-transfer states (Refs. 1 and 4). Normally, any admixture of charge-transfer states prevents localization and causes cancellation of the total spin. To counterpoise this effect we include the Coulomb repulsion of electrons in its reduced Hubbard form.

Both the experiment (Refs. 1–3) and theoretical analysis (Refs. 4 and 5) indicate that the system comprises two components: (i) electrons localized at the DMeFc sites and (ii) electrons localized at the TCNE sites. Hereafter they will be referred to as  $d$  system and  $\pi$  system, respectively.  $d$  and  $\pi$  electrons differ by their  $g$  factors. The contribution from charge-transfer states involving the ligands is accounted by the hopping term coupling the singly occupied orbital of TCNE with the vacant orbital of  $(DMeFc)^+$ . For the hopping term to be notable the DMeFc vacant orbital should have sufficient contribution from the ligand (i.e.,  $Cp^*$  ring)  $\pi$  orbitals because hopping can indeed take place only between the TCNE and the  $Cp^*$  ring  $\pi$  orbitals. Hence, electrons in the  $\pi$  system are actually distributed over orbitals of two kinds. These are the singly occupied  $\pi$  orbitals of TCNE and the DMeFc vacant orbitals of appropriate symmetry.

It would be natural to think that the two components of our system ( $d$  and  $\pi$  electrons) interact. Since no direct interaction between electrons on the DMeFc and on the TCNE sites is available (see Ref. 5 and above) we assumed<sup>6</sup> that a Kondo-type term on the DMeFc site should appear to account probable coupling between the localized electron and the electron back transferred from TCNE to the vacant orbital of DMeFc. This interaction is of the Coulomb origin and the most important contribution to it is the *intra-atomic* Heisenberg exchange<sup>7,8</sup> (i.e., the spin dependent part of the Coulomb interaction). The same interaction is responsible for the validity of Hund's rule in atoms.

Now we summarize our starting assumptions.

(i)  $d$  electrons at the DMeFc sites are perfectly localized.

(ii)  $\pi$  electrons at the TCNE sites are also almost localized but the states with electrons back transferred from the TCNE sites to the empty orbitals of DMeFc are also included.

(iii)  $d$  electrons are coupled with  $\pi$  electrons transferred back to the DMeFc  $\pi$  orbitals by a Kondo-type exchange interaction of *intra-atomic* origin.

The assumptions (i)–(iii) formulate the problem of magnetic order in the Miller-Epstein compounds as a

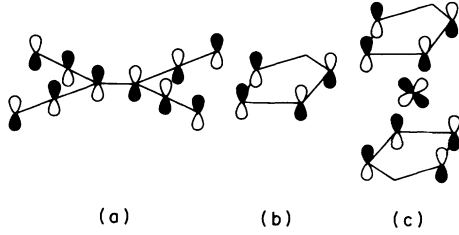


FIG. 2. Orbitals involved in the model. Different orientations of dark and light lobes correspond to different signs of MO coefficients. (a)  $b_{3g}$  orbital of TCNE (acceptor orbital). (b)  $e_{1x}$  orbital of Cp. (c)  $e'_{1gx}$  orbital of DMeFc (ligand orbital).

particular case of the general problem on a magnetic insulator. The general theory of the magnetic insulating state has been developed by Anderson.<sup>7</sup> We will apply the general theory of Ref. 7 to the model Hamiltonian,<sup>6</sup> but before we specify the site orbitals involved in the model and elucidate the origin and the sign of the Kondo-type term in the model Hamiltonian.

### C. Orbitals involved in the model

The lowest unoccupied molecular orbital of TCNE is the  $b_{3g}$   $\pi$  orbital [Fig. 2(a)]. When the radical anion is formed an extra electron occupies it. According to Ref. 6 this orbital is considered as the site orbital for the TCNE site. Hereafter it will be referred to as the *acceptor* orbital.

The orbitals of the DMeFc sites deserve special consideration. Direct calculations concerning electronic structure of both DMeFc and  $(\text{DMeFc})^+$  are absent in the literature. Following Smart and co-workers,<sup>9</sup> we invoke the data on electronic structure of ferrocene (Fc) and the ferricinium cation  $[(\text{Fc})^+]$  to model molecular orbitals (MO) of the decamethylated derivatives [DMeFc and  $(\text{DMeFc})^+$ ].

Shustorovich and Dyatkina<sup>10</sup> proposed an approximate model for the MO's of Fc which involves both  $\pi$  orbitals of the rings and valence orbitals of Fe. More recent calculations by Zerner, Loew, and co-workers<sup>11</sup> confirmed numerically the results of Ref. 10 concerning Fc and clarified some features of the electronic structure of  $(\text{Fc}^+)$ . According to Ref. 10 the highest occupied MO in Fc is doubly degenerated and belongs to the  $e_{2g}$  manifold. Atomic orbitals  $d_{\delta}$  ( $d_{xy}$  and  $d_{x^2-y^2}$ ) of the  $\text{Fe}^{2+}$  ion give the main contribution to it. (We use here the symmetry labeling of the orbitals adopted in Ref. 12.) Unpaired electron in the  $(\text{Fc})^+$  cation occupies one of the strongly

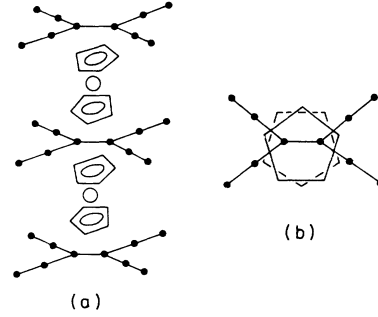


FIG. 3. Idealized geometry of the DMeFc-TCNE stack. (a) General view. (b) View along the stack axis.

localized degenerate MO's of the  $e_{2g}$  symmetry.<sup>11</sup> According to Ref. 5 in the  $(\text{DMeFc})^+$  cation the degeneracy of the triply occupied  $e_{2g}$  manifold is lifted and it is the  $d_{x^2-y^2}$  atomic orbital which gives the main contribution to the singly occupied orbital. The Fe orbitals of the  $d_{\pi}$  type ( $d_{xz}$  and  $d_{yz}$ ) contribute largely to the vacant MO's of  $(\text{DMeFc})^+$ .

