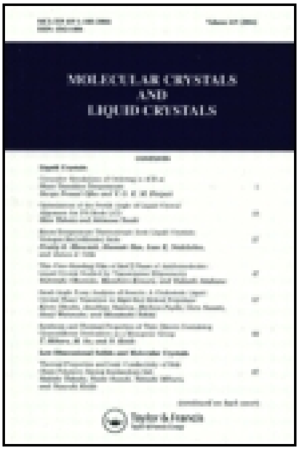

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Application of A Spin-1 Model to Describe Localized Delocalized Transitions in Mixed Valence Molecular Solids

K. Boukheddaden [a] , J. Linares [a] , S. Galam [a b] , A. Bousseksou [a] , J. Nasser [a] & F. Varret [a]

[a] Département de Recherches Physiques, URA CNRS n[ddot]71 UPMC, 4 Place Jussieu, F75252, Paris cedex 05, France

[b] Groupe de Physique des Solides, URA CNRS n[ddot]17, P6-P7, F75251, Paris, France

Version of record first published: 04 Oct 2006.

To cite this article: K. Boukheddaden , J. Linares , S. Galam , A. Bousseksou , J. Nasser & F. Varret (1993): Application of A Spin-1 Model to Describe Localized Delocalized Transitions in Mixed Valence Molecular Solids, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 234:1, 263-268

To link to this article: http://dx.doi.org/10.1080/10587259308042925

Mol. Cryst. Liq. Cryst. 1993, Vol. 234, pp. 263–268
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

APPLICATION OF A SPIN-1 MODEL TO DESCRIBE LOCALIZED DELOCALIZED TRANSITIONS IN MIXED VALENCE MOLECULAR SOLIDS

K.BOUKHEDDADEN, J. LINARES, S. GALAM *, A. BOUSSEKSOU, J. NASSER, F. VARRET

Département de Recherches Physiques, URA CNRS n°71 UPMC , 4 Place Jussieu, F75252 Paris cedex 05, France
* Groupe de Physique des Solides, URA CNRS n°17 P6-P7 F75251 Paris, France

Abstract A S=1 Ising interacting system described by a Blume-Emery-Griffith Hamiltonian is proposed to reproduce the different temperatures-dependencies of mixed valence biferrocenium derivatives.

INTRODUCTION

Hendrickson[1] have recently reported the results of various studies of mixed valences biferrocenium derivatives (Fig. 1). Depending on the counteranion and on the X-substituent a continuous or discontinuous transition is found as well as a thermal equilibrium between valence-trapped and valence-detrapped states.

The most comprehensive model for molecular mixed valences is that of Piepho, Krausz and Schatz (PKS)[2]. This model is adequately visualized, in the Born-Oppenheimer approach, by a configurational diagram. When two orbitals (d_{xy} and $d_{x^2-y^2}$)on each moiety of biferrcenium are considered the "extended PKS model" [3]

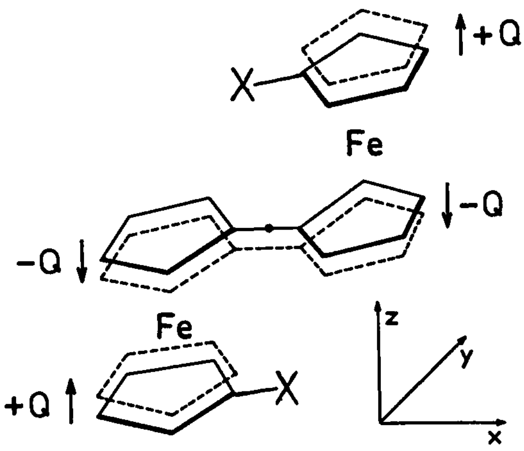

Fig.1 Schematic view of the biferrocenium cation

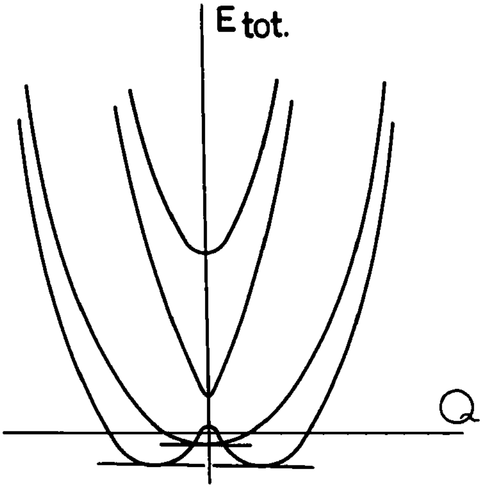

Fig. 2 Configurational diagram (adiabatic energy vs Q)

configurational diagram display 4 curves instead of 2 (Fig. 2). In this report we consider only the lower curve of each pair of PKS curves and we use a discrete level approach in the mean field approximation.

