Chemical Physics 153 (1991) 371–378
North-Holland

Ferromagnetism of charge-transfer crystals

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Received 9 January 1990; in final form 19 November 1990

A model explaining ferromagnetic ordering in organo-metallic charge-transfer molecular stack is constructed. A model Hamiltonian is proposed to describe a separate stack. The wave function of the ferromagnetic state of the stack is found in the UHF approximation.

1. Introduction

Recently, Miller and co-workers have reported the discovery of ferromagnetic order in the organometallic charge-transfer salt of decamethylferrocenium (DMFc) and tetracyanethylene (TCNE) at temperatures below $T_c = 4.8$ K [1–6].

The ferromagnetic DMFc–TCNE crystals consist of the one-dimensional stacks which are formed by the alternating molecules DMFc and TCNE (see fig. 1) [6]. Both the *intra*stack and *inter*stack distances between the Fe atoms are too large [2,6] for direct interaction between them to take place. Therefore, in papers [4,6] it was assumed that the bulk ferromagnetic state arises due to some effective exchange interaction between the unpaired electrons on the Fe^{3+} ions and the electrons of the $\mathrm{TCNE}^{\dot{-}}$ radical-anions. The effective exchange interaction, as Miller and his co-workers stated [4,6], arose due to resonance interactions of the d-electrons of Fe^{3+} and the unpaired electrons of $\mathrm{TCNE}^{\dot{-}}$. Such an approach both to the intrastack and the intrastack ordering is right only in general, since the corresponding resonance (hopping) integrals are extremely small because the distance between the Fe atom and the plane of the TCNE molecule is as large as 5.2 Å [2].

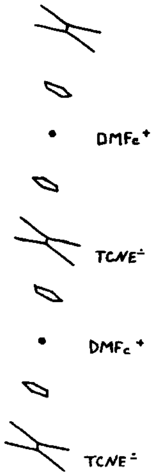


Fig. 1. The structure of a separate stack in the DMFc–TCNE crystal. Methyl groups are not shown.

Miller and Epstein (ME) [4,6] proposed a model of electronic structure of the ferromagnetic crystal DMFc–TCNE. In the ME model the electronic structure of the crystal is determined by unpaired electrons located on the e_{2g} (d_{xy}) orbitals of the Fe atoms and on the b_{3g} orbitals of the TCNE molecules. Inexplicitly it means that the ground-state wave function of the crystal is the antisymmetrized product of one-electron functions localized on the Fe and on the TCNE sites. In the ME model these localized electrons interact ferromagnetically because of the configurational admixing of the triplet excited state with an electron transferred from the Fe site to TCNE to the ground state.

This simple model seems to be acceptable at least in its part concerned with d-electrons. The localization of d-electrons is highly probable and a perturbative treatment of their resonance interactions seems to be valid as it will be discussed in detail below. At the same time the ME model meets a severe objection.

This objection is concerned with the very existence of the effective ferromagnetic exchange interaction between the unpaired d-electrons on the Fe^{3+} ions and the unpaired electrons on $TCNE^{\dot{-}}$. The corresponding constant of the kinetic exchange was estimated by ME as:

$$I_{\text{ferro}} \sim \beta^2_{\text{Fe-TCNE}} / \Delta E_{\text{CT}} \, ,$$

where $\beta_{\text{Fe-TCNE}}$ is the resonance integral between the d-orbitals of the Fe atom and the orbital of $TCNE^{\dot{-}}$ occupied by the unpaired electron, and ΔE_{CT} is the energy of the corresponding charge transfer state. As it was pointed out in ref. [7] this interaction is extremely weak because the resonance integrals $\beta_{\text{Fe-TCNE}}$ are very small. The authors of ref. [7] note that some alternative charge-transfer process involving the ligands (the substituted cyclopentadienyl anions) should exist to produce the ferromagnetic state.