To describe localized electrons at the DMeFc sites ( $d$  system) we take, according to Refs. 5 and 6, one singly occupied orbital per  $(\text{DMeFc})^+$  cation. This orbital involves a contribution from the ring  $\pi$  orbitals but the main contribution is that from the  $d_{x^2-y^2}$  orbital of the  $\text{Fe}^{3+}$  ion. Hereafter these orbitals will be referred to as *d orbitals*. The simplest model of the  $\pi$  system proposed in Ref. 6 involves the singly occupied acceptor orbital on each  $(\text{TCNE})^-$  and one MO on each DMeFc site. For the idealized geometry of the stack (Fig. 3) proposed in paper<sup>5</sup> only one  $\pi$  orbital of the  $\text{Cp}^*$  ring overlaps with the  $b_{3g}$  orbital of the  $(\text{TCNE})^-$  radical anion. That is the  $e_{1x}$  orbital [see Fig. 2(b)]. It is occupied in the  $(\text{Cp}^*)^-$  anion but due to mixing with the empty  $d_{xz}$  orbital it contributes to the  $e'_{1gx}$  vacant orbital<sup>10</sup> [Fig. 2(c)]. Thus the  $e'_{1gx}$  orbital of  $(\text{DMeFc})^+$  overlaps with the acceptor orbital. The  $e'_{1gx}$  MO is included into our model because it is the orbital of lowest energy giving rise to nonvanishing hopping with the acceptor orbitals.<sup>11</sup> Although it has significant contribution from the Fe atomic orbitals it is referred to as the *ligand* orbital (LO) irrespective of its actual composition.

## III. MODEL FOR ELECTRONIC STRUCTURE OF DMeFc-TCNE STACK

### A. Contributions to the total energy and the Hamiltonian

The model Hamiltonian for the DMeFc-TCNE stack, formulating the above ideas, has the form<sup>6</sup>

$$\begin{aligned}
 H = & - \sum_{n,\sigma} (\alpha_L L_{n\sigma}^\dagger L_{n\sigma} + \alpha_A A_{n\sigma}^\dagger A_{n\sigma}) + t_{\parallel} \sum_{n,\sigma} (L_{n\sigma}^\dagger A_{n\sigma} + A_{n\sigma}^\dagger L_{n-1\sigma} + \text{H.c.}) + \gamma_L \sum_n \hat{n}_{Ln\alpha} \hat{n}_{Ln\beta} + \gamma_A \sum_n \hat{n}_{An\alpha} \hat{n}_{An\beta} \\
 & - W \sum_{n,\sigma} d_{n\sigma}^\dagger d_{n\sigma} + U \sum_n d_{n\alpha}^\dagger d_{n\alpha} d_{n\beta}^\dagger d_{n\beta} + K \sum_n S_{Ln} S_{dn} ; \\
 \hat{n}_{Ln\sigma} = & L_{n\sigma}^\dagger L_{n\sigma}, \quad \hat{n}_{An\sigma} = A_{n\sigma}^\dagger A_{n\sigma}; \quad S_{Ln} S_{dn} = \frac{1}{2} (S_{Ln}^+ S_{dn}^- + S_{dn}^+ S_{Ln}^-) + S_{Ln}^z S_{dn}^z ; \\
 S_{Ln}^+ = & L_{n\alpha}^\dagger L_{n\beta}, \quad S_{Ln}^- = L_{n\beta}^\dagger L_{n\alpha}, \quad S_{dn}^+ = d_{n\alpha}^\dagger d_{n\beta}, \quad S_{dn}^- = d_{n\beta}^\dagger d_{n\alpha} ; \\
 S_{Ln}^z = & \frac{1}{2} (L_{n\alpha}^\dagger L_{n\alpha} - L_{n\beta}^\dagger L_{n\beta}), \quad S_{dn}^z = \frac{1}{2} (d_{n\alpha}^\dagger d_{n\alpha} - d_{n\beta}^\dagger d_{n\beta}) .
 \end{aligned} \tag{1}$$

Here  $L_{n\sigma}^\dagger$  is the creation operator of an electron on the LO of DMeFc,  $A_{n\sigma}^\dagger$  is the creation operator of an electron on the acceptor orbital,  $d_{n\sigma}^\dagger$  is the creation operator of an electron on the  $d$  orbital of DMeFc;  $n$  is the DMeFc-TCNE unit number;  $\sigma$  is the electron spin projection; its positive and negative values are denoted by the subscripts  $\alpha$  and  $\beta$ , respectively.

In Eq. (1) the first term is the attraction energy of a  $\pi$  electron to the cores of (DMeFc) $^+$  and TCNE, which are proportional to  $\alpha_L$  and  $\alpha_A$ , respectively. The second term describes the electron hopping in the  $\pi$  system. The third and the fourth terms are the Hubbard ones describing the Coulomb repulsion of electrons with opposite spin projections occupying the same site orbital: on DMeFc and on TCNE, respectively. The fifth term describes the attraction of  $d$  electrons to cores. The sixth term is the Coulomb repulsion of electrons with opposite spin projections occupying the same  $d$  orbital. The last term<sup>7,8</sup> (the Kondo term) describes the spin dependent part of the in-

tramolecular Coulomb interaction (intramolecular exchange) of unpaired  $d$  electrons with the electrons on the LO. Its spin independent part is omitted because it will not affect the form of the result and thus can be accounted for by the specific choice of parameters.