S=1 ISING-LIKE MODEL

Since the height of the barrier of the double-well curve[1] is ca. 300 cm^{-1} , and the gap between the single-well curve and the corresponding excited curve is certainly larger, it is reasonable to consider only the lower curve of each pair of PKS curve.

Our model consists of a discrete level scheme (Fig. 2) described by a fictitious S=1 spin. The level in the single-well correspond to $S_z=0$ (with two fold degeneracy) and levels in the double-well to $S_z= \pm 1$

In the solid state, we describe interacting S=1 systems by the Blume-Emery-Griffiths[4] Hamiltonian (introduced to describe $^3He-^4He$ properties).

$$\hat{\mathcal{H}} = \sum_{<i,j>} - J_{ij}\ \hat{\sigma}_i\ \hat{\sigma}_j - \sum_{<i,j>} K_{ij}\ \hat{\sigma}_i^2\ \hat{\sigma}_j^2 - \sum_i \Delta_i\ \hat{\sigma}_i^2 \qquad (\text{eq.1})$$

where $\hat{\sigma}_i$ is the projection of the i^{th} spin on the quantization axis. J and K are the interactions terms due to the intermolecular crystal field. The eigenvalues of $\hat{\mathcal{H}}$ are $\sigma_k = 0, \pm 1$. All contributions to eq.1 are relevant to the mixed valence problem:

- $\Delta_i\ \hat{\sigma}_i^2$ express the energy difference between the singlet and doublet of the isolated i^{th} molecule; it originates from the intra-molecular low-symmetry ligand-field. It is a single-spin symmetry breaking field;

- $J_{ij}\ \hat{\sigma}_i\ \hat{\sigma}_j$ is a contribution to the pair energy which lifts the degeneracy of the doublet states by spontaneous symmetry breaking;

- $K_{ij}\ \hat{\sigma}_i^2\ \hat{\sigma}_j^2$ is a second contribution to the pair energy, which does not lift the degeneracy of the doublet.

RESULTS AND DISCUSSION

The mean field approximation leads to the one-site Hamiltonian:

$$\hat{\mathcal{H}} = \frac{1}{2}(J\ m^2 + K\ q^2) + \Delta\hat{\sigma}^2 - J\ m < \hat{\sigma} > - K\ q\ \hat{\sigma}^2$$

where the two order paramters are defined by: $m = < \hat{\sigma} >$ and $q = < \hat{\sigma}^2 >$. J and K include the number of first neigbors ($J = zJ_{ij}$, $K = zK_{ij}$). The eigenstates of $\hat{\mathcal{H}}$ are $\sigma = +1, -1, 0$, with eigenvalues $A+B_-$, A, $A+B_+$ respectively, where $A = \frac{1}{2}(J\ m^2 + K\ q^2)$ and $B_{\pm} = \Delta \pm J\ m - K\ q^2$

The partition fonction $\mathbb{Z}$ and the free energy $\mathbb{F} = - k_B T\ \mathrm{Ln}(\mathbb{Z})$ are derived:

$$\mathbb{Z} = (2 + 2\, e^{\beta(Kq - \Delta)}\, \mathrm{ch}(\beta Jm))\, \exp\left(-\frac{\beta}{2}(Jm^2 + Kq^2)\right)$$

$$\mathbb{F} = \frac{1}{2}(Jm^2 + Kq^2) - k_B T\, \mathrm{Ln}(2 + 2\, e^{\beta(Kq-\Delta)}\, \mathrm{ch}(\beta Jm))$$

Minimization of $\mathbb{F}$ with respect to m and q leads the coupled system:

$$m = \frac{2\, e^{\beta(Kq - \Delta)}\, \mathrm{sh}(\beta Jm)}{2 + 2\, e^{\beta(Kq - \Delta)}\, \mathrm{ch}(\beta Jm)}$$

$$q = \frac{2\, e^{\beta(Kq - \Delta)} \mathrm{ch}(\beta Jm)}{2 + 2\, e^{\beta(Kq - \Delta)}\, \mathrm{ch}(\beta Jm)}$$

According to the values of the coupling parameters J, K, and low-symmetry ligand-field Δ, three typical situations are obtained.

