

Toward a Theory of the Room-Temperature Organometallic Charge-Transfer Ferromagnet

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We propose a hypothetical spatial arrangement of the components and a model for electronic structure of the room-temperature organometallic ferromagnet $V(\text{TCNE})_x \cdot y\text{CH}_2\text{Cl}_2$ (TCNE = tetracyanoethylene). The ferrimagnetic ground state arises because of weak electron hopping between the d orbital of V^{2+} ions and singly occupied orbitals of $\text{TCNE}^{\cdot-}$. For the ground state this interaction is treated by means of a variational unrestricted Hartree–Fock method. We describe the excited states of the ferrimagnetic crystal by an effective spin Hamiltonian which arises within the perturbational approach to the intersite hopping. The chemical bonding in the new class of organometallic magnetic materials is discussed briefly.

I. Introduction

Since the discovery of organometallic ferromagnets based on the charge-transfer salt of decamethylferrocene (DMeFc) with tetracyanoethylene (TCNE) by Miller, Epstein, and co-workers,¹ progress in this area has been remarkable. The Curie temperature (T_c) of the DMeFc–TCNE salt is 4.8 K. Hoffman and co-workers² reported that the analogous salt of decamethylmanganocenium (DMeMc) with tetracyanoquinodimethane (TCNQ) has $T_c = 6.2$ K, and Yee and co-workers³ have found that the DMeMc–TCNE salt has $T_c = 8.8$ K. Very recently Miller, Epstein, and co-workers⁴ reported the synthesis of a room-temperature ferromagnet—a remarkable breakthrough in the area of organometallic magnetism.

The air- and moisture-sensitive black amorphous precipitate obtained from the reaction of bis(benzene)vanadium ($V(\text{C}_6\text{H}_6)_2$) with TCNE in dichloromethane solution exhibits both spontaneous magnetization and hysteresis in its magnetization curve at room temperature.⁴ This behavior contrasts sharply with that of the series of compounds reported previously^{1–3} which exhibit magnetic order only at extremely low temperatures (several kelvin). Incidentally, the chemical composition of the room-temperature ferromagnet is completely different from that of the low-temperature ones. While the low-temperature Miller–Epstein compounds contain metallocenium cations^{1–3} which retain cyclopentadienyl ligands, in the reaction yielding the room-temperature Miller–Epstein ferromagnet the benzene rings attached to the vanadium atom are lost and the composition of the precipitate can be expressed as $V(\text{TCNE})_x \cdot y\text{CH}_2\text{Cl}_2$ where x is about 2 and y is about 0.5. That brought the authors of refs 4–6 to the idea that the high Curie temperature of the V–TCNE compound (it is estimated to be 400 K—even higher than the decomposition temperature^{4,5}) is a consequence of direct interaction between the nitrogen atoms of TCNE molecules and vanadium atoms not screened by the cyclopentadienyl ligands. This idea is ingenious, but because of the lack of structural information, it has not yet evolved into a theory which would describe the magnetic interaction in the V–TCNE compound on the molecular level. The experimental data on the magnetic susceptibility and on magnetization of the room-temperature ferromagnet were fit^{5,6} to phenomenological models with effective

antiferromagnetic coupling of the spins localized on V and TCNE sites.⁴ However, the particular features of the electronic structure of the material which are responsible for the effective spin–spin interactions remain unclear.

Though almost nothing is known about the actual structure of the V–TCNE ferromagnet, any possible structure must satisfy some general conditions based upon experimental data from refs 4–6. Any V–TCNE sublattice must (i) correspond to the observed composition $V(\text{TCNE})_2$, (ii) form a three-dimensional network of V atoms and TCNE molecules without pronounced anisotropy, and (iii) be loose enough to accommodate solvent molecules and still comply with the observed density of about 1 g/cm^3 .⁷ Such a sublattice need not actually exist on the long range scale but is probably an acceptable approximation for short range domains.

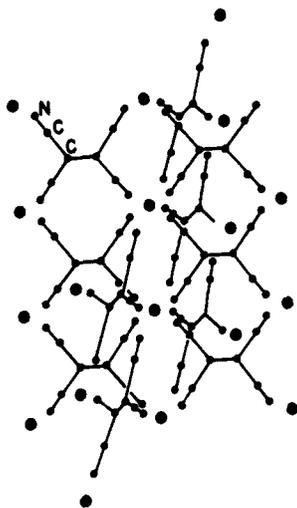
In order to describe the electronic structure of V–TCNE, we will use the theory of the magnetic insulating state,⁸ in which effective interaction between local magnetic moments is explained by weak delocalization of local electronic states. This idea has recently been implemented^{9–12} for analysis of electronic structure and magnetic interactions in low-temperature Miller–Epstein ferromagnets.

The paper is organized as follows: in section II we describe a hypothetical crystal structure for the V–TCNE compound and the electronic structure of the ions constituting the crystal. In section III we describe the one-electron states and the interactions involved in the model Hamiltonian for that crystal. In section IV we consider the electronic ground state of the crystal in the framework of the proposed model. In section V we perform the perturbational treatment of one-electron hopping, leading to the spin Hamiltonian for excited states of the crystal, and we make some numerical estimates of its parameters. In section VI we consider the nature of bonding in the V–TCNE sublattice. Section VII concludes with some discussion and remarks.

II. V–TCNE Sublattice

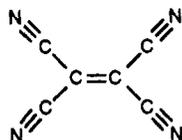
A. Geometry. One simple structure which satisfies the $V(\text{TCNE})_2$ stoichiometry is presented in structure 1. It contains a cubic (or cubic with tetragonal distortion) lattice of vanadium atoms (1). The vanadiums are surrounded by planar TCNE molecules, which are placed in the vertical faces of cubes. Each vanadium atom interacts with eight different TCNE molecules, or, more precisely, with the nitrogen atoms of eight TCNE

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molecules (2). We assume that the TCNE fragments keep their planar structure in the room-temperature ferromagnet as well (see below).