### B. Exchange interaction

The last term in Eq. (1) is of particular importance. In Ref. 6 we used the Hamiltonian equation (1) with  $K > 0$ . The intramolecular exchange was assumed to be of kinetic origin. However the  $e'_{1gx}$  LO does not overlap with the singly occupied  $d$  orbital of the  $e_{2g}$  symmetry. The singly occupied acceptor  $b_{3g}$  orbital also does not overlap with the  $d$  orbital. Therefore neither intramolecular nor intermolecular kinetic exchange is possible. By contrast the *intramolecular* exchange integral has large *intra-atomic* contributions which gives a total negative sign of  $K$ . The exchange integral is given by the formula

$$K = -2(dL|Ld), \quad (dL|Ld) = e^2 \int dr \int dr' \psi_d^*(r) \psi_L(r) |r-r'|^{-1} \psi_L^*(r') \psi_d(r'), \quad (2)$$

where  $\psi_d(r)$  and  $\psi_L(r)$  are the corresponding coordinate one electron wave functions (orbitals). The coefficients of the expansions of the LO and the  $d$  orbital over the Fe atomic orbitals and the  $\pi$  orbitals of the Cp\* rings have been found by Shustorovich and Dyatkina:<sup>10</sup>

$$\begin{aligned} \psi_L(r) &= \sqrt{1 - C_{xz}^2} \psi_{e_{1gx}}(r) - C_{xz} \psi_{xz}(r), \\ \psi_d(r) &= \sqrt{1 - C_{x^2-y^2}^2} \psi_{e_{2g}}(r) - C_{x^2-y^2} \psi_{x^2-y^2}(r), \end{aligned}$$

where  $\psi_{e_{1g}}(r)$  and  $\psi_{e_{2g}}(r)$  are the symmetric linear combinations of the pure  $e_1$  and  $e_2$   $\pi$  orbitals of the two Cp\* rings, respectively, in the coordinate representation,  $\psi_{xz}(r)$  and  $\psi_{x^2-y^2}(r)$  are the  $d_{xz}$  and  $d_{x^2-y^2}$  orbitals of the Fe atom, respectively,  $C_{xz}$  and  $C_{x^2-y^2}$  are the coefficients found in Ref. 10 numerically.

Substituting the expressions for  $\psi_L(r)$  and  $\psi_d(r)$  into the formula for  $K$  and assuming two-center exchange integrals to be zero (for more details see Ref. 13 where the intermediate neglect by differential overlap approximate treatment of two electron integrals has been extended to transition metal complexes) we obtain

$$\begin{aligned} K &= -2(dL|Ld) = -2C_{xz}^2 C_{x^2-y^2}^2 (\delta\pi|\pi\delta), \\ (\delta\pi|\pi\delta) &= 3F^2(dd)/49 + 20F^4(dd)/441, \end{aligned} \quad (3)$$

where  $(\delta\pi|\pi\delta)$  stands for the two-electron Coulomb interaction integral between the  $d_{xz}(d_\pi)$  and  $d_{x^2-y^2}(d_\delta)$  atomic orbitals;  $F^2(dd)$  and  $F^4(dd)$  are the Slater-Condon parameters of the intra-atomic Coulomb interaction.

## IV. ELECTRONIC STRUCTURE OF THE STACK

Now we construct the description for the electronic structure of the separate stack in accordance with ideas by Anderson<sup>7</sup> concerning the general theory of magnetic interaction in insulators. The main idea of Ref. 7 is that the local one-electron states in magnetic crystals do not coincide with the states of free constituent ions. The latter should be modified to account for the influence of the crystal lattice. We construct such modified states for the donor-acceptor stack with the Hamiltonian equation (1). First we find the Bloch states which contain information on the electronic structure of the crystal. Second we transform the Bloch states into the local Wannier states. The Wannier states approximate the modified states of the ions in the crystal. Then the exchange interactions between the Wannier states will be accounted for and the effective Heisenberg Hamiltonian for the separate stack will be constructed.

### A. Hartree-Fock state and Bloch states

In order to find the Bloch states for electrons in the stack we use the equation of motion method and then apply the unrestricted Hartree Fock (UHF) approximation to solve these equations.

The equations of motion for the annihilation operators  $L_{n\sigma}$ ,  $A_{n\sigma}$ , and  $d_{n\sigma}$  have the form ( $\hbar=1$ )

$$\begin{aligned} i\partial L_{n\sigma}/\partial t &= [L_{n\sigma}, H], \quad i\partial A_{n\sigma}/\partial t = [A_{n\sigma}, H], \\ i\partial d_{n\sigma}/\partial t &= [d_{n\sigma}, H]. \end{aligned}$$