(i) Fig 3 : order-disorder transition of second order; it can be obtained in cases of well isolated d_{xy} groundstate, leading to the simple PKS case. It is obtained when $J \neq 0$ (>0) and $J > \Delta - K$.

(ii) Fig 4 : order-disorder transition of first-order; it requires a tight thermodynamic competition between d_{xy} and $d_{x^2-y^2}$ orbitals (such as all three states are thermally accessible). It is obtained when $J - \Delta + K \sim kT$, with a sufficient large value of K.

(iii) Progressive conversion from trapped to delocalized , it occurs when coupling parameters are weak. In this case the proportion between trapped and delocalized states follows the mass action law.

Concerning the spectroscopic measurements it is important to note that the observed spectra depend essentially on the measuring frequency of the technique, compared to electron transfer rates in the system. It is clear from both experimental data[1] and recent vibronic calculations we performed on a pair of coupled molecules, that the transfer rate between the two wells of the double-well curve is faster than the Mössbauer measuring frequency (which is

~ 10^8 s^{-1}) : therefore Mössbauer spectra are sensitive to the average distortion, i.e. to the order parameter **m**, and this basically explains the "fusion-type" behavior reported by Sano et al [5] . At reverse, a fast technique such a I.R., which is faster than the electron transfer rate in most cases[1] , will reveal a trapped state at all temperatures.

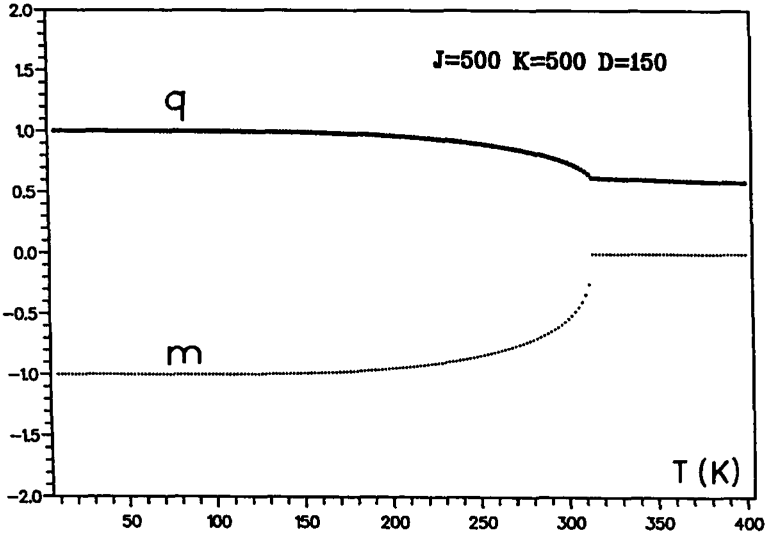

Fig. 3 Second-order order-disorder transition

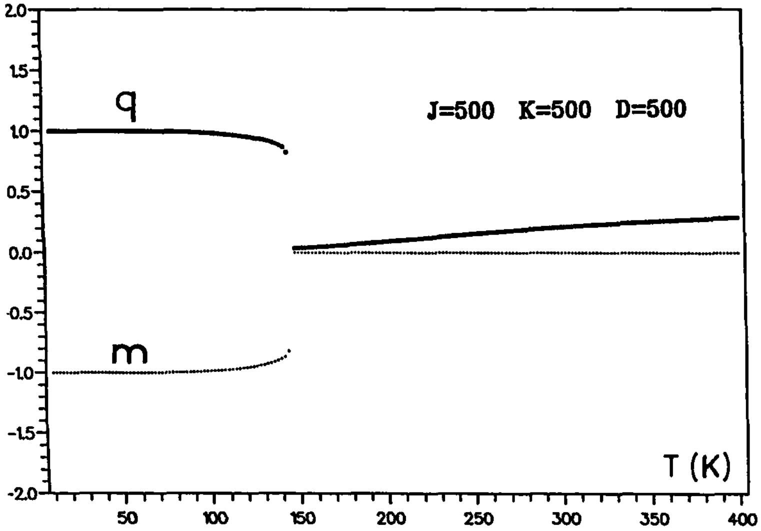

Fig. 4 First-order order-disorder transition

The relaxation rates between d_{xy} and $d_{x^2-y^2}$ orbitals are not known; it seems that these rates might be smaller than the Mössbauer frequency in some cases where the Mössbauer reveal the coexistence of components typical for trapped and delocalized states over a large temperature range. