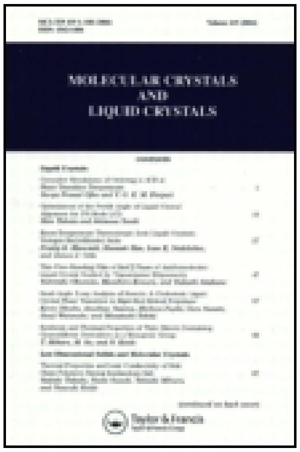

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Mixed-Valence Molecule-Based Compounds: Charge Ordering and Magnetic Properties

Sophia Klokishner [a] & Anatolii Hincu [a]

[a] State University of Moldova, Kishinev, Moldova

To cite this article: Sophia Klokishner & Anatolii Hincu (1997): Mixed-Valence Molecule-Based Compounds: Charge Ordering and Magnetic Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 305:1, 341-351

To link to this article: http://dx.doi.org/10.1080/10587259708045071

Mol. Cryst. Liq. Cryst., 1997, Vol. 305, pp. 341–351
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science Publishers
Printed in India

MIXED-VALENCE MOLECULE-BASED COMPOUNDS:CHARGE ORDERING AND MAGNETIC PROPERTIES

SOPHIA KLOKISHNER, ANATOLII HINCU
State University of Moldova,Kishinev , Moldova

Abstract A model of charge ordering in crystals comprising trinuclear mixed-valence complexes is proposed. Qualitatively different types of temperature behaviour of the mean value of crystal dipole moment (order parameter) are shown to be possible. These types of dependences lead to one, two and three phase transitions. The phase transitions predicted are elucidated to be of the first and the second kind.The anomalous behaviour of the magnetic moment is shown to arise from non-magnetic electric dipole-dipole interaction between molecules.

INTRODUCTION

Mixed-valence (MV) molecular clusters contain ions with different degrees of oxidation bridged by ligands in a molecular system. At present a class of crystals comprising MV molecular clusters is known to exhibit charge ordering. The most important examples are provided by biferrocenium salts[1,2], trinuclear MV metal acetate compounds $[M_3O(O_2CCH_3)_6(L)_3]S$ [3-8], where M is a transition metal element such as iron or manganese, L is a ligand and S is a solvate molecule. The phase transitions in these compounds have been proved by Mossbauer spectroscopy and variable temperature heat capacity. The reported heat capacity data show that depending on the structure of constituent molecules trinuclear MV metal acetates exhibit one[8], two[7] and four phase transitions.[4] The vast experimental material has stimulated the appearance of a new trend within the MV theory and this is the investigation of interacting clusters. The microscopic theory of charge ordering in binuclear MV compounds was framed in.[9-18] The problem of phase transitions in trinuclear MV compounds is much more complicated. Till now phenomenological description has only been done.[19-21] Besides the phenomenological hamiltonians of intercluster interaction the models previously suggested for trinuclear systems do not take into consideration the intracluster Heisenberg and double exchange as well as the dependence of tunnel splitting on the cluster full spin. Meanwhile as it will be seen below, these are the factors that determine the essential properties of trinuclear MV systems. Since the magnetic properties of MV clusters are closely dependent on the migration rate of "extra" electrons charge ordering is accompanied by modification of magnetic properties. Nevertheless the problem of magnetic behaviour of trinuclear MV charge-ordered systems was not examined, because interacluster magnetic interactions were not taken into account.[19-21] In the present paper a microscopic model of charge ordering in crystals comprising trinuclear MV complexes is proposed, the peculiarities of phase transitions and magnetic properties of such systems are under examination.