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The structure proposed clearly satisfies requirements i–iii, listed in the Introduction. It corresponds to the approximate stoichiometry, it is loose, and if the lattice parameters are $a = b = 8.54$ Å and $c = 7.20$ Å, then the density corresponding to the formula $V(\text{TCNE})_{2.1}^{1/2}\text{CH}_2\text{Cl}_2$ is equal to 1.11 g/cm³. The type of coordination of TCNE to the V atom suggested here is listed among others in ref 6. It actually exists in another organometallic ferromagnet, $[\text{MnTPP}]^+[\text{TCNE}]^-$.^{7b}

B. Electronic Structure of Constituent Ions. On the basis of IR spectroscopic data, the authors of ref 4 proposed that in the room-temperature ferromagnet vanadium atoms occur in the form of the V^{2+} ions and TCNE occurs in the form of TCNE^- , as in the low-temperature Miller–Epstein ferromagnets.¹ The lowest unoccupied molecular orbital of TCNE is the b_{3g} orbital of π character. This orbital lies at rather low energy, since TCNE is a good organic acceptor. We will refer to the b_{3g} orbital of TCNE as the *acceptor* orbital. When the radical anion is formed, an extra electron occupies this orbital. TCNE^- are known to be planar,¹ and we assume them to be planar in the V–TCNE compound as well.

Free V^{2+} have three electrons in their d-shell. In the cubic field of our suggested structure, the splitting pattern for d-orbitals is inverted, two below three, compared to that in the octahedral field. If x and y axes are chosen to coincide with a and b crystallographic axes, respectively, and the z axis coincides with the c axis, then the cubic harmonics labeled d_{xz} , d_{yz} , and $d_{x^2-y^2}$ lie above and those labeled d_{z^2} , d_{xy} , below. In the distorted cubic environment the degeneracy is lifted. We assume for the sake of simplicity that tetragonal symmetry is nevertheless conserved, so that the orbitals d_{xz} and d_{yz} remain doubly degenerate. We also assume the distortion puts these degenerate orbitals at higher energy so that three electrons are probably distributed in three lower orbitals ($d_{x^2-y^2}$, d_{z^2} , and d_{xy}).

Since the nitrogen–vanadium separation is quite large, the splitting probably does not exceed the critical value separating high spin complexes from low spin ones, so the V^{2+} ions are in

the high spin state ($S = 3/2$), in agreement with the data analysis performed in ref 4.

The above analysis suggests that in the case of the room-temperature V–TCNE ferromagnet we have a magnetic insulator. The general theory of the magnetic insulating state was developed by Anderson.⁸ In our qualitative considerations presented just above, we treated the local magnetic states as states of free constituent ions. In contrast with that, Anderson's theory assumes these states to be slightly delocalized. The main idea of ref 8 is that, in order to construct the local one-electron states of the crystal, one should modify the states of the free ions to take into account the influence of the crystal lattice upon them. The way to construct such modified states is as follows: First, we write the model Hamiltonian formulating the above-mentioned qualitative features of geometrical and electronic structure of the crystal. That Hamiltonian necessarily will contain electron–electron interaction terms, which do not allow one to solve for the ground state exactly. To accomplish that, we will use the self-consistent field approximation and factorize these terms. The problem then becomes a linear one. We will proceed to find the Bloch states for the factorized linear problem; these states contain information on the electronic structure of the crystal. Finally, we transform the Bloch states into local Wannier states. The Wannier states approximate the modified states of the ions in the crystal. They give the description of the electronic ground state of the crystal in terms of the local states, which are in some sense close to the states of free ions. In order to estimate the characteristic energy of magnetic excitations, we construct the effective spin Hamiltonian. Its effective exchange parameter gives us the scale of characteristic energies of magnetic excitations.

III. Model Hamiltonian

In order to write the Hamiltonian explicitly, we must specify the set of one-electron basis states involved in the model. The qualitative discussion above suggests that acceptor orbitals of two TCNE molecules in each unit cell must be included. To describe electrons in the V^{2+} ions, we consider three lower d-orbitals ($d_{x^2-y^2}$, d_{z^2} , and d_{xy}) per site. For the geometry proposed above, only the d_{xy} orbital has a nonvanishing overlap with the acceptor orbitals of the adjacent TCNE molecules. For that reason we take into account electron hopping between d_{xy} orbitals of vanadium ions and b_{3g} orbitals of adjacent TCNE molecules.

To consider effects of electron–electron repulsion, we (as suggested in refs 9–12) include the on-site Hubbard terms for TCNE molecules. Description of electron–electron interactions in the vanadium ions is not so simple, because we need to reproduce the high spin ground state of the V^{2+} ions predicted by Hund's rule. Hund's rule emerges from the reduced form of the interaction operator for d-electrons^{14–16} which we will use.

The model Hamiltonian for the V–TCNE sublattice, formulating the above ideas, has the form

$$H = \sum_{\mathbf{r}} (H_d(\mathbf{r}) + H_A(\mathbf{r}) + H_{dA}(\mathbf{r})) \quad (1)$$

Summation over \mathbf{r} is extended to all unit cells of the crystal. The operator $H_d(\mathbf{r})$ describes electrons in three d-orbitals of the vanadium ion in the \mathbf{r} th unit cell. Operator $H_A(\mathbf{r})$ describes electrons in two acceptor orbitals of two TCNE^- ions in the \mathbf{r} th unit cell. Operator $H_{dA}(\mathbf{r})$ describes electron hopping interaction between d-states and acceptor states.

$$H_A(\mathbf{r}) = -\alpha_A \sum_{\sigma} (n_{\xi_{r\sigma}} + n_{\eta_{r\sigma}}) + \gamma_A (n_{\xi_{r\uparrow}} n_{\xi_{r\downarrow}} + n_{\eta_{r\uparrow}} n_{\eta_{r\downarrow}}) \quad (2a)$$

$$n_{\xi_{r\sigma}} = \xi_{r\sigma}^{\dagger} \xi_{r\sigma}, \quad n_{\eta_{r\sigma}} = \eta_{r\sigma}^{\dagger} \eta_{r\sigma}$$

Operators $\xi_{r\sigma}^{\dagger}$ ($\xi_{r\sigma}$) and $\eta_{r\sigma}^{\dagger}$ ($\eta_{r\sigma}$) are the operators creating (annihilating) an electron with spin projection σ on the acceptor orbitals of the TCNE molecules extended in the x and y directions,

respectively, in the r th unit cell. In eq 1 the first term is the energy of attraction of an electron to the core of TCNE. The second term is the Hubbard one, describing the Coulomb repulsion of electrons with opposite spin projections occupying the same acceptor site orbital.