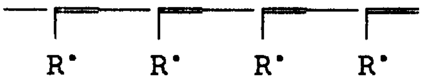
In addition to the comments of ref. [7] we should note that the π-orbitals of the molecules forming the stacks seem to be coupled due to the intrastack resonance interaction. The electrons which in the ME model are localized on the TCNE sites are on the contrary probably delocalized over all stack and this delocalization should be taken into account somehow. The proposed picture includes both the localized electrons placed on the d-orbitals of the DMFc sites and the delocalized electrons occupying the π-orbitals of TCNE and the ligand orbitals of DMFc. The d-orbitals are not mixed to the delocalized orbitals by the resonance interaction, but it does not mean that the localized electrons do not interact with the delocalized ones. The perturbative treatment of the weak resonance interaction leads to the effective intramolecular exchange interaction of the localized d-electrons with electrons in *ligand* orbitals of the $DMFc^+$ cation. (The similar picture was proposed in [8,9] to describe the interaction of local spins in the d-shell of the Cu atoms with itinerant electrons in the quasi-one-dimensional semiconductor copper phthalocyanine iodide). This intramolecular kinetic exchange is inherently *anti*ferromagnetic. Its constant K can be estimated by the formula:

$$K \simeq 4\beta^2_{\text{Fe-Cp}} / \Delta E'_{\text{CT}} \, ,$$

where $\beta_{\text{Fe-Cp}}$ is the resonance integral between the d-orbital of the Fe atom and a ligand orbital of the $DMFc^+$ cation. Obviously $K \gg I_{\text{ferro}}$, because $\beta_{\text{Fe-Cp}}$ is greater than $\beta_{\text{Fe-TCNE}}$ by several orders of magnitude and $\Delta E'_{\text{CT}}$ and ΔE_{CT} differ no more than by several times.

The above consideration on electronic structure of the separate stack can be summarized as follows. Each $DMFc^+$ cation bears in its d-shell one unpaired electron. These electrons are localized and can be characterized by their spin projection $\pm\frac{1}{2}$. Other electrons are delocalized and can be characterized by the wave numbers of the orbitals spread over the entire stack. The localized electrons can be treated as local $\frac{1}{2}$-spins which interact with the delocalized electrons by some effective exchange interaction. The delocalized orbitals involve both the π-orbitals of the TCNE molecules and the π-orbitals of the permethylated cyclopentadienyl ligands as well. The delocalization and the intramolecular exchange together effectively include in the consideration the charge-transfer states involving d-shell, ligands, and acceptor molecules in accord with suggestions of ref. [7].

The above picture closely resembles those that arose in the Kondo problem [10] and in the RKKY model for the interaction of magnetic impurities in metals [11]. For the first time such an approach was applied to the quasi-one-dimensional crystals in refs. [8,9]. Recently in our paper [12] the similar considerations were applied to the organic ferromagnet composed of polyene chains with radical substituents. In that case



we encounter a very similar situation: The electrons in the π-conjugated system are delocalized whereas unpaired electrons in the radical substituents are localized and interact with delocalized ones by means of some effective exchange.

In the present paper we propose a model Hamiltonian for the ferromagnetic DMFc–TCNE stack which includes the above-mentioned effects of delocalization and intramolecular antiferromagnetic exchange. Although the proposed model does not contain the ferromagnetic effective exchange the variational wave function with ferromagnetic order can be constructed.

2. Theory

As we mentioned in section 1 the electronic structure of a separate stack of the charge-transfer ferromagnet DMFc–TCNE resembles that of the polymer ferromagnet [12]. Therefore it can be described by using a model analogous to the model of the polymer ferromagnet proposed in ref. [12].

In the DMFc–TCNE crystal the DMFc and TCNE molecules alternate and form stacks (see also fig. 1):

$DMFc^+$
$TCNE^{\dot{-}}$
$DMFc^+$
$TCNE^{\dot{-}}$

which are aligned in the *a*-direction. The intermolecular separations between adjacent molecules in the stack are large enough to consider molecules comprising the the stack separately. Therefore it would be natural to begin the discussion of the electronic structure of the stack from the description of electronic structures of the constituting molecules.