After some algebra we obtain

$$\begin{aligned}
i\partial L_{n\alpha}/\partial t &= -\alpha_L L_{n\alpha} + t_{\parallel}(A_{n+1\alpha} + A_{n\alpha}) + \gamma_L L_{n\beta}^{\dagger} L_{n\beta} L_{n\alpha} + \frac{1}{2} K L_{n\alpha} S_{dn}^z + \frac{1}{2} K L_{n\beta} S_{dn}^-, \\
i\partial L_{n\beta}/\partial t &= -\alpha_L L_{n\beta} + t_{\parallel}(A_{n+1\beta} + A_{n\beta}) + \gamma_L L_{n\alpha}^{\dagger} L_{n\alpha} L_{n\beta} - \frac{1}{2} K L_{n\beta} S_{dn}^z + \frac{1}{2} K S_{dn}^+ L_{n\alpha}, \\
i\partial A_{n\sigma}/\partial t &= -\alpha_A A_{n\sigma} + t_{\parallel}(L_{n-1\sigma} + L_{n\sigma}) + \gamma_A A_{n-\sigma}^{\dagger} A_{n-\sigma} A_{n\sigma}, \\
i\partial d_{n\alpha}/\partial t &= -W d_{n\alpha} + U d_{n\beta}^{\dagger} d_{n\beta} d_{n\alpha} + \frac{1}{2} K d_{n\alpha} S_{Ln}^z + \frac{1}{2} K d_{n\beta} S_{Ln}^-, \\
i\partial d_{n\beta}/\partial t &= -W d_{n\beta} + U d_{n\alpha}^{\dagger} d_{n\alpha} d_{n\beta} - \frac{1}{2} K d_{n\beta} S_{Ln}^z + \frac{1}{2} K S_{Ln}^+ d_{n\alpha}.
\end{aligned} \tag{4}$$

The UHF approximation is got by replacing the products of three fermion operators according to the rule

$$c_1^{\dagger} c_2 c_3 \rightarrow \langle c_1^{\dagger} c_2 \rangle c_3 - \langle c_1^{\dagger} c_3 \rangle c_2.$$

The averages  $\langle \dots \rangle$  are to be taken over the UHF single determinant state which is to be found. We choose the form of the averages semi-empirically. The averages of the form  $\langle c_{\sigma}^{\dagger} c_{-\sigma} \rangle$  are set to be zero. This reflects the fact that the UHF state is to be an eigenstate of the spin projection operator. Hence all the averages of the type  $\langle S_{Ln}^+ \rangle$ ,  $\langle S_{Ln}^- \rangle$ ,  $\langle S_{dn}^+ \rangle$ , and  $\langle S_{dn}^- \rangle$  become zero. The averages of the type  $\langle d_{n\alpha}^{\dagger} L_{n\sigma} \rangle$  are also set to be zero because electron hopping between LO's and  $d$  orbitals is neglected.

It is known from the experiment<sup>14</sup> that no superstructure is observed both in the Mössbauer spectra and in the crystal structure of the Miller-Epstein ferromagnet. Therefore all the averages are indeed  $n$  independent. After some algebra we obtain the equations of motion in the UHF approximation with the above symmetry conditions imposed on

$$\begin{aligned}
i\partial L_{n\sigma}/\partial t &= -\alpha_L L_{n\sigma} + t_{\parallel}(A_{n+1\sigma} + A_{n\sigma}) \\
&\quad + \gamma_L \langle n_{L-\sigma} \rangle L_{n\sigma} + K \sigma \langle S_d^z \rangle L_{n\sigma}, \\
i\partial A_{n\sigma}/\partial t &= -\alpha_A A_{n\sigma} + t_{\parallel}(L_{n-1\sigma} + L_{n\sigma}) \\
&\quad + \gamma_A \langle n_{A-\sigma} \rangle A_{n\sigma}, \\
i\partial d_{n\sigma}/\partial t &= \varepsilon(\sigma) d_{n\sigma}, \\
\varepsilon(\sigma) &= -W + U \langle d_{n-\sigma}^{\dagger} d_{n-\sigma} \rangle + K \sigma \langle S_L^z \rangle.
\end{aligned} \tag{5}$$

Here the quantities  $\langle n_{L\sigma} \rangle$ ,  $\langle n_{A\sigma} \rangle$ ,  $\langle S_d^z \rangle$ , and  $\langle S_L^z \rangle$  are the  $n$ -independent averages of the operators  $\hat{n}_{Ln\sigma}$ ,  $\hat{n}_{An\sigma}$ ,  $S_{dn}^z$ , and  $S_{Ln}^z$  over the UHF state.

It can be easily seen from Eqs. (5) that  $d$  orbitals are not mixed with  $\pi$  orbitals. All the  $d$  spin orbitals irrespective to  $n$  have the same energy  $\varepsilon(\sigma)$  which however depends on the spin projection of the  $d$  electron. Because  $K$  is negative (see Sec. III B) the orbital energy  $\varepsilon(\sigma)$  is lower when the product  $\sigma \langle S_L^z \rangle$  is positive. According to the usual rules of orbital filling, electrons occupy localized  $d$  orbitals and they all have the spin projection  $S$  which corresponds to the lower energy. All the  $d$  orbitals are singly occupied, for the excessive electrons cannot occupy these orbitals because of the strong intra-atomic Coulomb repulsion ( $U$ ). The averages  $\langle d_{n\sigma}^{\dagger} d_{n\sigma} \rangle$  are all equal to unity for  $\sigma = S$  and are vanishing for  $\sigma = -S$ ,  $\langle S_d^z \rangle = S$ . Previously, the same result concerning the alignment of spins of  $d$  electrons was obtained in Ref. 6. One can see that the states  $d_{n\sigma}$  are solutions of the equa-

tions of motion (5) and thus are the Bloch states. At the same time they are perfectly localized so that no additional localization is needed to obtain the Wannier states.

The one-electron states in the  $\pi$  system can be readily found from the first and the second equations of motion. Let us consider the stack containing  $N$  DMeFc-TCNE units and impose on the cyclic (Born-von Kármán) boundary conditions. Since each unit cell provides two orbitals ( $b_{3g}$  and  $e'_{1gx}$ ) to the  $\pi$  system two sets of the Bloch states appear. Let the annihilation operators  $g_{k\sigma}$  and  $f_{k\sigma}$  be the solutions of the linearized equations of motion, i.e., they annihilate an electron with the spin projection  $\sigma$  in one of the two Bloch states with the wave number  $k$ . The annihilation operators for the Bloch states obey the equations

$$\begin{aligned}
i\partial g_{k\sigma}/\partial t &= \varepsilon_{k\sigma}^-(S) g_{k\sigma}, \\
i\partial f_{k\sigma}/\partial t &= \varepsilon_{k\sigma}^+(S) f_{k\sigma}.
\end{aligned}$$

Taking  $g_{k\sigma}$  and  $f_{k\sigma}$  in the form

$$\begin{aligned}
g_{k\sigma} &= x_{k\sigma} a_{k\sigma} + y_{k\sigma} 1_{k\sigma}, \\
f_{k\sigma} &= -y_{k\sigma}^* a_{k\sigma} + x_{k\sigma}^* 1_{k\sigma}, \\
|x_{k\sigma}|^2 + |y_{k\sigma}|^2 &= 1, \\
1_{k\sigma} &= (1/\sqrt{N}) \sum_n \exp(-ikn) L_{n\sigma}, \\
a_{k\sigma} &= (1/\sqrt{N}) \sum_n \exp(-ikn) A_{n\sigma}, \\
k &= (2\pi/N)j, \quad j = -N/2, \dots, N/2,
\end{aligned} \tag{6}$$

we obtain the expansion coefficients  $x_{k\sigma}$  and  $y_{k\sigma}$  which are  $S$  dependent

$$\begin{aligned}
x_{k\sigma} &= \cos\theta_{k\sigma}, \quad y_{k\sigma} = e^{-ik/2} \sin\theta_{k\sigma}, \\
\sin 2\theta_{k\sigma} &= -\frac{2\varepsilon_0(k)}{[\Delta\varepsilon_{\sigma}(S)^2 + 4\varepsilon_0^2(k)]^{1/2}},
\end{aligned} \tag{7}$$

and the orbital energies

$$\begin{aligned}
\varepsilon_{k\sigma}^{\pm}(S) &= -\bar{\alpha} + \gamma_L \langle n_{L-\sigma} \rangle / 2 + \gamma_A \langle n_{A-\sigma} \rangle / 2 \\
&\quad + K \sigma S / 2 \pm \frac{1}{2} [\Delta\varepsilon_{\sigma}^2(S) + 4\varepsilon_0^2(k)]^{1/2}, \\
\Delta\varepsilon_{\sigma}(S) &= |\Delta\alpha + \gamma_L \langle n_{L-\sigma} \rangle - \gamma_A \langle n_{A-\sigma} \rangle + K \sigma S|, \\
\varepsilon_0(k) &= 2t_{\parallel} \cos k / 2, \\
\bar{\alpha} &= (\alpha_L + \alpha_A) / 2, \\
\Delta\alpha &= \alpha_A - \alpha_L > 0.
\end{aligned} \tag{8}$$

Both the experiment<sup>1</sup> and the theoretical analysis performed in Ref. 6 indicate that the charge distribution in the  $\pi$  system of the ferromagnetic stack is very inhomogeneous;  $\pi$  electrons are concentrated on the TCNE sites. In the framework of the present approach this fact can be described if we assume that the ratio  $t_{\parallel}/\Delta\varepsilon_{\sigma}(S)$  is small. In this limit the expansion coefficients are

$$\begin{aligned} x_{k\sigma} &= 1 - [t_{\parallel}/\Delta\varepsilon_{\sigma}(S)]^2(1 - \cos k) , \\ y_{k\sigma} &= -2e^{-ik/2}[t_{\parallel}/\Delta\varepsilon_{\sigma}(S)]\cos k/2 . \end{aligned} \quad (9)$$

From Eqs. (7) and (9) one can see that in the limit of small  $t_{\parallel}/\Delta\varepsilon_{\sigma}(S)$  the Bloch states  $g_{k\sigma}$  are largely formed by the acceptor site orbitals, whereas the main contribution to the  $f_{k\sigma}$  states is from the ligand orbitals on the donor sites.

The expressions, Eqs. (7) and (8), defining the Bloch states of the  $\pi$  system, contain the averages over the UHF state, so in order to get the Bloch states exactly we need to know the wave function for the UHF state and to perform the self-consistency procedure. The UHF wave function for electrons in the  $\pi$  system is the antisymmetrized product of the filled Bloch states. The states to be filled can be selected heuristically. Two experimental observations<sup>1</sup> are important in that respect. First, it is known that  $\pi$  electrons are almost completely localized at the acceptor sites. Second, we know that the total spin of the ground state corresponds to two unpaired electrons per formula unit. These conditions can be satisfied simultaneously if we fill the  $g_{k\sigma}$  states (largely acceptor states) and, moreover, only those with  $\sigma = S$ . Such a filling may seem to be very unnatural but it does not contradict the standard procedure for construction of the UHF state. Indeed in the limit of small  $t_{\parallel}/\Delta\varepsilon_{\sigma}(S)$  the energies for the  $g_{k\sigma}$  Bloch states are

$$\varepsilon_{k\sigma}^{-}(S) = -\alpha_A + \gamma_A \langle n_{A-\sigma} \rangle - \frac{4t_{\parallel}^2 \cos^2 k/2}{\Delta\varepsilon_{\sigma}(S)} . \quad (10)$$

For the  $f_{k\sigma}$  states they are

$$\varepsilon_{k\sigma}^{+}(S) = -\alpha_L + \gamma_L \langle n_{L-\sigma} \rangle + K\sigma S + \frac{4t_{\parallel}^2 \cos^2 k/2}{\Delta\varepsilon_{\sigma}(S)} . \quad (11)$$