The reduced Hamiltonian¹⁴⁻¹⁶ for d-states has the form

$$H_d(\mathbf{r}) = -\sum_{\sigma} (\alpha_f n_{f\sigma} + \alpha_u n_{u\sigma} + \alpha_v n_{v\sigma}) + (U + 2J) \times \\ (n_{f\uparrow} n_{f\downarrow} + n_{u\uparrow} n_{u\downarrow} + n_{v\uparrow} n_{v\downarrow}) + (U + J/2) \sum_{\sigma, \sigma'} (n_{f\sigma} n_{u\sigma'} + \\ n_{f\sigma} n_{v\sigma'} + n_{u\sigma} n_{v\sigma'}) - 4J(S_{f\uparrow} S_{u\uparrow} + S_{f\uparrow} S_{v\uparrow} + S_{u\uparrow} S_{v\uparrow}) \quad (2b)$$

In this equation $f_{r\sigma}^+$ ($f_{r\sigma}$), $u_{r\sigma}^+$ ($u_{r\sigma}$), and $v_{r\sigma}^+$ ($v_{r\sigma}$) are the creation (annihilation) operators of an electron with spin projection σ on the d_{xy} , d_{z^2} , and $d_{x^2-y^2}$ orbitals, respectively, of the vanadium ion in the r th unit cell. The first term in the above operator is the one-electron energy of the orbitals (proportional to α_f , α_u , and α_v , respectively) and reflects their crystal field splitting as well.

The electron-electron repulsion part of the above Hamiltonian contains the term describing the interaction of two electrons with opposite spins occupying the same d-orbital (that proportional to $U + 2J$), the term describing repulsion between electrons occupying different d-orbitals at the same vanadium site (that proportional to $U + J/2$), and the exchange terms having the form of scalar products of spin operators.

The electron number operators $n_{f\sigma}$, $n_{u\sigma}$, and $n_{v\sigma}$ are defined as usual. The spin product terms are defined by the well-known relations

$$S_i S_j = 1/2(S_i^+ S_j^- + S_j^+ S_i^-) + S_i^z S_j^z \\ S_i^+ = c_{i\uparrow}^+ c_{i\downarrow}, \quad S_i^- = c_{i\downarrow}^+ c_{i\uparrow}, \quad S_i^z = 1/2(c_{i\uparrow}^+ c_{i\uparrow} - c_{i\downarrow}^+ c_{i\downarrow})$$

Parameters describing the electron-electron interaction in the d-shell of vanadium ions are the average Coulomb integral (U) and the average exchange integral (J) calculated for different cubic harmonics.^{14,15}

The electron hopping operator has the form

$$H_{dA}(\mathbf{r}) = -t \sum_{\sigma} ((\xi_{r\sigma}^+ \xi_{r\sigma} + \eta_{r\sigma}^+ \eta_{r\sigma}) - (\xi_{r\sigma}^+ \xi_{r+a\sigma} + \eta_{r\sigma}^+ \eta_{r+b\sigma}) + \\ (\xi_{r\sigma}^+ \xi_{r+c\sigma} + \eta_{r\sigma}^+ \eta_{r+c\sigma}) - (\xi_{r\sigma}^+ \xi_{r+a+c\sigma} + \eta_{r\sigma}^+ \eta_{r+b+c\sigma})) + hc \quad (2c)$$

It is responsible for extension of one-electron states over the crystal. The hopping parameter t is proportional to the overlap between the orbitals. For that reason we retain only the terms corresponding to the hopping between the d_{xy} orbitals of vanadium ions and acceptor orbitals on all TCNE sites adjacent to the given V site.

IV. Electronic Structure of the Crystal

A. Delocalized Representation of the Ground State. In order to find the ground state for the crystal, we apply the unrestricted Hartree-Fock (UHF) approximation to factorize the terms of electron-electron interaction in the Hamiltonian. The UHF approximation consists of replacing the products of four fermion operators according to the rule

$$c_1^+ c_2^+ c_3^+ c_4 \rightarrow \langle c_1^+ c_2 \rangle \langle c_3^+ c_4 \rangle - \langle c_1^+ c_4 \rangle \langle c_2^+ c_3 \rangle$$

The averages $\langle \dots \rangle$ must be taken over the UHF single determinant state which is yet to be found. The general form of the averages can be chosen semiempirically to satisfy certain a priori symmetry conditions. For instance, we set averages of the form $\langle c_{\sigma}^+ c_{-\sigma} \rangle$ to be zero. This is equivalent to requiring that the UHF state must be an eigenstate of the spin projection operator. Hence all the averages of the form $\langle S_i^+ \rangle$ or $\langle S_i^- \rangle$ are zero. We also would like to preserve the local symmetry of the V^{2+} sites. For that reason we also set to zero averages having the form $\langle f_{r\sigma}^+ u_{r\sigma} \rangle$ or $\langle f_{r\sigma}^+ v_{r\sigma} \rangle$.

The spatial dependence of the averages is also established semiempirically. As a first approximation we take the averages to be the same for all unit cells. The quantities $\langle n_{i\sigma} \rangle$ and $\langle S_i^z \rangle$ are then the r -independent averages of the operators $n_{i\sigma}$ and $S_{i\sigma}^z$ over the ground state.

Keeping in mind the symmetry-conditioned restrictions on the form of the averages imposed above, we obtain, after some algebra, the electronic energy of the crystal per unit cell in the UHF approximation:

$$E = -\alpha_A (\langle n_{\xi} \rangle + \langle n_{\eta} \rangle) + \gamma_A (\langle n_{\xi\uparrow} \rangle \langle n_{\xi\downarrow} \rangle + \\ \langle n_{\eta\uparrow} \rangle \langle n_{\eta\downarrow} \rangle) - (\alpha_f \langle n_f \rangle + \alpha_u \langle n_u \rangle + \alpha_v \langle n_v \rangle) + \\ (U + 2J) (\langle n_{f\uparrow} \rangle \langle n_{f\downarrow} \rangle + \langle n_{u\uparrow} \rangle \langle n_{u\downarrow} \rangle + \langle n_{v\uparrow} \rangle \langle n_{v\downarrow} \rangle) + \\ (U + J/2) (\langle n_f \rangle \langle n_u \rangle + \langle n_f \rangle \langle n_v \rangle + \langle n_u \rangle \langle n_v \rangle) - \\ 4J (\langle S_f^z \rangle \langle S_u^z \rangle + \langle S_f^z \rangle \langle S_v^z \rangle + \langle S_u^z \rangle \langle S_v^z \rangle) - t \sum_{\sigma} P_{\sigma} \quad (3)$$