2.1. Electronic structure of TCNE

TCNE is a molecule with closed electronic shell. Its lowest unoccupied molecular orbital (LUMO) is of π-character and belongs to the b_{3g} irreducible representation of the D_{2h} point group. The energy of the LUMO is quite low, and this molecule is a good electron acceptor. When the radical-anion is formed an extra electron occupies the b_{3g}-orbital. It changes the bond lengths but the molecular symmetry remains intact [2,6].

2.2. Electronic structure of the DMFc$^+$ cation

The electronic structure of the DMFc$^+$ cation is relevant to the problem of the ferromagnetic order in the considered system. The DMFc molecule is a d^6-complex. So six of its electrons are placed on the strongly localized nonbonding 3d-orbitals of the Fe atom. The other electrons are placed on the delocalized bonding orbitals of the $C_5(CH_3)_5$ (Cp*) ligands and on 4s and 4p orbitals of Fe. The main question is the nature of the highest occupied MO in DMFc and of the singly occupied MO in the DMFc$^+$ cation. In the literature two viewpoints on this subject are presented [13–19]. The first one, adopted by Miller and Epstein [4,6], is that the highest occupied orbital of ferrocene (Fc) and also of DMFc is doubly degenerate. This viewpoint is supported by MO–LCAO calculations both on ab initio and semiempirical levels [13,15,16,18]. However, it contradicts to that arising from analysis of the (d–d)-excitation spectra of metallocenes and decamethylmetallocenes. The experimental data both on Fc [20] and on DMFc [19,20] unequivocally suggest that the highest occupied d level is nondegenerate. This viewpoint is also supported by an X_α calculation [17]. The experiments carried out to find the singly occupied orbital in the Fc$^+$ cation did not clarify the situation. Indeed both the photoelectron spectra of Fc [14] and ab initio calculation [15] suggest that the ground state of the ferricinium cation is the $^2E_{2g}$ state and that the unpaired electron occupies the degenerate e_{2g} orbital (d_{xy}). The more recent calculations [17,18] suggest that the ground state of the cation is the $^2A_{1g}$ state and the singly occupied orbital is the a_{1g}-orbital (d_{z^2}) (Here we use the symmetry notation adopted in ref. [21]). Moreover the relative level positions in the gas phase are not relevant because in the crystal they can be changed due to surrounding effects (see also ref. [7]). At any rate it is known that one electron from the nonbonding 3d-orbital of each DMFc molecule is removed and the d^5-complex DMFc$^+$ having total spin $\frac{1}{2}$ is formed.

However, the calculations [18] revealed some interesting features of the electronic structure of Fc$^+$. It turns out that an unpaired electron occupies a strongly localized MO. In ref. [18] it was shown that the d-orbital gives 86% contribution to the singly occupied orbital whereas other orbitals are delocalized over the molecule in a greater extent. Indeed d-orbital is even more localized because the Hartree–Fock approximation usually overestimates delocalization. Therefore we consider the singly occupied d-orbital to be perfectly local.

Now we can distinguish two systems of orbitals in DMFc$^+$. The first one, consisting of the localized d-orbitals of the Fe^{3+} ion is analogous to the system of the side group orbitals of the polymer ferromagnet

[12]. The second one is composed of the delocalized π-orbitals of the Cp* ligands and the overlapping 4s and 4p orbitals of Fe. Hereinafter the second set of orbitals will be referred to as the ligand orbitals (LO) of DMFc.

2.3. A model for the electronic structure of the stack

The above discussion suggests some important features for the adequate model for the electronic structure of the DMFc–TCNE stack which seem to be missed in the ME model [4,6] (see section 1).

One of the characteristic features of the electronic structure of the stack in the ME model is that the electrons are perfectly localized. The localized structure is visualized in the ME model by ferromagnetically interacting local spins with $S=\frac{1}{2}$ placed on the DMFc and TCNE sites, which represent unpaired electrons in the d-shells of the Fe atoms or on the LUMOs of the TCNE molecules respectively. Although for d-electrons this picture is acceptable (d-electrons are indeed localized) it may be inappropriate for electrons in TCNE because of the resonance interaction between π-orbitals of TCNE and π-orbitals of the Cp* rings.