The states  $g_{k\sigma}$  and  $f_{k\sigma}$  are divided by the gap  $\Delta\varepsilon_{\sigma}(S)$  of the order of 1 eV (see below), so the  $g_{k\sigma}$  states, having lower energy, must be filled first. The energies of the  $g_{k\sigma}$  Bloch states with  $\sigma = S$  are lower than the energy of the lowest state with  $\sigma = -S$  for all  $|k| < k_1$ :

$$\begin{aligned} \cos(k_1/2) &= \left[ \frac{\Delta\varepsilon_S(S)}{\Delta\varepsilon_{-S}(S)} \right]^{1/2} \\ &= \left[ \frac{|\Delta\alpha + K/4|}{|\Delta\alpha - K/4|} \right]^{1/2} . \end{aligned}$$

So electrons are placed in the Bloch state of lower energy and all the  $g_{kS}$  states with  $|k| < k_1$  are occupied. It gives rise to the electron density  $\rho_S^0 = k_1/\pi$  with the spin projection  $S$ . Due to the Hubbard term  $\gamma_A \langle n_{AS} \rangle$  in the orbital energy this density shifts upward all the energies of

the  $g_{k-S}$  states by the quantity  $\gamma_A \rho_S^0$ . The relation  $\gamma_A \rho_S^0 \gg t_{\parallel}^2/\Delta\varepsilon$  [ $\Delta\varepsilon$  stands for  $\Delta\varepsilon_S(S)$ ] seems to be satisfied (see below) and therefore the remaining electrons cannot enter the  $g_{k\sigma}$  Bloch states with the spin projection  $\sigma = -S$  and also occupy the  $g_{kS}$  states but with larger  $k$ . So the UHF state for  $\pi$  electrons, which satisfies the experimental limitations imposed above, is obtained by complete filling of all the  $g_{kS}$  Bloch states. In that case the averages  $\langle n_{L\sigma} \rangle$  and  $\langle n_{A\sigma} \rangle$  are given by

$$\begin{aligned} \langle n_{A\sigma} \rangle &= \frac{1}{\pi} \int_0^{k_{F\sigma}} |x_{k\sigma}(S)|^2 dk , \\ \langle n_{L\sigma} \rangle &= \frac{1}{\pi} \int_0^{k_{F\sigma}} |y_{k\sigma}(S)|^2 dk , \end{aligned} \quad (12)$$

with the Fermi wave numbers  $k_{FS} = \pi$  and  $k_{F-S} = 0$ .

### B. Effective Heisenberg Hamiltonian for the stack

In the previous section we have constructed the delocalized Bloch states for the  $\pi$  system of the separate stack. According to Sec. IV A  $d$  electrons in the stack occupy perfectly local states. Their one-electron states are already local Wannier states. The one-electron states of  $\pi$  electrons are the Bloch states  $g_{kS}$  mainly concentrated on the acceptor sites. To obtain the Anderson's description we must transform the Bloch states  $g_{kS}$  into the local Wannier states and account the exchange interaction between the Wannier states for  $d$  and  $\pi$  electrons.

The Wannier states by definition are given by

$$\begin{aligned} w_{mS} &= (1/\sqrt{N}) \sum_k \exp(ikm) g_{kS} \\ &= (1/\sqrt{N}) \sum_k \exp(ikm) (x_{kS} a_{kS} + y_{kS} 1_{kS}) \\ &= \sum_n (U_{mn} A_{nS} + V_{mn} L_{nS}) , \\ U_{mn} &= (1/N) \sum_k \exp[ik(m-n)] x_{kS} , \\ V_{mn} &= (1/N) \sum_k \exp[ik(m-n)] y_{kS} . \end{aligned} \quad (13)$$

Substituting the values Eq. (9) of  $x_{kS}$  and  $y_{kS}$  into the above expressions Eq. (13) for the Wannier functions we obtain

$$\begin{aligned} U_{mm} &= 1 - (t_{\parallel}/\Delta\varepsilon)^2 , \\ U_{mm\pm 1} &= \frac{1}{2}(t_{\parallel}/\Delta\varepsilon)^2 , \\ V_{mm} &= -t_{\parallel}/\Delta\varepsilon , \quad V_{mm-1} = -t_{\parallel}/\Delta\varepsilon . \end{aligned} \quad (14)$$

The  $m$ th local Wannier function is mainly concentrated on the  $m$ th acceptor (TCNE) site but it also has contributions from the LO of the adjacent (DMFc)<sup>+</sup> cations which are of the first order in the small parameter  $t_{\parallel}/\Delta\varepsilon$  and those from the nearest-neighbor acceptor orbitals which are of the second order in  $t_{\parallel}/\Delta\varepsilon$ .

In line with Ref. 7 the spatial part (quantities  $U_{mn}$  and  $V_{mn}$ ) for the acceptor centered local Wannier states of the opposite ( $-S$ ) spin projection will be taken to be

equal to those of the Wannier states corresponding to the spin projection  $S$  [Eq. (14)].

Now we are in a position to write the spin Hamiltonian describing the low energy excitations of the stack. The spin-dependent part of the Coulomb interaction between the electrons occupying the Wannier states of two types (the perfectly local states for  $d$  electrons and the acceptor centered Wannier states for  $\pi$  electrons) naturally has the form of the Heisenberg spin Hamiltonian:

$$H_{\text{exch}} = J \sum_m (s_{dm} s_{Am} + s_{d,m-1} s_{Am}) . \quad (15)$$

Taking into account that the two center Coulomb exchange terms are vanishing (Ref. 13) and retaining only the intra-atomic ones we get the effective exchange constant in the form

$$\begin{aligned} J &= -2(w_m d_m | d_m w_m) \\ &= -2(w_m d_{m-1} | d_{m-1} w_m) \\ &= K V_{mm}^2 \\ &= K V_{m,m-1}^2 \\ &= -2C_{xz}^2 C_{x^2-y^2}^2 (\delta\pi | \pi \delta) (t_{\parallel} / \Delta\epsilon)^2 < 0 . \end{aligned}$$

The operators  $s_{dm}$  are precisely the spin operators of  $d$  electrons ( $S_{dm}$ ), whereas the operators  $s_{Am}$  are those of the electrons occupying the Wannier orbital centered on the  $m$ th TCNE site and having some density on the ligand orbitals of two adjacent DMeFc molecules.