MOLECULAR FIELD STATES

In order to demonstrate the effects with utmost clarity a model crystal consisting of MV d^1-d^1-d^0- clusters of C_{3V} symmetry is considered. These clusters are the simplest trimeric systems in which Heisenberg exchange operates along with the double exchange. The full cluster spin acquires the values S=0,1. The energy spectrum of an isolated MV d^1-d^1-d^0 cluster consists of four exchange-resonance levels with the energies[22]:

$$\varepsilon\left({}^{2s+1}A\right) = (2P+J)(-1)^s, \varepsilon\left({}^{2s+1}E\right) = (-1)^s(-P+J), \tag{1}$$

where J is the Heisenberg exchange parameter, P is the transfer parameter, A=A_1 and A_2, for spins S=0 and 1 respectively, A_1, A_2, E are the irreducible reprezentations of the C_{3V} point group. In the delocalized A- and E- states the mean value of the cluster dipole moment vanishes. In the states with fixed valency clusters possess significant dipole moments exceeding those for ordinary ferroelectrics for which characteristic values of ionic displacements are of the order of 0.05A . Therefore the intercluster dipole-dipole interaction affects appreciably the charge distribution of the migrating hole and can stabilize the charge-ordered phase. The crystal Hamiltonian has the form:

$$H = \sum_n H_n - \frac{1}{2}\sum_{n,m}\sum_{\alpha,\beta} K^{\alpha\beta}(n-m) d_n^\alpha d_m^\beta, \tag{2}$$

$$K^{\alpha\beta}(n-m) = R_{nm}^{-3}(\delta_{\alpha\beta} - 3\frac{R_{nm}^{\alpha} R_{nm}^{\beta}}{R_{nm}^{2}}), \qquad ,\beta = x, y \tag{3}$$

where H_n is the Hamiltonian of an isolated cluster with the eigenvalues determined by Equation (1),the second term is the dipole-dipole interaction , n,m number interacting clusters, R_n and R_m are their position vectors, $R_{nm}=R_n-R_m$, d_n^{α} is the matrix of the component of the n-th cluster dipole moment. The matrices d_n^x and d_n^y consist of three-dimensional blocks numbered by the full spin value S and its projection M.. These blocks have the form:

$$d_{\bar{n}}^{x}(S) = \frac{d_0}{2} \begin{array}{c} \begin{array}{ccc} {}^{2s+1}A & {}^{2s+1}E_{\alpha}, & {}^{2s+1}E_{\beta} \end{array} \\ \begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \end{array} , \quad d_{\bar{n}}^{y}(S) = \frac{d_0}{2} \begin{array}{c} \begin{array}{ccc} {}^{2s+1}A & {}^{2s+1}E_{\alpha}, & {}^{2s+1}E_{\beta} \end{array} \\ \begin{pmatrix} 0 & 0 & \sqrt{2} \\ 0 & -1 & 0 \\ \sqrt{2} & 0 & 1 \end{pmatrix} \end{array} , \tag{4}$$

where d_0 =-eR is the dipole moment of an isolated cluster with the fully localized hole, R being the distance between the ion with the fully localized hole and the centre of the triangle formed by three cluster ions, α =x,y, β=y,x for spins S=0 and S=1 respectively [23]

In the molecular field approximation the crystal Hamiltonian decomposes into the sum of single-cluster Hamiltonians:

$$\widetilde{H}_n = H_n - (L_{xx}\bar{d}^x + L_{xy}\bar{d}^y)d_n^x - (L_{yy}\bar{d}^y + L_{xy}\bar{d}^x)d_n^y, \; L_{\alpha\beta} = \sum_m K^{\alpha\beta}(n-m) \tag{5}$$

Here $L_{\alpha\beta}$ are the structural parameters depending on the mutual positions of clusters in the crystal lattice, $\bar{d}^x$ and $\bar{d}^y$ are the thermal average values of the x and y components of the dipole moment:

$$\bar{d}^{\alpha} = \frac{Tr\left[\exp\left(-\frac{\widetilde{H}}{kT}\right)d_n^{\alpha}\right]}{Tr\left[\exp\left(-\frac{\widetilde{H}}{kT}\right)\right]}, \qquad \alpha = x, y, \qquad \widetilde{H} = \sum_n \widetilde{H}_n \tag{6}$$

Further we shall proceed from the real structure of crystals comprising trinuclear MV complexes.[3-8] Taking into account the strong screening of cluster cations by ligands we restrict the interactions to the nearest neighbour sites and consider only the interaction of a MV molecule with six other molecules in the neighbouring stacks as it occurs in basic transition metal acetates.[3-8] In this approximation the only molecular field parameter remains nonvanishing $L_{xx} = L_{yy} = L,\ L_{xy} = 0$. Assuming the parameter L to be positive we shall discuss only the ferroelectric type ordering. Further on we shall deal with the magnitude of the vector of the mean dipole moment $\bar{d}$ and the angle φ that indicates the direction of this vector in the xy-plane:

$$\bar{d}^x = \bar{d}\cos\varphi; \qquad \bar{d}^y = \bar{d}\sin\varphi \tag{7}$$

From the set of equations (6) we obtain that the angle φ providing the minimum of the crystal free energy takes on the the values $\varphi_1 = \frac{\pi}{2}, \varphi_2 = \frac{7}{6}\pi; \varphi_3 = \frac{11}{6}\pi$. These values of the angle φ indicate at which ion of a cluster the hole is mainly localized. It should be stressed that this localization is only partial. So in the charge-ordered phase of ferroelectric type the dipole moments of all MV molecules are aligned along one direction defined by one of the possible values of the angle φ. The magnitude of the mean dipole moment $\bar{d}$ is considered as the order parameter. In characterizes the degree of "extra" hole localization. Below some critical temperatures the crystal is disordered, and the order parameter vanishes. Equations (6) have a number of non-trivial solutions for $\bar{d}$(T) determined by relations between the exchange parameter J, the transfer parameter P and the typical energy of dipole-dipole interaction.

Within the framework of the approximations accepted the expressions for cluster energy levels $\varepsilon_i(S)$ look as follows:

$$\begin{gathered}
\varepsilon_{1,2}(0) = \frac{1}{2}[P - D \pm 3W(0)]; \varepsilon_3(0) = -P + D; \\
\varepsilon_{4,5}(1) = -2J - \frac{1}{2}[P + D \mp 3W(1)]; \varepsilon_6(1) = -2J + P + D; \\
(S) = \left[P^2 + D^2 + (-1)^S \frac{2PD}{3}\right]^{\frac{1}{2}}; D = \frac{L\bar{d}d_0}{2}
\end{gathered} \tag{8}$$

As it is seen from Equations (8) the intercluster interaction results in the splitting of the orbital doublets ^{1}E and ^{3}E levels.

PHASE TRANZITIONS

The temperature dependence of the order parameter is defined by the energy spectrum of an isolated cluster and dipole-dipole interaction. We introduce two dimensionless parameters x= $J/|P|$ and y= P/Ld_0^2. The first one indicates the mutual position of the isolated cluster levels. The second parameter describes the competition between intracluster delocalization and dipole-dipole interaction. Further we shall consider the qualitative modifications in the order parameter temperature dependence provided that paramiters x and y change.

A Single Phase Transition

If the conditions P>0, x<-0.5 or p<0, x>0.5 are imposed, the ground state of an isolated cluster is an E-level. In this case with increase of parameter y the phase transition temperature decreases due to the suppression of charge ordering by hole delocalization. (Figure 1). From Figure1 it is also seen that increase of parameter y results in the change of the phase transition order. Under condition y<1 the first-order phase transitions take place. At y=1.5 the order parameter already vanishes continuously and not abruptly that evidences the phase transition of the second order. At the same time with increase of parameter y the maximum value of the order parameter tends to 1/2 d$_0$. The results obtained can be

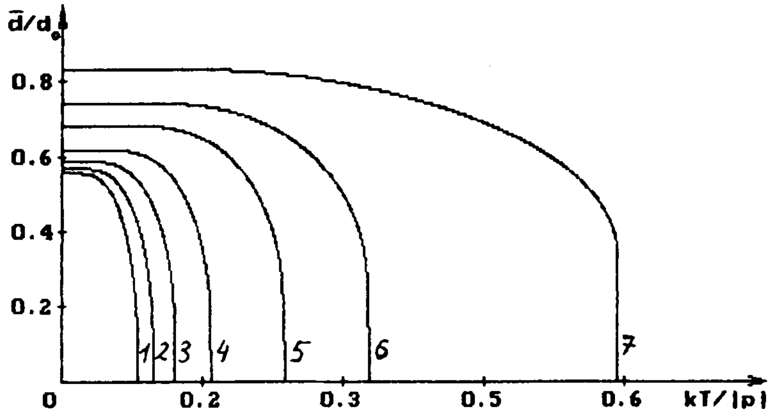

FIGURE 1 Temperature dependence of the order parameter in the case of one phase transition and $P>0$, x=-0.7. (1) y=3, (2) 2.5, (3) 2, (4) 1.5, (5) 1, (6) 0.75, (7) 0.5.

interpreted as follows. In the states $^{2s+1}E_x$ and $^{2s+1}E_y$ of an isolated cluster the mean dipole moments are equal in magnitude and opposite directed along the y- axis (see Equation

(4)). As a result the thermal average of the dipole moment in this state is equal to zero. Meanwhile only a small perturbation splitting the ${}^{2s+1}E$- level is sufficent to produce a nonvanishing thermal average. As a matter of fact for weak molecular fields the excited ${}^{2s+1}A$ -level does not affect the order parameter temperature behavior. In this case the equation for $\bar{d}$ (T) takes the form:

$$\frac{\bar{d}}{d_0} = \frac{1}{2}\tanh\left(\frac{2\bar{d}T_c}{d_0 T}\right), \qquad kT_c = \frac{1}{4}Ld_0^2 \qquad (9)$$

and describes the phase transitions of the second order. At low temperatures $\bar{d}(0)=d_0/2$. Thus for the considered case even the very weak molecular field promotes the "extra" hole localization. However the increase of parameter $|y|$ leads to the narrowing of the temperature range in which the charge-ordered phase stabilizes. When $P > 0, x > -0.5$ and $P < 0, x < 0.5$ the orbital singlets ${}^3A_2$ and ${}^1A_1$ are respectively the ground states of the system of non-interacting clusters. In singlet states the mean values of dipole moment components vanish (4). A singlet state acquires a dipole moment when an E-state with the same spin is admixed to it by the molecular field. Hence in this case charge ordering appears to be energetically favoured, if the characteristic energy of intercluster interaction surpasses the energy gap $3|P|$ between a singlet and a doublet with the same spin. Figure 2 demonstrates that for y<1/3 there is a single phase transition of the first order.

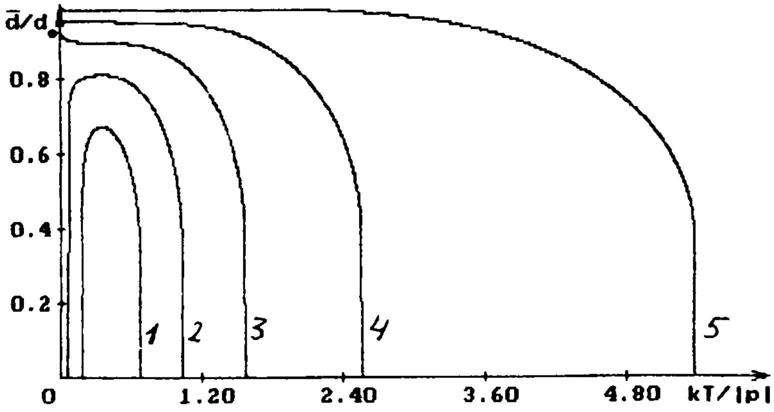

Figure 2 Temperature dependence of the order parameter in the case of one or two phase transitions and $P<0$, x=0.1.(1)y=-0.5, (2) - 0.4, (3) - 0.3, (4) - 0.2, (5) - 0.1.