As in the case of the polymer ferromagnet [12] (see also section 1) we encounter the situation when some electrons (namely d-electrons) are localized whereas the others are delocalized. Therefore we adopt the following model to describe the electronic structure of the stack.

To describe d-electrons (d-system) it suffices to take into account one 3d-orbital per Fe atom occupied by a single electron each. According to ref. [7] (see also section 1) we will consider only one non-degenerate d-orbital per Fe atom regardless of its origin.

To describe delocalized electrons (organic system) in the stack it is necessary to take into account both the LO of DMFc$^+$ and π-orbitals of TCNE. The simplest model of the delocalized system should involve at least one orbital of TCNE and one LO of DMFc$^+$. For TCNE it is reasonable to choose the b_{3g} orbital. The proper choice of the DMFc$^+$ orbital is determined by the contributions of different electronic configurations to the ground state of the organic system (OS) of the stack. Obviously only the contributions of the configurations with an electronic back transferred from the TCNE site to an unoccupied LO of DMFc$^+$ are significant. Thus in the proposed model some unoccupied LO of DMFc$^+$ is assumed to take part in the formation of the delocalized OS. Here we do not include explicitly the contribution of the back transfer of an electron from the TCNE site into the d-shell. These configurations are effectively taken into account by the exchange term in eq. (1).

The model Hamiltonian of the DMFc–TCNE stack has the following form:

$$
\begin{aligned}
H= & -\sum_{n,\sigma}\left(\alpha_1 c^+_{1n\sigma}c_{1n\sigma}+\alpha_2 c^+_{2n\sigma}c_{2n\sigma}\right) \\
& -t_{\parallel}\sum_{n,\sigma}\left(c^+_{1n\sigma}c_{2n\sigma}+c^+_{2n\sigma}c_{1n+1\sigma}+\text{h.c.}\right) \\
& +\gamma_1\sum_{n} c^+_{1n\alpha}c_{1n\alpha}c^+_{1n\beta}c_{1n\beta}+\gamma_2\sum_{n} c^+_{2n\alpha}c_{2n\alpha}c^+_{2n\beta}c_{2n\beta} \\
& -W\sum_{n,\tau}A^+_{n\tau}A_{n\tau}+K\sum_{n}\sum_{\sigma,\tau}\sigma\tau c^+_{1n\sigma}c_{1n\sigma}A^+_{n\tau}A_{n\tau}\,. \qquad (1)
\end{aligned}
$$

Here $c^+_{1n\sigma}$ is the creation operator of an electron on the LO of DMFc, $c^+_{2n\sigma}$ is the creation operator of an electron on TCNE, $A^+_{n\tau}$ is the creation operator of an electron on the 3d DMFc orbital; n is the DMFc–TCNE unit number in the stack. In eq. (1) the first term is the attraction energy of an electron in the OS to the cores of DMFc$^+$ and TCNE, which are proportional to α_1 and α_2, respectively. The second term describes the electron hopping in the OS. The third and the fourth terms describe the Coulomb repulsion of the electrons with opposite spin projections occupying the same orbital: on DMFc and on TCNE, respectively. The fifth term describes the attraction of d-electrons to core. The sixth term describes the effective intramolecular exchange interaction of unpaired d-electrons in the OS (on the LO).

We have not yet specified the unoccupied LO involved in the OS of the stack. As it was mentioned in section 1 the effective exchange integral is proportional to the squared resonance integral between the singly occupied d-orbital and corresponding LO. Due to uncertainties of the symmetry assignment of the singly occupied d-orbital and to effects of the local symmetry breaking in the crystal (see section 2.2) the symmetry of the LO remains uncertain. The LO should be vacant and have at least small overlap with the singly occupied d-orbital for the kinetic intramolecular exchange to exist.

The Hamiltonian (1) is very similar to that of the polymer ferromagnet [12]. Thus the procedure proposed in ref. [12] to find the approximate ground state of the polymer ferromagnet can be applied as well to the Hamiltonian (1).