where

$$P_{\sigma} = (((\xi_{r\sigma}^+ \xi_{r\sigma}) + (\eta_{r\sigma}^+ \eta_{r\sigma})) - ((\xi_{r\sigma}^+ \xi_{r+a\sigma}) + (\eta_{r\sigma}^+ \eta_{r+b\sigma})) + \\ ((\xi_{r\sigma}^+ \xi_{r+c\sigma}) + (\eta_{r\sigma}^+ \eta_{r+c\sigma})) - ((\xi_{r\sigma}^+ \xi_{r+a+c\sigma}) + \\ (\eta_{r\sigma}^+ \eta_{r+b+c\sigma}))) + cc \\ \langle n_i \rangle = \sum_{\sigma} \langle n_{i\sigma} \rangle$$

The electronic energy must be optimized in order to find the averages corresponding to the UHF ground state. The standard method of parametrizing the averages is to introduce the Bloch states as linear combinations of the site states. It can be seen, however, from eq 2, that the averages $\langle n_{u\sigma} \rangle$, $\langle n_{v\sigma} \rangle$, $\langle S_u^z \rangle$, and $\langle S_v^z \rangle$ enter the above expression for the energy in such a form that the participation of the respective orbitals in the linear combinations of the site states does not decrease the energy. For that reason they will not be included explicitly in the subsequent optimization procedure.

The averages can be parametrized with use of the Fourier transformation. For the Fourier transforms $\xi_{k\sigma}$, $\xi_{k\sigma}$, and $\eta_{k\sigma}$ of the site states $\xi_{r\sigma}$, $\xi_{r\sigma}$, and $\eta_{r\sigma}$, we introduce a new set of orthonormal one-electron states $Z_{k\sigma}$, $\Psi_{k\sigma}$, and $T_{k\sigma}$:

$$Z_{k\sigma} = \cos \theta_{k\sigma} \xi_{k\sigma} + \sin \theta_{k\sigma} (S_{xk}^* \xi_{k\sigma} + S_{yk}^* \eta_{k\sigma}) \\ \Psi_{k\sigma} = -\sin \theta_{k\sigma} \xi_{k\sigma} + \cos \theta_{k\sigma} (S_{xk}^* \xi_{k\sigma} + S_{yk}^* \eta_{k\sigma}) \\ T_{k\sigma} = (S_{yk} \xi_{k\sigma} - S_{xk} \eta_{k\sigma}) \quad (4)$$

where

$$Q_{xk} = 1 - \exp(-ik_x) + \exp(-ik_z) - \exp(-ik_x - ik_z) \\ Q_{yk} = 1 - \exp(-ik_y) + \exp(-ik_z) - \exp(-ik_y - ik_z) \\ S_{xk} = Q_{xk} (Q_{xk}^* Q_{xk} + Q_{yk}^* Q_{yk})^{-1/2}, \\ S_{yk} = Q_{yk} (Q_{xk}^* Q_{xk} + Q_{yk}^* Q_{yk})^{-1/2}$$

The averages defined above can be expressed now as functions of the variation parameters $\theta_{k\sigma}$.

$$\langle n_{\xi\sigma} \rangle = (1/N) \sum_{\mathbf{k}} [n_{T_{k\sigma}} S_{xk}^* S_{yk} + n_{Z_{k\sigma}} \sin^2 \theta_{k\sigma} S_{xk}^* S_{xk} + \\ n_{\Psi_{k\sigma}} \cos^2 \theta_{k\sigma} S_{xk}^* S_{xk}] \\ \langle n_{\eta\sigma} \rangle = (1/N) \sum_{\mathbf{k}} [n_{T_{k\sigma}} S_{xk}^* S_{xk} + n_{Z_{k\sigma}} \sin^2 \theta_{k\sigma} S_{yk}^* S_{yk} + \\ n_{\Psi_{k\sigma}} \cos^2 \theta_{k\sigma} S_{yk}^* S_{yk}] \\ \langle n_{f\sigma} \rangle = (1/N) \sum_{\mathbf{k}} [n_{Z_{k\sigma}} \cos^2 \theta_{k\sigma} + n_{\Psi_{k\sigma}} \sin^2 \theta_{k\sigma}] \quad (5)$$

Here N is the number of the unit cells and $n_{i\sigma} = 0, 1$ ($i = Z, \Psi$,

and T) are the occupation numbers for the corresponding states. The occupation numbers satisfy the normalization condition:

$$\sum_{i, \mathbf{k}, \sigma} n_{i\mathbf{k}\sigma} = 5N$$

The sum of the averages of electron-transfer operators P_σ in eq 2 does not depend on r and has the form

$$P_\sigma = (2/N) \sum_{\mathbf{k}} \sin \theta_{\mathbf{k}\sigma} \cos \theta_{\mathbf{k}\sigma} \times \\ (Q^*_{x\mathbf{k}} Q_{x\mathbf{k}} + Q^*_{y\mathbf{k}} Q_{y\mathbf{k}})^{1/2} (n_{Z\mathbf{k}\sigma} - n_{\Psi\mathbf{k}\sigma}) \quad (6)$$

The averages thus defined must be inserted into the general expression for the energy. For any given distribution of the state occupation numbers $n_{i\mathbf{k}\sigma}$, the energy is a smooth function of the variation parameters $\theta_{\mathbf{k}\sigma}$. However, the very form of this function depends on that distribution (i.e. on the particular mode of filling) in a singular manner. We will choose the type of filling heuristically, based upon the relative magnitude of parameters of the Hamiltonian, eq 1.

