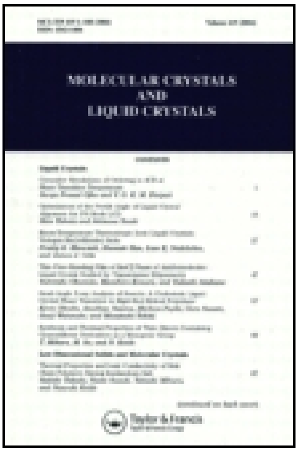

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High Nuclearity Mixed-Valence Clusters. Theoretical Approaches

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HIGH NUCLEARITY MIXED-VALENCE CLUSTERS. THEORETICAL APPROACHES.

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Abstract A general approach is developed in order to calculate the energy levels and magnetic properties of high nuclearity mixed valence clusters. The approach considers all the relevant electronic processes, namely (i) interelectronic Coulomb repulsion between the moving electrons, which depend on the different distributions of the electronic pairs over the available metal sites; (ii) single and double electron transfer processes, which promotes the electron delocalization; (iii) magnetic exchange interactions. This approach is applied here to tetranuclear iron (II)-iron (III) clusters for symmetries comprised between tetrahedral and square planar.

INTRODUCTION

The interplay between electron delocalization and magnetic interactions play a key role in the properties of several kinds of bulk magnetic materials, including superconductors and molecular magnets, and also in mixed-valence clusters of current interest in biology (iron-sulfur ferredoxins) and inorganic chemistry (heteropolyblues). Simple theory of the double exchange deals with delocalization of one electron (or hole) over a restricted number of sites.[1] For a dimeric MV entity this theory predicts that electron delocalization stabilizes a ferromagnetic ground state, even in presence of antiferromagnetic exchange interactions. However, this conclusion can not be extended to higher nuclearity MV systems. For example, it has been shown that in a trinuclear MV clusters the nature of the ground spin state depends on the topology of the cluster and on the sign of the double exchange (transfer) parameter. In fact, in these clusters electron delocalization can also results in the stabilization of antiferromagnetic and intermediate ground spin states.[2]

With the aim of having a better understanding of the spin-state structures and magnetic properties of higher nuclearities MV clusters we have developed a general approach based on group theory which exploit all the symmetries of the system (spin space and molecular symmetries) in order to make treatable the problem. This approach considers all the relevant electronic processes, namely (i) interelectronic Coulomb repulsion between the moving electrons, which depend on the different distributions of the electronic pairs over the available metal sites; (ii) single and double electron transfer processes, which promotes the electron delocalization; (iii) magnetic exchange interactions.

For relatively simple systems (two delocalized electrons moving over a highly symmetrical metal network and interacting with one ore two magnetic sites) the problem can be solved by hand as has been shown in the case of metal-oxide clusters containing electronic pairs delocalized over 12 or 18 metal atoms (heteropolyblues with Keggin and Wells-Dawson structures).[3]

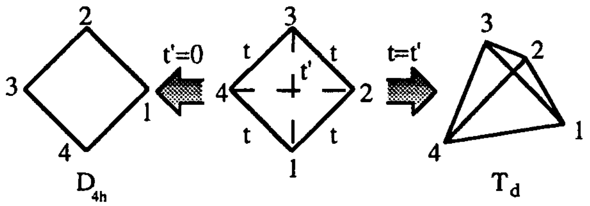
For larger spins carried by the metals, or for larger moving electron numbers, etc, the problem becomes cumbersome and really intractable by hand. Nevertheless, the basic processes, are unchanged. Merely, they are used an exceedingly large number of times. As a consequence it was appealing to build a program able to organize and perform all the required elementary operations. Such a program has been developed. It allows to treat any kind of molecular symmetry: it requires to be furnished with the corresponding multiplication table and irreducible representations basis. The amplitude of the localized spins, as well as their number and that of the moving electrons are only limited by the available computer room Any two function transfer integral, as well as four function Coulomb terms may be included in the computation. In a first step, this program has been applied successfully to tetranuclear iron (II)-iron (III) clusters for symmetries comprised between tetrahedral and square planar.