As in ref. [12] we use the UHF approximation to calculate the ground state of the stack. With use of the equation of motion method in ref. [12] it was shown that the ground state wave function can be taken in the form of an antisymmetrized product of the wave function Φ_1 of localized electrons which all have the same spin projection $-S/2$ (d-system) and of the wave function of delocalized electrons in the organic system (Φ_2):

$$\Phi = \Phi_1 \wedge \Phi_2 \,,$$

$$\Phi_1 = \prod_n A^{+}_{n,-S/2} |0\rangle \,,$$

$$\Phi_2 = \prod_{|k| < k_F} g^{+}_{k\beta} g^{+}_{k\alpha} |0\rangle, \quad k_F = \tfrac{1}{2}\pi \,,$$

$$g^{+}_{k\sigma} = \cos\theta_{k\sigma}(S)\; \alpha^{+}_{k\sigma} + \sin\theta_{k\sigma}(S)\; b^{+}_{k\sigma} \,,$$

$$a^{+}_{k\sigma} = \frac{1}{\sqrt{N}} \sum_n \exp(\mathrm{i}kn) c^{+}_{1n\sigma} \,,$$

$$b^{+}_{k\sigma} = \frac{1}{\sqrt{N}} \sum_n \exp(\mathrm{i}kn) c^{+}_{2n\sigma} \,, \qquad (2)$$

where $g^{+}_{k\sigma}$ is the creation operator of an electron with spin projection σ on the occupied molecular orbital with wave number k. The parameters $\theta_{k\sigma}(S)$ are determined by the self-consistency conditions for the one-dimensional donor–acceptor crystal provided that the wave function Φ_2 of delocalized electrons has the zero projection of its total spin:

$$\tan 2\theta_{k\sigma}(S) = \frac{2t_{\parallel}(1+\cos k)}{\Delta\alpha + \Delta\gamma/2 - \delta_{-\sigma}(S)\bar{\gamma} - \frac{1}{2}K\sigma S} \,,$$

$$\delta_{\sigma}(S) = \frac{1}{2\pi} \int_0^{k_F} \cos 2\theta_{k\sigma}(S)\, \mathrm{d}k \,, \quad k_F = \tfrac{1}{2}\pi \,, \qquad (3)$$

where $\Delta\alpha = \alpha_1 - \alpha_2$, $\Delta\gamma = \gamma_2 - \gamma_1$, $\bar{\gamma} = \gamma_1 + \gamma_2$. The quantities $\delta_\alpha(\mathrm{S})$ and $\delta_\beta(\mathrm{S})$ determine the electron spin densities in the OS. The spin density on the DMFc site is

$$Q_{\mathrm{spin}} = S(\delta_\alpha(S) - \delta_\beta(S)) \,.$$

The spin density on TCNE is $-Q_{\mathrm{spin}}$. The charge densities on the sites are

$$Q_{\mathrm{TCNE}} = \tfrac{1}{2} + \delta_\alpha(S) + \delta_\beta(S) \,,$$

$$Q_{\mathrm{DMFc}} = \tfrac{1}{2} - \delta_\alpha(S) - \delta_\beta(S) \,.$$

The electronic structure of the OS of the stack has, in accord with eqs. (2) and (3), the following features. Due to nonzero total spin of the stack some nonvanishing spin density arises on the orbitals of DMFc$^+$ and TCNE which are involved in the OS. The spin density in the OS alternates on the neighboring molecules. Analogous result on the alternating spin density of delocalized π-electrons in the polymer ferromagnet was obtained in ref. [12].

The variable S determines both the sign of the spin densities in the OS and the orientation of the local d-electron spins and it can be either +1 or −1. The total spin of the stack is proportional to its length and amounts $\frac{1}{2}$ per formula unit. Thus the ground state of the stack exhibits ferromagnetic order.