Two And Three Phase Transitions

Investigation of Equation(6) shows that for parameter values

$$P > 0, \quad -0.2 < x < 0.5, \quad \frac{1}{3} < y < y_1(x) \qquad (10)$$

or

$$P < 0, \quad -0.5 < x < 0.2, \quad y_2(x) < y < -\frac{1}{3} \qquad (11)$$

(where $y_1(x)$ and $y_2(x)$ are defined numerically) two nearby first-order phase transitions may be observed at temperatures T_{c1} and T_{c2} (Figure 2).In such a way the system is disordered not only at high temperatures $T \geq T_{c2}$, but also at low temperatures $T \leq T_{c1}$. The charge ordered phase takes place in a finite temperature range $T_{c1} < T < T_{c2}$. The physical reason of two phase transitions consists in following. Under conditions (11) the ground level is the orbital singlet $^1A_1$ followed by the close ^3E - multiplet. In this case the energy gap $3P$ between the states $^1A_1$ and ^1E arising from hole delocalization exceeds the intercluster interaction. So at low temperatures when only the ground $^1A_1$ level is populated the paraphase is the energetically favourable state of the system. At the same time as it was shown above for an E-state the conditions of charge-ordered phase stabilization are softer. Therefore the thermal population of the ^3E -state leads to the suppression of the "extra" hole delocalization, and charge ordering takes plase. Further increase in temperature leads to the population of the level ^1E, the thermal fluctuations destroy the molecular field and the crystal again becomes non-ordered. Computer calculations show that for $P > 0, -0.5 < x \leq -0.2$ or $P < 0,\ 0.2 \leq x < 0.5$ and certain values of parameter y three phase transitions are possible . The temperature dependence in this case is presented in Figure 3.

MAGNETIC PROPERTIES

The temperature dependence of the order parameter leads to the temperature dependence of the energy levels (8) obtained in the molecular field approximation. This gives rise to the anomalous temperature behaviour of the magnetic moment. The characteristic attribute of the magnetic moment is its low-temperature limit defined by the spin of the

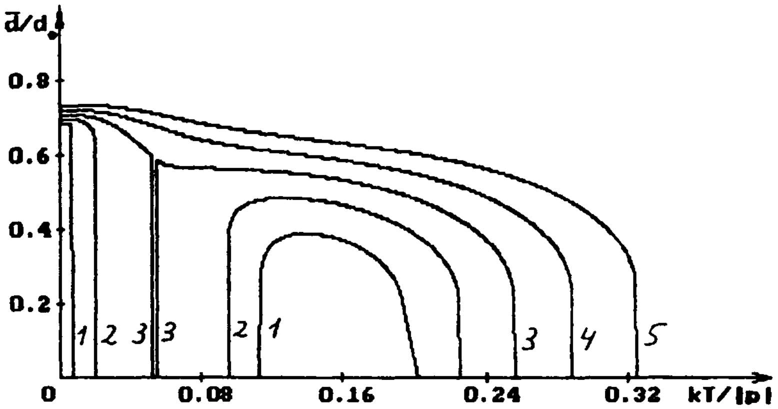

FIGURE 3 Temperature dependence of the order parameter in the case of one or three phase transitions and $P<0$, $x=0.35$.(1) $y=-1$,(2)-0.95,(3)- 0.9,(4)-0.85,(5)-0.8.

cluster ground state. In a system of interacting clusters the ground state spin is determined by the competition of inter- and intracluster interactions. Two different schemes of cluster levels in the molecular field approximation are presented in Figure 4 . Figure 4a describes the temperature behaviour of the energy levels in the case of two phase transitions. In the charge-ordered phase the molecular field removes the degeneracy of E-levels and decreases the energy of the ground state. At any temperatures the ground state corresponds to the spin S=0. The low-temperature limit of the magnetic moment acquires the value 0. Qualitatively another picture is presented in Figure 4b. In the ground state of the disordered phase S=0 and $\mu(0)=0$. While decreasing temperature the crossover of the levels occurs and thus the ground state changes. Then the magnetic moment of crystal per one cluster corresponds to S=1. The temperature dependence of the magnetic moments for both cases under consideration is presented in Figure 5. The essential qualitative difference from the magnetic moment of the system of non-interacting clusters takes place in the case of a crossover of the ground state and the excited one. Curve 5 describes the magnetic moment for the system of interacting clusters; in the low temperature limit we obtain $\mu(0)=2.83\mu_B$. For the non-interacting clusters $\mu(0)=0$ (Figure 5, curve 1). We note that such anomalous behavior of the magnetic