ENERGY LEVELS OF THE TETRANUCLEAR Fe(II)-Fe(III) CLUSTERS

We present here the influence of the double exchange on the spin-state structure of the cluster, as well as the evolution of the spin-state energies with its geometry. We take into account as electronic processes the single electron transfers, t and t', and the electron repulsion, U, which is relevant when two electrons are moving. Depending on the number of delocalized electrons three different cases can be considered namely 1Fe(II)-3Fe(III) ($d^6d^5d^5d^5$), 2Fe(II)-2Fe(III) ($d^6d^6d^5d^5$) and 3Fe(II)-1Fe(III) ($d^6d^6d^6d^5$). We assume that due to crystal field effects the metal ions have orbitally non-degenerate ground states.

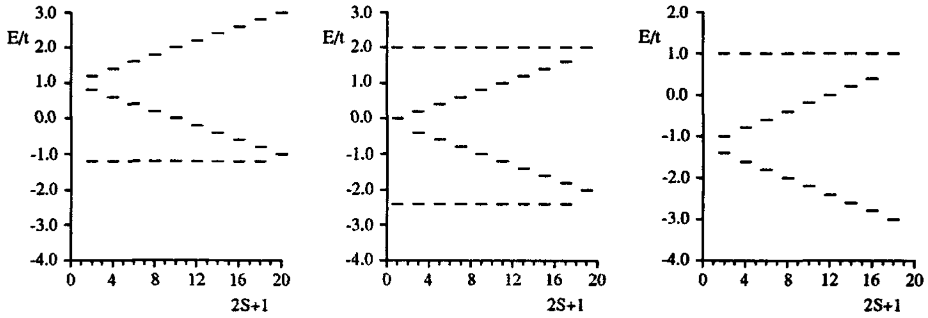
Influence of the double exchange.

From a topological point of view the transfer network of the MV cluster can be visualized as follows:



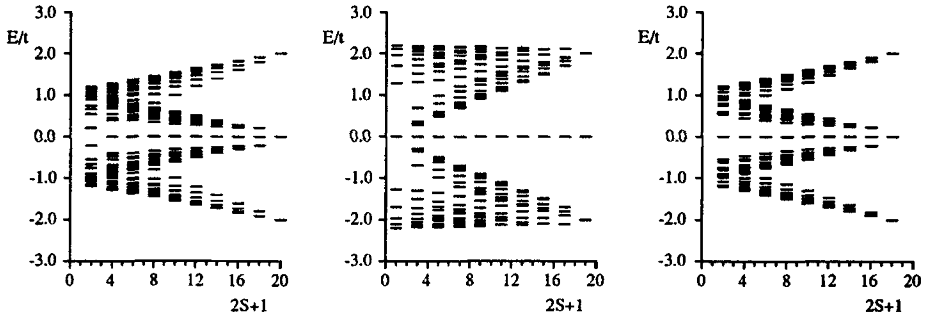
where t and t' account for the two different transfer pathways in the cluster. Thus, the general case where t≠t' accounts for D_{2d} symmetry, while by continuous variation of the transfer parameters we can go from a tetrahedral T_d structure of the metal ions to a square planar D_{4h} structure.

For the tetrahedral geometry unsymmetrical arrangements of levels are observed in the three cases (Figure 1), so as the ground spin state depends on the sign of the transfer parameter and on the number of moving electrons. Thus, in the case with one "extra" electron ($d^6d^5d^5d^5$), double exchange stabilizes the ferromagnetic spin state (S_{max}=19/2) when t is negative. For positive t the ground level is a fully degenerate one which comprises states with spin multiplicities between S_{min}=1/2 and S=17/2; the ferromagnetic spin state is slightly excited (0.2t). For the $d^6d^6d^6d^5$ system the energy spectrum is quite similar to the previous case, but is reversed with respect to the sign of t. This difference can be related with the fact that now a hole, instead of an electron, is migrating. A second difference is that now the fully degenerate level comprises states with spin multiplicities between S_{min} and S_{max}. Finally, the intermediate $d^6d^6d^5d^5$ system present an unexpected "quasi" symmetrical energy spectrum in which fully degenerate levels are observed either for positive as for negative t values (for t > 0 the ground level comprises states with spin multiplicities between S_{min}=1/2 and S=17/2, while for t > 0 this comprises spin states between S_{min} and S_{max}). This is a very important result that indicates that in this particular case double exchange is completely unable to stabilize a particular spin configuration. Therefore, the structure of the low lying levels as well as the ground spin state will be determined in this case by effects of smaller magnitude compared to double exchange, as for example magnetic exchange interactions, distortions from the T_d symmetry, or local anisotropy of the magnetic ions.