2.4 Model calculation on the separate stack

We used the self-consistency eq. (3) to calculate the electronic structure of a separate DMFc–TCNE stack. So we encountered the problem of parameterization of the model. As can be easily seen the results of the calculations are only dependent on the difference $\Delta\alpha = \alpha_1 - \alpha_2$ and not on the values of α_1 and α_2 themselves. We adopt the energy gauge $\alpha_1 = 0$ and $\Delta\alpha$ becomes

$$\Delta\alpha = \Delta E + A + E_M - I \,,$$

where I is the ionization potential of d-electron (the first ionization potential of DMFc), ΔE is the energy of the excitation of d-electron to LO, A is the electron affinity of the TCNE molecule, and E_M is the Madelung energy per formula unit. According to ref. [7] the parameters of the ionic crystals are lying close to the neutral-ionic interface where the Madelung energy E_M coincides with the $I-A$ energy. Therefore $\Delta\alpha$ is about ΔE which amounts several electronvolts [7,18,19]. These $\Delta\alpha$ are obviously very large. This result indicates on very large difference between one-electron energies of the sites.

The most difficult problem is to estimate the intrastack resonance parameter $t_{\parallel}$ coupling the b_{3g}-orbital of TCNE and the LO of DMFc. The crystal structure of the ferromagnetic phase is not known for certain. The TCNE moieties are disordered [2,6] and therefore the exact values of $t_{\|}$ are unknown. Moreover, for the higher orbitals with multiple nodes the intermolecular resonance integrals are very sensitive to the geometry variations [22]. Existing experimental data on the charge distribution in the DMFc–TCNE salt [2,6] suggest it to be strongly inhomogeneous which is characteristic for narrow band solids. At any rate the resonance integrals cannot be large. The characteristic values of $t_{\|}$ in the narrow and solid should satisfy the conditions [23]:

$$\Delta\alpha/t_{\|} \approx \gamma_1/t_{\|} \approx \gamma_2/t_{\|} \geqslant 3 \div 5 .$$

In this limit the solution of the self-consistency equations (eq. (3)) has the following features. The absolute values of $\delta_\alpha(S)$ and $\delta_\beta(S)$ are close to their limiting value $\frac{1}{4}$. They are positive and therefore the electron density on the TCNE site is close to unity. The values of $\delta_\alpha(S)$ and $\delta_\beta(S)$ slightly differ because of the exchange interaction of delocalized electrons with the local spins and therefore the alternating spin densities arise in the OS. For example, for the parameter values

$$\Delta\alpha/t_{\|}=3, \quad \gamma_1/t_{\|}=\gamma_2/t_{\|}=5, \quad K/t_{\|}=2.5 ,$$

we obtain the spin density Q_{spin} on the LO of DMFc to be about 0.20 and the charge density Q_{TCNE} to be about 0.7.

3. Discussion

The UHF method was previously applied to the hypothetical polymer ferromagnet composed of the polyene chains with radical substituents (see ref. [12] and references therein). The main result of ref. [12] is that the exchange interaction between delocalized electrons in the conjugated π-system and local spins in the radical substituents aligns the latter in the same direction, and therefore gives the high spin ground state. The UHF result of ref. [12] is consistent with the exact topological considerations based upon the Ovchinnikov theorem on the total spin of alternant conjugated hydrocarbons [24].

The Miller ferromagnet considered in the present paper to some extent resembles the polymer ferromagnet. As in the polymer ferromagnet one part of electrons in the Miller ferromagnet can be described with use of local spins, but the other part remains delocalized as electrons in the conjugated π-system do. The UHF method was successful in the case of the polymer ferromagnet and it was a heuristic suggestion to apply the same method to the Miller ferromagnet.

Let us discuss the relations of our model with that of ME. First of all we note a correlation between the two approaches. Indeed in both the models d-electrons are treated as local spins. The difference arises when the electrons in the organic system (OS) are described. The ME model describes these electrons as local spins as well. In our model electrons in the OS are described as delocalized ones. Electron density, however, is distributed very inhomogeneously, and it is mainly concentrated on the TCNE sites. This result is in accordance with observed bond lengths in the TCNE moiety in the crystal which coincide with those in the TCNE$^{\dot{-}}$ radical-anion [2,6]. The strong inhomogeneity of the calculated charge distribution in the OS fairly corresponds with the experimental observations and supports the idea of the narrow electronic bands in the DMFc–TCNE ferromagnet.