The above picture correlates with the experimental observations reviewed in Ref. 1. In the temperature region from 16 to 60 K the magnetic susceptibility can be fitted to the one-dimensional ferromagnetic spin- $\frac{1}{2}$  Heisenberg model with  $J = -30$  K. We utilize these data on susceptibility in order to estimate the parameters of our model and to check its consistency.

Substituting the Slater-Condon parameters  $F^2(dd)$  and  $F^4(dd)$  from Ref. 13 and the quantities  $C_{xz}^2$  and  $C_{x^2-y^2}^2$  (which amounts to 0.65 and 0.86, respectively) from Refs. 10 and 11 we obtain  $K = -10^4$  K. The experimental value of  $J$  can therefore be reproduced with  $t_{\parallel} / \Delta\epsilon = 0.055$ . The latter is small enough for our approximation to be valid.

The value of the hopping integral  $t_{\parallel}$  can be estimated independently for the idealized geometry of Ref. 5. It is the hopping integral between the  $b_{3g}$   $\pi$  orbital of TCNE and the  $e_{1x}$   $\pi$  orbital of the Cp ring (calculated according to Ref. 15) multiplied by the coefficient of the latter orbital in the expansion of the  $e'_{1gx}$  MO of Fc (see Sec. III B). Thus the estimated hopping integral amounts to 900 K. Inserting the latter value in the condition  $\gamma_A \rho_S^0 \gg t_{\parallel}^2 / \Delta\epsilon$  (see Sec. IV B) we obtain  $\gamma_A \gg 600$  K which is reasonable because the intramolecular repulsion constants are usually estimated to be of the order of 1 eV, i.e.,  $10^4$  K. That makes the filling procedure of Sec. IV A consistent. The value of  $\Delta\alpha$  thus amounts to  $1.5 \times 10^4$  K. The latter value seems to be satisfactory in view of Ref. 6 where the order of  $\Delta\alpha$  has been estimated to be about the energy required to transfer an electron from the  $d$  orbital to the

ligand orbital in the free DMeFc molecule. The corresponding excitation in our case is the ( $d_{\delta} \rightarrow d_{\pi}$ ) excitation. According to Refs. 9 and 11 its energy ranges from  $2.5 \times 10^4$  to  $3.5 \times 10^4$  K. We see that all the parameters of the model proposed are mutually consistent and do not contradict the known experimental facts.

## V. DISCUSSION

As Miller, Epstein, and co-workers mentioned in their recent review (Ref. 16) a microscopic model for the magnetic ordering in the charge transfer organometallic crystals has not been evolved yet. Several working paradigms are considered as reasonable. Two common features of the different existing approaches are worthwhile to be outlined. First, in all the models electrons at  $d$  sites and those on the TCNE sites are treated as local  $\frac{1}{2}$  spins interacting with their nearest neighbors. Thus the problem is reduced to the spin Hamiltonian of the Heisenberg type. Second, the orbitals occupied by unpaired (magnetic) electrons are considered as if they were orbitals of free ions [ $\text{Fe}^{3+}$  and  $(\text{TCNE})^-$ , respectively]. The models differ in a particular mechanism of the interaction between the electrons occupying the orbitals of free ions. In the original ME model the interaction between the local spins is the direct kinetic exchange<sup>1,4</sup> (charge transfer) between the triply occupied doubly degenerate manifold of  $(\text{DMeFc})^+$  and  $(\text{TCNE})^-$ . Soos and McWilliams<sup>5</sup> mentioned that the spin-dependent part of the Coulomb interaction of electrons occupying the local orbitals is also ferromagnetic. However both the interactions become very weak for the intersite separations of about 5 Å and cannot explain the observed value of the effective exchange parameter of about 30 K. To avoid this difficulty Soos and McWilliams<sup>5</sup> proposed also to consider charge transfer between the TCNE sites and  $\pi$  orbitals of the Cp\* rings instead of direct charge-transfer between TCNE and Fe orbitals. The orbitals of Cp\* however were taken as those of free  $(\text{Cp}^*)^-$  anion and no definite conclusion on the sign or the magnitude of the interaction were obtained. It is known, however, as pointed out by Anderson,<sup>7</sup> that the models considering the one-electron states of the free ions as true one-electron states of magnetic electrons in crystals are incorrect because the former are to be modified to account for the crystal structure. The successive method to do it was also proposed by Anderson.<sup>7</sup> It is the following: (1) to find the Bloch states of the crystal (they will contain all the information on the crystal electronic structure); (2) to transform the delocalized Bloch states to the local Wannier states, and (3) to consider interactions between electrons occupying the local Wannier states.