The total number of electrons to be distributed is 5 per unit cell. We assume that the parameters of the Hamiltonian eq 1 describing the electron-electron repulsion, both intraatomic (U and J), and intramolecular (γ_A), are much greater than the electron-transfer parameter t . For that reason the limit of separated V^{2+} cations and $TCNE^-$ anions is a good initial approximation. In the free ion limit all the averages of the form $\langle n_{i\sigma} \rangle$ are either zero or unity and for no i is $\langle n_{i\sigma} \rangle$ unity for both values of the spin projection σ . The exchange terms in the Hamiltonian make the spin projections of all the electrons in the vanadium sites the same. Thus the averages $\langle S^z_i \rangle$, $\langle S^z_u \rangle$, and $\langle S^z_v \rangle$ are the same; we denote their common value by S . In terms of the delocalized states defined above, the free ion limit is equivalent to setting all of the variational parameters $\theta_{\mathbf{k}\sigma}$ to zero and to setting all of the occupation numbers $n_{Z\mathbf{k}\sigma} = 1$. Then all the ζ -states are singly occupied by electrons with spin projection S . Two other electrons with the same spin projection occupy the isolated (u and v) orbitals in each unit cell. The single occupancy of the acceptor states in the free ion limit can be reproduced if one fills completely all the T and Ψ states with electrons having spin projection S' , such that for all \mathbf{k} , $n_{T\mathbf{k}S'} = n_{\Psi\mathbf{k}S'} = 1$. If the electron-transfer term vanishes, then the states with arbitrary mutual orientation of the spin projections in the vanadium and $TCNE$ ions are degenerate. The electronic wave function of the crystal in the free ion limit therefore reads

$$\Psi_{\text{free}} = \prod_{\mathbf{r}} \xi_{rS}^+ \eta_{rS}^+ \zeta_{rS}^+ \mu_{rS}^+ \nu_{rS}^+ |0\rangle$$

This function usually serves as a starting point for perturbative treatment of an admixture of electron-transfer states (see below). However, we are going to treat these states in the framework of the variational approach, using a trial wave function with parameters $\theta_{\mathbf{k}\sigma}$.

$$\Psi_{\text{trial}} = \prod_{\mathbf{k}} \Psi_{\mathbf{k}S}^+ \Upsilon_{\mathbf{k}S}^+ Z_{\mathbf{k}S}^+ \prod_{\mathbf{r}} \mu_{rS}^+ \nu_{rS}^+ |0\rangle \quad (7)$$

Though the above wave function of the free ion limit has been presented as a product of local one-electron states of free ions, it will coincide with the trial function of eq 7, provided the variational parameters $\theta_{\mathbf{k}\sigma}$ are set to zero. So in its extreme form eq 7 describes the completely localized free ion limit as well.

Though the electron delocalization is weak, it nevertheless gives some gain in energy as compared to the free ion limit. One can see that only $Z_{\mathbf{k}\sigma}$ and $\Psi_{\mathbf{k}\sigma}$ states contribute to P_σ —the sum of averages which is responsible for the energy lowering. Moreover, if for some \mathbf{k} the states $Z_{\mathbf{k}\sigma}$ and $\Psi_{\mathbf{k}\sigma}$ are both occupied, their contributions to P_σ cancel each other. Since all the states $Z_{\mathbf{k}\sigma}$ are occupied, the only way to maximize the energy gain from delocalization is to fill all the $\Psi_{\mathbf{k}\sigma}$ states. Then we have $S' =$

$-S$ and the trial wave function becomes

$$\Psi_{\text{trial}} = \prod_{\mathbf{k}} \Psi_{\mathbf{k}\sigma}^+ \Upsilon_{\mathbf{k}\sigma}^+ Z_{\mathbf{k}\sigma}^+ \prod_{\mathbf{r}} \mu_{rS}^+ \nu_{rS}^+ |0\rangle$$

Now the function to be optimized—the electronic energy per unit cell (eq 3)—is completely defined.

The equations for the vibrational parameters $\theta_{\mathbf{k}\sigma}$ of the trial function become

$$\partial E / \partial \theta_{\mathbf{k}\sigma} = 0$$

and after substituting of the averages eqs 5 and 6, we obtain

$$-2t \cos 2\theta_{\mathbf{k}\sigma} (Q^*_{x\mathbf{k}} Q_{x\mathbf{k}} + Q^*_{y\mathbf{k}} Q_{y\mathbf{k}})^{1/2} (n_{Z\mathbf{k}\sigma} - n_{\Psi\mathbf{k}\sigma}) + \\ (\epsilon_{A\sigma} - \epsilon_{\zeta\sigma}) \sin 2\theta_{\mathbf{k}\sigma} = 0$$

$$\epsilon_{A\sigma} = -\alpha_A + \gamma_A \langle n_{A-\sigma} \rangle$$

$$\epsilon_{\zeta\sigma} = -\alpha_\zeta + (U + 2J) \langle n_{\zeta-\sigma} \rangle +$$

$$(U + J/2) (\langle n_v \rangle + \langle n_u \rangle) - 4J\sigma (\langle S^z_v \rangle + \langle S^z_u \rangle) =$$

$$-\alpha_\zeta + (U + 2J) \langle n_{\zeta-\sigma} \rangle + 2(U + J/2) - 8J\sigma S$$

Here we set $\langle n_{\xi\sigma} \rangle = \langle n_{\eta\sigma} \rangle = \langle n_{A\sigma} \rangle$. The variational parameters can be found easily:

$$\cos \theta_{\mathbf{k}\sigma} = \left(\frac{1}{2} \left(1 + \frac{\Delta\epsilon_\sigma}{(\Delta\epsilon_\sigma^2 + 4t^2(Q^*_{x\mathbf{k}} Q_{x\mathbf{k}} + Q^*_{y\mathbf{k}} Q_{y\mathbf{k}}))^{1/2}} \right) \right)^{1/2}$$

or

$$\sin \theta_{\mathbf{k}\sigma} = \left(\frac{1}{2} \left(1 - \frac{\Delta\epsilon_\sigma}{(\Delta\epsilon_\sigma^2 + 4t^2(Q^*_{x\mathbf{k}} Q_{x\mathbf{k}} + Q^*_{y\mathbf{k}} Q_{y\mathbf{k}}))^{1/2}} \right) \right)^{1/2}$$

where

$$\Delta\epsilon_\sigma = \epsilon_{\zeta\sigma} - \epsilon_{A\sigma} \quad (8)$$