The two models differ in the spin density. In the ME model the spin density on the TCNE site is strictly 1 whereas in our model it is about 0.2 (see section 2.4).

The value of the projection of the total spin (and correspondingly the saturation magnetization) of the stack turns out to be incorrect in our method. It was shown [2,6] that the experimental value of the saturation magnetization can be reproduced if the spin projection is ±1 per formula unit, whereas in our model the spin projection per formula unit equals to $\pm\frac{1}{2}$. Nevertheless the ME model of the ground state fails to explain the origin of the ferromagnetic order in the separate stack without invoking the kinetic ferromagnetic exchange based upon the direct resonance interaction between d-electrons and electrons in TCNE. However such an interaction seems to be ruled out by the analysis of ref. [7].

On the other hand the suggestion of ref. [7] on the important role of the charge-transfer states involving π-orbitals of the Cp* ligands turned out to be very useful. However, the authors of ref. [7] oversimplified the picture of the ligand orbitals. They restricted themselves to the π-orbitals of the Cp* rings and did not take into account diffuse 4s- and 4p-orbitals on the Fe atoms. The latter, however, are known to give an important contribution to the ligand orbitals and are always considered in the framework of any standard quantum chemical calculation (see in particular refs. [13–19]). The diffuse Fe orbitals drastically change all of the picture of the ligand orbitals of the $DMFc^+$ cation as compared to that of ref. [7] producing additional ligand levels which can overlap with orbitals of TCNE. For example in the idealized geometry adopted in ref. [7] only the occupied e_1-orbital of Cp* overlaps with the TCNE b_{3g}-orbital which we included in the organic system. If 4s- and 4p-orbitals are added the e_1-orbital also gives contribution (due to mixing with diffuse orbitals of the metal) to some vacant orbital which thus will overlap with the TCNE b_{3g}-orbital.

In the present paper we stress the role of delocalization of organic electrons (i.e. of the charge-transfer configurations) in the formation of the ferromagnetic ground state of the separate stack. It would be interesting to discuss different classes of configurations with charge-transfer contributing to the ground state. Any admixture of configurations with direct charge transfer between d-system and TCNE is ruled out, but the role of the charge-transfer configurations involving the Cp* ligands is stressed by the analysis given in paper [7]. Assuming the ligand orbital to be empty we include inexplicitly (in the framework of the UHF procedure) the configurations with an electron back transferred from the b_{3g}-orbital of TCNE to the DMFc ligand orbital. These configurations were absent in ref. [7] but as we managed to show this process plays a decisive role in the formation of the ferromagnetic ground state.

The mechanism of effective interaction between the local spins used in the present theory resembles the RKKY mechanism, which is well known in the theory of magnetic impurities [11]. Both in the RKKY theory and in the theory proposed the key role is played by the exchange interaction of the local spins with the delocalized electrons (band electrons). The effective interaction of the regularly displaced local spins with the system of the delocalized electrons causes the ground state of the stack to have ferromagnetic order in the system of the local spins. This interaction also results in the alternation of the spin density in the OS of the stack.

4. Conclusion

In this paper the important role of delocalization of electrons in the stacks is shown. The ordering in the charge-transfer ferromagnets arises because of both delocalization of electrons in the organic system and antiferromagnetic exchange interaction between delocalized electrons in the OS and localized ones in the d-system. This viewpoint strongly differs from the heuristic model [1–6] for the mechanism of the ordering in Miller ferromagnets. Because the main purpose of the present paper was to provide a framework for discussion of the ferromagnetism in the charge-transfer crystals, the calculations performed are mere illustrations since the parameterization problem remains unsolved and shall demand much work.

Acknowledgments

The authors would like to thank the referees for their profound and suggestive comments which helped us to clarify our paper.

The authors are grateful to Drs. V. Ya. Krivnov, A.M. Berezhkovskii, V.M. Ryaboy, and A.V. Soudackov for valuable discussions, and to Dr. A. Yu. Cohn for help during the preparation of the manuscript.

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