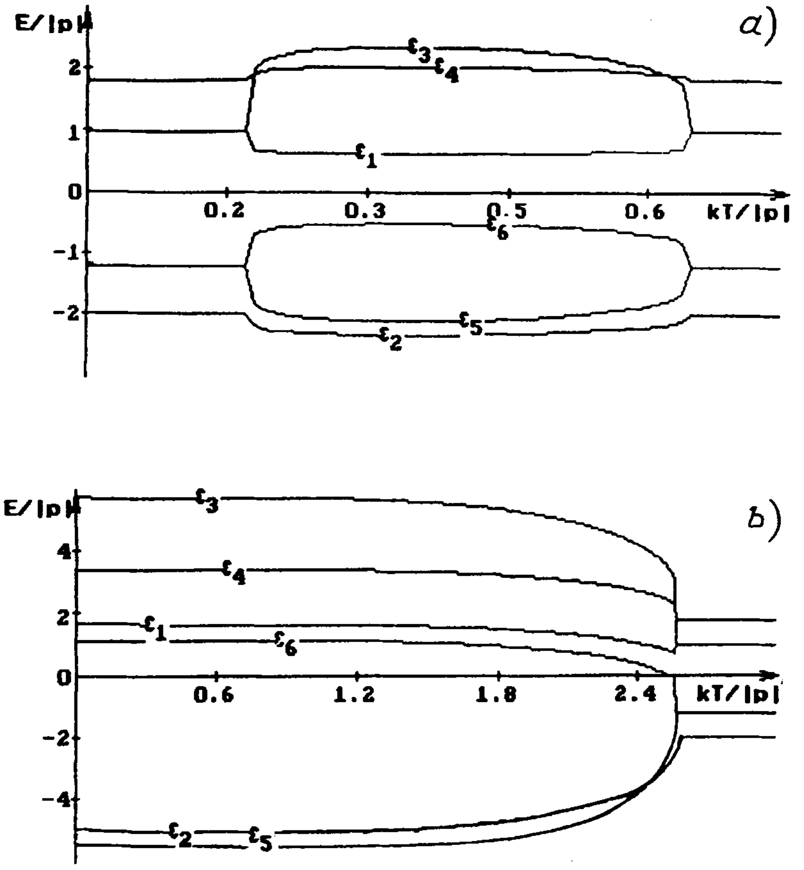

FIGURE 4 Temperature behaviour of the energy levels of the MV d^1-d^1-d^0 cluster in the molecular field approximation for $P<0$ and $x=0.1$. a) $y=-0.5$, b) $y=-0.2$.

moment in fact arises from the non-magnetic electric dipole-dipole interaction between clusters. The phase transition from the disordered phase to the charge-ordered one is accompanied by a transition between the non-magnetic and the paramagnetic state of the crystal.

The model above developed involves all relevant interactions such as intercluster Heisenberg and double exchange, intercluster dipole-dipole interaction. Even in the

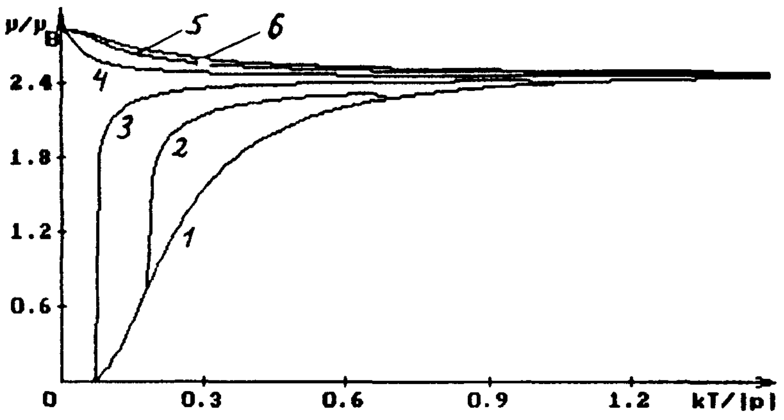

FIGURE 5 Temperature dependence of the effective magnetic moment in the case of $P<0$ and $x=0.1$.(1) $y=\infty$, (2) - 0.5, (3) - 0.4, (4) - 0.3, (5) - 0.2, (6) - 0.1.