In the present paper we carried out Anderson's program for the model Hamiltonian<sup>6</sup> [Eq. (1)] describing the separate stack. For the states localized on the TCNE sites the calculations were carried out explicitly (Sec. IV). For the states of the  $\text{Fe}^{3+}$  ions we have found the Wannier states inexplicitly, by replacing the states of free ions by the molecular states involving the  $\text{Cp}^*\pi$  orbitals and taking the latter as the true Wannier states. The whole derivation has been successful because we dealt with a

molecular crystal where intermolecular interactions are weak. Stronger interactions [intramolecular ones between states of the  $\text{Fe}^{3+}$  ion and those of the ligands in the  $(\text{DMeFc})^+$  cation] had been accounted before in the course of quantum chemical calculations on ferrocene<sup>10</sup> and ferricinium cation.<sup>11</sup>

The ground-state wave function of the stack can be presented as the antisymmetrized product of the wave function  $\Phi_d$  for  $d$  electrons and of the wave function  $\Phi_\pi$  for  $\pi$  electrons:

$$\Phi = \Phi_d \otimes \Phi_\pi,$$

$$\Phi_d = \prod_n d_{nS}^\dagger |0\rangle, \quad \Phi_\pi = \prod_n w_{nS}^\dagger |0\rangle.$$

It reflects the basic features of the electronic structure of DMeFc-TCNE proposed by Miller and Epstein.<sup>1,4</sup> In the above ground state the electrons are localized on the DMeFc and TCNE sites and their spins are all aligned in the same direction. The ground state fairly fits into the spin Hamiltonian model with the effective ferromagnetic interaction (in accordance with proposals by Miller and Epstein<sup>1,4</sup>). The Heisenberg Hamiltonian describes also the low energy excitations of the system. Thus we transformed the model Hamiltonian involving parameters of electronic structure of the constituent molecules and of their interactions [Eq. (1)] to the effective Heisenberg Hamiltonian [Eq. (18)] describing the experimental data in the local spin picture.

In our present paper as in the previous one (see Ref. 6) we used the UHF method in order to find the contribution of the charge-transfer states involving the  $\text{Cp}^*$  ligands. Close results concerning the ground state of the Hamiltonian equation (1) and its low energy excitations can be obtained in the framework of the standard operator perturbation theory with the hopping term as a perturbation.<sup>17</sup>

The approach to the magnetism of the Miller-Epstein compounds proposed in the present paper can be directly generalized to derivatives of other metallocene cations  $(\text{MCp}^*_2)^+$  bearing larger local spins in their  $d$  shells. The effective exchange interaction will be ferromagnetic for all metallocene cations where the ligand orbitals (with a large contribution from the metal  $d_\pi$  orbitals) are kept to be empty and unpaired electrons occupy  $d$  orbitals of different symmetry ( $d_\delta$  or  $d_\sigma$ ). Such a situation takes place for all  $M = \text{Fe}, \text{Mn}, \text{Cr}$ , and the effective interaction must be ferromagnetic in the corresponding  $\text{MCp}^*_2$ -TCNE salts. The case of the  $\text{CrCp}^*_2$ -TCNE salt is particularly important because originally Miller and Epstein<sup>4</sup> predicted it to be ferrimagnetic and the effective exchange to be antiferromagnetic in it. In the framework of our approach the effective exchange in  $\text{CrCp}^*_2$ -TCNE, contrarily, must be ferromagnetic, which is confirmed by recent experiments due to Broderick and Hoffman.<sup>18</sup>

An important example of the true variation of the sign of the effective exchange is provided by the  $\text{NiCp}^*_2$ -TCNE salt. It should be noted that in general the picture proposed in the present paper does not apply to the case of antiferromagnetic  $\text{NiCp}^*_2$ -TCNE. The reason is that

in the  $(\text{NiCp}^*_2)^+$  cation the unpaired electron occupies one of the *ligand* orbitals (LO's) which are always empty for all other metals in this series and which can overlap with the singly occupied orbital of  $(\text{TCNE})^\pm$  directly. According to general considerations of Refs. 7 and 8 the direct overlap gives rise to antiferromagnetic interaction of the order  $t_\parallel^2/\Delta\epsilon$  [ $\Delta\epsilon$  is the characteristic energy of the state with an electron transferred from  $(\text{TCNE})^\pm$  to  $(\text{NiCp}^*_2)^+$ ] between the local spins. The sign of the interaction is therefore in perfect agreement with experiment.<sup>1</sup> The energy of the interaction is of the same order of magnitude as that of the ferromagnetic exchange  $K(t_\parallel/\Delta\epsilon)^2$  since  $K$  and  $\Delta\epsilon$  are estimated to be of the same order. Experimental data of Ref. 1 show, however, that the antiferromagnetic exchange is weaker than the ferromagnetic one almost by the order of magnitude (for more details see Ref. 17).

## VI. CONCLUSION

In the present paper we demonstrated the role of the interplay between the delocalization and the localization of electronic states in the stacks of the ferromagnetic charge-transfer crystals. The effective exchange in the charge-transfer ferromagnets arises because of both slight delocalization of electrons in the  $\pi$  system and strong on site ferromagnetic exchange interaction between electrons in the  $\pi$  system and those in the  $d$  system. Contributions of the two delocalization processes are important. The first process is the delocalization of the ring  $\pi$  orbitals onto the Fe atoms inside the  $(\text{DMeFc})^+$  cations. This is nothing other than the usual delocalization of molecular one-electron states.

The second delocalization process is the delocalization of the TCNE centered Wannier states to the ligand orbitals of the adjacent  $(\text{DMeFc})^+$  cations (i.e., the charge transfer involving the ligands). This delocalization is weak (of the order of  $t_\parallel/\Delta\epsilon$ ), but it suffices to explain the observed ferromagnetic exchange parameter because the intramolecular Kondo exchange term is very strong.

The viewpoint on the origin of the ferromagnetism in the charge-transfer organometallic crystals presented in this paper strongly differs from the heuristic model of Miller, Epstein, and Reiff<sup>1</sup> and Miller and Epstein<sup>4</sup> for the mechanism of the ordering in the Miller ferromagnets. Contrarily our results concerning the ground-state wave function for the separate stack and the picture of the low energy excitations fairly corresponds with the picture proposed by Miller and Epstein.

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