Parameters of our Hamiltonian eq 1 are such that the delocalization is weak, or formally $|t/\Delta\epsilon_\sigma| \ll 1$. In that limit the variational parameters are defined by the identities

$$\cos \theta_{\mathbf{k}\sigma} = 1 - \left(\frac{t}{\Delta\epsilon_\sigma} \right)^2 (Q^*_{x\mathbf{k}} Q_{x\mathbf{k}} + Q^*_{y\mathbf{k}} Q_{y\mathbf{k}}) / 2$$

or

$$\sin \theta_{\mathbf{k}\sigma} = \frac{t}{\Delta\epsilon_\sigma} (Q^*_{x\mathbf{k}} Q_{x\mathbf{k}} + Q^*_{y\mathbf{k}} Q_{y\mathbf{k}})^{1/2}$$

The averages of the particle number operators $\langle n_{i\sigma} \rangle$ entering the expressions for $\Delta\epsilon_\sigma$ can be expressed as sums over the Brillouin zone:

$$\langle n_{\xi S} \rangle = \langle n_{A S} \rangle = (1/N) \sum_{\mathbf{k}} \sin^2 \theta_{\mathbf{k} S} S^*_{x\mathbf{k}} S_{x\mathbf{k}} =$$

$$4(t/\Delta\epsilon_S)^2 = \langle n_{\eta S} \rangle$$

$$\langle n_{\zeta S} \rangle = (1/N) \sum_{\mathbf{k}} \cos^2 \theta_{\mathbf{k} S} = 1 - 8(t/\Delta\epsilon_S)^2$$

$$\langle n_{\zeta - S} \rangle = \langle n_{A - S} \rangle = (1/N) \sum_{\mathbf{k}} [S^*_{y\mathbf{k}} S_{y\mathbf{k}} + \cos^2 \theta_{\mathbf{k}\sigma} S^*_{x\mathbf{k}} S_{x\mathbf{k}}] =$$

$$1 - 4(t/\Delta\epsilon_{-S})^2 = \langle n_{\eta - S} \rangle$$

$$\langle n_{\zeta - S} \rangle = (1/N) \sum_{\mathbf{k}} \sin^2 \theta_{\mathbf{k} - S} = 8(t/\Delta\epsilon_{-S})^2$$

The above expressions, together with the definition of $\Delta\epsilon_\sigma$ (eq 8), form the set of self-consistency equations for the averages. They can be solved iteratively; their solution completely defines the trial wave function corresponding to the lowest possible (in the UHF approximation) energy.

B. Localized Representation of the Ground State. In the previous section we found the ground state of electrons in the

V(TCNE)₂ crystal within the UHF approximation. The electronic wave function in the UHF approximation (eq 7) is a product of the Bloch states which are delocalized over the entire crystal. The energies associated with the Bloch states form energy bands. As we mentioned in the previous section, the parameters of the Hamiltonian satisfy the condition $t/|\Delta\epsilon_\sigma| \ll 1$. In this limit the energy bands have the form

$$\begin{aligned}\bar{\epsilon}_{\mathbf{k}\sigma} &= \epsilon_{A\sigma} - \frac{t^2(Q_{x\mathbf{k}}^*Q_{x\mathbf{k}} + Q_{y\mathbf{k}}^*Q_{y\mathbf{k}})}{|\Delta\epsilon_\sigma|} \\ \epsilon_{\mathbf{k}\sigma}^0 &= \epsilon_{A\sigma} \\ \epsilon_{\mathbf{k}\sigma}^+ &= \epsilon_{\zeta\sigma} + \frac{t^2(Q_{x\mathbf{k}}^*Q_{x\mathbf{k}} + Q_{y\mathbf{k}}^*Q_{y\mathbf{k}})}{|\Delta\epsilon_\sigma|}\end{aligned}$$

One of the bands is dispersionless, two others are very narrow. That all indicates that a localized description of the electronic structure of the V(TCNE)₂ crystal may be more appropriate than the delocalized one obtained in the previous section.

To construct the local description, we must turn to Wannier functions centered on the crystal sites. Note that since the u and v states did not participate in the optimization procedure, they do not form bands and thus are not delocalized. They can be considered as the Wannier states for corresponding electrons. For the delocalized bands the Wannier states are of two types: (1) vanadium-centered states with predominant contributions from the ionic ζ states, and (2) TCNE-centered states largely formed from the b_{3g} orbitals of x or y TCNE radical anions.

The Wannier functions are by definition

$$\begin{aligned}z_{r\sigma} &= (N)^{-1/2} \sum_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}) Z_{\mathbf{k}\sigma} \\ x_{r\sigma} &= (N)^{-1/2} \sum_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}) (S_{x\mathbf{k}}\psi_{\mathbf{k}\sigma} + S_{y\mathbf{k}}^*\nu_{\mathbf{k}\sigma}) \\ y_{r\sigma} &= (N)^{-1/2} \sum_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}) (S_{y\mathbf{k}}\psi_{\mathbf{k}\sigma} - S_{x\mathbf{k}}^*\nu_{\mathbf{k}\sigma})\end{aligned}$$

In the weak hopping limit we have

$$\begin{aligned}z_{r\sigma} &= (1 - 4(t/\Delta\epsilon_\sigma)^2)\zeta_{r\sigma} + t/\Delta\epsilon_\sigma(\xi_{r\sigma} + \xi_{r+c\sigma} - \xi_{r+a\sigma} + \\ &\quad \xi_{r+a+c\sigma} + \eta_{r\sigma} + \eta_{r+c\sigma} - \eta_{r+b\sigma} + \eta_{r+b+c\sigma}) \\ x_{r\sigma} &= (1 - 2(t/\Delta\epsilon_\sigma)^2)\xi_{r\sigma} - t/\Delta\epsilon_\sigma(\zeta_{r\sigma} + \zeta_{r-c\sigma} - \zeta_{r-a\sigma} + \zeta_{r-a-c\sigma}) \\ y_{r\sigma} &= (1 - 2(t/\Delta\epsilon_\sigma)^2)\eta_{r\sigma} - t/\Delta\epsilon_\sigma(\zeta_{r\sigma} + \zeta_{r-c\sigma} - \zeta_{r-b\sigma} + \zeta_{r-b-c\sigma})\end{aligned}$$

The entire Slater determinant remains unchanged under the transformation leading from delocalized Bloch states to local Wannier states. The trial wave function of the ground state of the crystal thus reads

$$\Psi_{\text{trial}} = \prod_{\mathbf{r}} x_{\mathbf{r}-\mathbf{S}}^+ y_{\mathbf{r}-\mathbf{S}}^+ z_{\mathbf{r}\mathbf{S}}^+ u_{\mathbf{r}\mathbf{S}}^+ v_{\mathbf{r}\mathbf{S}}^+ |0\rangle$$

It looks very similar to the wave function of the crystal in the free ion limit. The local atomic states of the free ion limit function are replaced here by slightly delocalized Wannier states. This takes into account the delocalizing effect of the resonance term in the Hamiltonian.