framework of this simplest model we have found one , two and three phase transitions resembling the experimental situation occuring in trinuclear MV metal acetates.[3-8] While writing about three phase transitions we bear in mind that only three of four phase transitions in $[Fl_3O(O_2CCH_3)_6(py)_3](py)$ (where py is pyridine) are attributed by the authors [4] to MV phenomenon. In contrast to our model the initial models[19-21] of cooperative phenomena in trinuclear MV compounds do not take into account the detailed structure of spin-delocalized states and yield one or two phase transitions. In future we intend to consider a more realistic model taking into account the real electronic structure of MV trinuclear iron and manganese complexes.

We are grateful to professor B.S.Tsukerblat for useful discussions of the paper.

REFERENCES

1.Sorai, A. Nishimori, D. N. Hendrickson, T.-Y. Dong, M.J. Cohn, J. Am. Chem.Soc., 109, 4266(1987).
2. J. Webb, P. M. Hagen, R.J. Witterbort, M. Sorai, D. N. Hendrickson, Inorg. Chem., 31, 1791 (1992).

3.S.M.Oh, T.Kambara, D. N. Hendrickson, M.Sorai, K. Kaji, S. E. Woehler, R. J. Witterbort, J. Am. Chem. Soc., 107, 5540 (1985).

4.M.Sorai, K. Kaji, D. N. Hendrickson, S. M. Oh, J. Am. Chem. Soc., 108, 702 (1986).

5.Y.Kaneko, M. Nakano, M. Sorai, Ho G. Jang, D. N. Hendrickson, Inorg. Chem. 28, 1067, 1989.

6.M.Nakano, M. Sorai, J. B. Vincent, G. Christon, Ho G. Jang, D. N. Hendrickson, Inorg. Chem., 26, 4608 (1989).

7.Y.Kaneko, M. Nakano, M. Sorai, Ho G. Jang, D. N. Hendrickson, Inorg. Chem, 28, 1067 (1989).

8.Ho G. Jang, J. B. Vincent, M. Nakano, J. C. Huffman, G. Christon, M. Sorai, R. J. Wittebort, D. N. Hendrickson, J. Am. Chem. Soc., 111, 7778 (1989);

9.S.I. Klokishner, B. S. Tsukerblat, JEPT Letters, 45, 31, 1987

10.S.I. Klokishner, B. S. Tsukerblat, Soviet Phys. Solid State, 29, 2679 (1987).

11.T.Kambara, D. N. Henderickson, T.- Yu. Dong, M.J. Cohn, J. Chem. Phys. 86, 2362 (1987).

12.I. Klokishner, B. S. Tsukerblat, Chem Phys. 125, 11 (1988).

13.Kambara, N. Sasaki, J. Coord. Chem, 18, 129(1988).

14.S.I. Klokishner, A. V. Koryachenko, B. S. Tsukerblat, Phys. Stat. Sol(b), 160 ,641 (1990).

15.A.V. Koryachenko, S. I. Klokishner, B. S. Tsukerblat, Chem. Phys., 150, 295(1991); 161, 141, (1992).

16.B.S. Tsukerblat, S. I. Klokishner, B. L. Kushkuley, Chem. Phys., 166, 97 (1992).

17.S.I. Klokishner, B. D. Geikhman, Phys. Stat. Sol(b), 188, 623 (1995).

18.J.Linares, K. Boukheddaden, F. Varret, Chem. Phys., 182, 1 (1994).

19.T.Kambara, D. N. Hendrickson, M. Sorai, S. M. Oh, J. Chem. Phys., 85, 2895 (1986)

20.R.M. Stratt, S. H. Adachi, J. Chem. Phys., 86, 7156 (1987).

21.S.H. Adachi, A. E. Panson, R. M. Stratt, J. Chem. Phys., 88, 1134 (1988).

22.M.I. Belinskii, Molec. Phys., 60, 793 (1987).

23.S.I.Boldyrev, V.Ya.Gamurar, B.S.Tsukerblat, A.V.Palii, Molec.Phys., 81, 621(1994).