(a) (b) (c)

FIGURE 1.Influence of the transfer on the energy spectrum of the cluster as a function of the spin multiplicity in the T_d case (t'/t=1). (a), (b) and (c) corresponds to the $d^6d^5d^5d^5$, $d^6d^6d^5d^5$ and $d^6d^6d^6d^5$ cases, respectively.



(a) (b) (c)

FIGURE 2. Influence of the transfer on the energy spectrum of the cluster as a function of the spin multiplicity in the D_{4h} case (t'/t=0). (a), (b) and (c) corresponds to $d^6d^5d^5d^5$, $d^6d^6d^5d^5$ and $d^6d^6d^6d^5$ systems, respectively.

Let us examine now the MV clusters with D_{4h} symmetry. In contrast to the T_d symmetry, a symmetrical energy diagram with respect to the sign reverse of the transfer parameter is obtained in the three cases, and furthermore the energy levels exhibit a large dispersion forming energy bands. However, the energy spectra of the systems involving. one "extra" electron (or hole) is significantly different from the case involving two "extra" electrons. Thus, in the $d^6d^5d^5d^5$ and $d^6d^6d^6d^5$ systems the stabilization of the spin states increases with the spin multiplicity, so as the ground spin state is always the ferromagnetic one. Conversely, in the $d^6d^6d^5d^5$ system a "quasi" degenerate ground level formed by an mixture of the different spin configurations with $S < S_{max}$ is observed; actually, the ground state corresponds to the antiferromagnetic one, but the differences in energy with the lower lying levels of the other spin multiplicities are quite small (for the first excited state this energy is 0.02 t).

Influence of the Coulomb repulsion

In the $d^6d^6d^5d^5$ system beside the transfer integral, we need to consider the interelectronic repulsion between the two moving electrons when the intermetallic distances are different. This is the case encountered in the square planar geometry, and when the tetrahedron is distorted. In the D_{4h} case, for example, two different interelectronic repulsions are possible, which correspond to the two different distributions of the electronic pair over the four metal sites. The difference in energy between these two repulsions define the interelectronic Coulomb parameter, U. In Figure 3 we show the influence of this parameter. As we can see, U produces a small unsymmetry in the energy spectrum, leading to a shift by U of the upper energy band and of the level situated at E = 0. However, the structure of the two energy bands remains unchanged, so as the relative energies of the low lying levels, and in particular the nature of the ground state, are not affected by the electron repulsion.

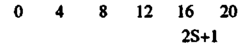


FIGURE 3. Influence of the Coulomb repulsion on the energy spectrum of the $d^6d^6d^5d^5$ D_{4h} cluster as a function of the spin multiplicity and U = t.

CONCLUSIONS

To predict the nature of the ground state of high nuclearity mixed-valence clusters is always difficult since there are significant differences between the double exchange theory for MV dimers and polynuclear MV clusters. Therefore, the development of theoretical approaches as that presented in this work, should allow to perform more accurate quantitative investigations on the energy spectrum of this kind of systems. In the next future we are intending to introduce new features in the computational program. First of all it will be rather easy to take into account different metals in the cluster. This let us to investigate the thermodynamic properties of polymetallic clusters opening a new set of fascinating problems. For example, the case of a MV chain with delocalized electrons and localized spin carriers. This will allow us to analyze the role of the delocalized electrons in the exchange between the spins carriers, or to simulate a magnetic interlayer coupling through non-magnetic metals.

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