V. Excitations and Effective Spin Hamiltonian

Now let us turn to the excited states of the V(TCNE)₂ crystal. In the previous section we have shown that electrons in the crystal can be treated as occupying localized Wannier states, which in turn do not differ strongly from the states of free ions. In that situation the spin Hamiltonian describing the low energy excitations of the crystal can be constructed by starting from the wave function of the free ion limit (see above). The effective

exchange in this Hamiltonian occurs due to one-electron hopping between the free ionic states; the magnitude of the corresponding parameter can be estimated in the framework of a perturbational treatment of the hopping.

We consider first a pair of noninteracting V²⁺ and TCNE⁻ ions described by the Hamiltonians, eqs 2a and 2b, respectively. The energy of the ground state of this pair reads

$$E_0 = -\alpha_A - \alpha_\zeta - \alpha_u - \alpha_v + 3U - 3/2J$$

Two states with one electron transferred between the two ions (from ζ to A and from A to ζ) contribute to the effective exchange interaction. Their energies are respectively

$$E_{\zeta \rightarrow A} = -2\alpha_A - \alpha_u - \alpha_v + \gamma_A + U - J/2$$

$$E_{A \rightarrow \zeta} = -2\alpha_\zeta - \alpha_u - \alpha_v + 6U + 7/2J$$

If the intersite hopping is negligible, the states with different mutual orientation of the spins in the ζ state and in the acceptor state are degenerate and equal to E_0 . The perturbational treatment of electron hopping between the sites leads, as usual, to a Heisenberg Hamiltonian for two $1/2$ spins:

$$H_h = K S_\zeta S_A$$

with the effective exchange constant of the form

$$K = 2t^2(\Delta E_{\zeta \rightarrow A}^{-1} + \Delta E_{A \rightarrow \zeta}^{-1})$$

where

$$\begin{aligned}\Delta E_{\zeta \rightarrow A} &= \alpha_\zeta - \alpha_A + \gamma_A - 2U + J = -\Delta\alpha + \gamma_A - 2U + J \\ \Delta E_{A \rightarrow \zeta} &= \alpha_A - \alpha_\zeta + 3U + 5J = \Delta\alpha + 3U + 5J \\ \Delta\alpha &= \alpha_A - \alpha_\zeta\end{aligned}$$

The same procedure can be applied to all the hopping terms $H_{dA}(\mathbf{r})$ (eq 2c), coupling the free ions in the lattice. The result comes out as a spin Hamiltonian of the form

$$\begin{aligned}H_{\text{spin}} &= -4J \sum_{\mathbf{r}} (S_{\zeta\mathbf{r}} S_{u\mathbf{r}} + S_{\zeta\mathbf{r}} S_{v\mathbf{r}} + S_{u\mathbf{r}} S_{v\mathbf{r}}) + \\ &K \sum_{\mathbf{r}} (S_{\zeta\mathbf{r}} S_{\xi\mathbf{r}} + S_{\zeta\mathbf{r}} S_{\eta\mathbf{r}} + S_{\xi\mathbf{r}} S_{\zeta\mathbf{r}+a} + S_{\eta\mathbf{r}} S_{\zeta\mathbf{r}+b} + S_{\xi\mathbf{r}} S_{\zeta\mathbf{r}+c} + \\ &\quad S_{\eta\mathbf{r}} S_{\zeta\mathbf{r}+c} + S_{\xi\mathbf{r}} S_{\zeta\mathbf{r}+a+c} + S_{\eta\mathbf{r}} S_{\zeta\mathbf{r}+b+c}) \quad (9)\end{aligned}$$

The Hamiltonian eq 9 is not a standard Hamiltonian of the Heisenberg type, usually used to describe magnetic properties of insulators.⁸ It contains two contributions of different origin: first, the strong interaction of the electron spins in the vanadium ions ($S_{\zeta\mathbf{r}}$, $S_{u\mathbf{r}}$, and $S_{v\mathbf{r}}$) and, second, weak interaction of the spin of an electron in the ζ state with the spins of electrons in the acceptor states (ξ and η). If the interaction between the spins on the vanadium and acceptor sites were to vanish, the system turns into a mixture of paramagnetic ions of two types. The ground state is then highly degenerate.

The excited states of the system as a whole are those with some fraction of the vanadium ions in their excited states with multiplicity other than $S = 3/2$ —the multiplicity of the ground state. The characteristic energy of these states is of the order of the intraatomic exchange interaction $J \propto 10^3$ K. In the presence of weak ($K \ll J$) interaction between spins on the different sites, the lower spin multiplet of the vanadium ions is split and states with different spin projection have different energy. That gives rise to the ferrimagnetic state of the V(TCNE)₂ crystal. The lowest elementary excitations are now flips of the acceptor $1/2$ spins with the energy of $2K$, and spin flips of the vanadium $3/2$ spins. The energies of the latter states can be estimated by using the explicit electronic wave functions for intermediate values of

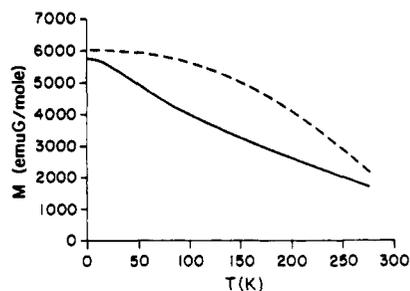


Figure 1. Saturation magnetization of $V(\text{TCNE})_2$ as a function of temperature. Solid line: The experimental values of the magnetization⁴ measured in the external field of 19.5 kG. Dashed line: Our calculation by eq 10 with the exchange constant $K = 180$ K.

the spin projection of the $^3/2$ multiplet of the vanadium ion. They are respectively

$$\begin{aligned} |S_V^z = 3/2\rangle &= |uv\zeta\rangle \\ |S_V^z = 1/2\rangle &= (|\bar{u}v\zeta\rangle + |u\bar{v}\zeta\rangle + |uv\bar{\zeta}\rangle)/3^{1/2} \\ |S_V^z = -1/2\rangle &= (|\bar{u}\bar{v}\zeta\rangle + |u\bar{v}\bar{\zeta}\rangle + |\bar{u}v\bar{\zeta}\rangle)/3^{1/2} \\ |S_V^z = -3/2\rangle &= |\bar{u}\bar{v}\bar{\zeta}\rangle \end{aligned}$$

Here the vertical bars stand for the Slater determinant built up from the spin orbitals between them. The horizontal bars denote the spin projection opposite to that in the ground state of the crystal. Substituting these functions in the Hamiltonian H_b , we get the energies of states with different spin projections on the vanadium site. They are 0, $4K/3$, $8K/3$, and $4K$ for states with $S_z = -3/2, -1/2, +1/2$, and $+3/2$, respectively. Interactions between elementary excitations located on different sites are weak, and the corresponding magnon bands are narrow. In that case, as in the case of narrow electronic bands (see above), the local description is more convenient than the band picture. As a zero approximation we will consider the elementary magnetic excitations described just above as the true excited states of the ferrimagnetic V-TCNE crystal.

This approximate picture of the magnetic excited states of the V-TCNE crystal may be used to interpret the temperature dependence of the saturation magnetization ($M(T)$). In ferromagnets the saturation magnetization decreases according to the Bloch $T^{3/2}$ law.¹⁷ In ferrimagnets, though, the temperature dependence of the saturation magnetization can be quite complicated.¹⁸ In order to obtain a formula for saturation magnetization, we applied the general method for deriving the $T^{3/2}$ law but replaced the usual magnon excitations by the excited states introduced above. The saturation magnetization at zero temperature ($M(0)$) was estimated as 6000 (emu G)/mol,⁴ corresponding to one $1/2$ spin per unit cell. It is directed along the applied field. Then flips of the $1/2$ spins located in the acceptor sites increase the magnetization, whereas flips of the $3/2$ spins on the vanadium sites decrease it. The number of populated excited states of the i th type per unit cell is given by the usual identity: $n_i = g_i[\exp(\epsilon_i/kT) - 1]^{-1}$. Finally we have

$$M(T) = M(0) + \Delta M(T)$$

where

$$\begin{aligned} \Delta M(t)/M(0) &= 2[\exp(2K/kT) - 1]^{-1} - [\exp(4K/3kT) - \\ &1]^{-1} - 2[\exp(8K/3kT) - 1]^{-1} - 3[\exp(4K/kT) - 1]^{-1} \end{aligned}$$

The graph of $M(T)$ obtained with use of the above formula, with $K = 180$ K, is presented in Figure 1 together with the experimental values⁴ of the magnetization in the external field 19.5 kG. They are in reasonable agreement.

VI. Bonding in the Room-Temperature Ferromagnet

The question of the nature of bonding always arises when we encounter a new class of materials. For that reason the description of bonding in the room-temperature organometallic ferromagnet is of much interest. In the previous sections we described the magnetic properties of the room-temperature organometallic ferromagnet. It is known, however, that the magnetic properties of the usual (inorganic) magnetic insulators are connected with low energy excitations of d-electrons which are not involved in bonding.^{8,19} Bonding in materials of that type (for example, magnetic transition metal oxides) arises from interactions leading to wide valence bands where the 4s orbitals of the metal ions and the occupied orbitals of light elements (oxygen) give the main contribution. The situation in magnetic insulators is similar to that in paramagnetic complexes of transition metals, as was recently discussed in ref 20. In paramagnetic transition metal complexes, the d-electrons which are responsible for paramagnetism are not involved in bond formation between the transition metal ions and ligands. On the other hand, the main contribution to delocalized bonding orbitals comes from the occupied orbitals of the ligands and from 4s orbitals of the transition metal ions.

The situation with bonding in the V-TCNE room-temperature ferromagnet is probably the same. The magnetic electrons are described by the Hamiltonian of eq 1, which does not include either orbitals or interactions contributing to the wide valence bands, those responsible for bonding between V and TCNE. For the geometry proposed in section I, the lone pair orbitals of the nitrogen atoms of TCNE overlap with the 4s orbital of vanadium. In the absence of vanadium all eight symmetry adapted combinations of the lone pair orbitals are occupied and no bonding is possible. At the same time, the lone pair orbitals do not interact much with each other and destabilization does not appear either. When the vanadium ion enters, the overlap with its 4s orbital slightly stabilizes the a_1 combination of the lone pair orbitals, which gives rise to some bonding between vanadium and TCNE. The interaction responsible for bond formation between the TCNE⁻ and Mn³⁺ ions in the chains of the quasi-one-dimensional ferromagnet $[\text{MnTPP}^+][\text{TCNE}^-]^{7a}$ is probably the same—the interaction between the nitrogen lone pair of the TCNE molecule and the 4s orbital of the Mn ion. Bonds of that type are inevitably very weak, but this is in agreement with the experimental data about the thermal instability of the room-temperature organometallic ferromagnet.

VII. Conclusion

In this paper we demonstrated the fine balance between delocalization and localization of electronic states in magnetic charge-transfer crystals. The effective exchange in the charge-transfer magnets arises because of slight delocalization of the magnetic states of the free ions. Though it is very weak, this delocalization turns out to be sufficient to maintain the overall magnetic order. Stronger delocalization, however, would result in spin cancellation and thus in destruction of the magnetic state.

We also formulated the heuristic ideas of Miller and Epstein^{1,4} concerning the origin of ferromagnetism in the charge-transfer organometallic crystals. Our results concerning the ground-state wave function for the V-TCNE sublattice and the picture of the energy excitations correspond fairly well with the picture proposed by Miller and Epstein.

We also made some comments on the difference between electronic states responsible for the magnetic structure of a crystal and those responsible for bonding. It must be stressed again that two different classes of electronic states in the solid are responsible for those two distinct classes of phenomena. The magnetic properties are determined by weakly interacting local electronic states, close to the states of free ions (atoms). Bonding phenomena are related to strongly interacting delocalized states, close to the Bloch states in solids.

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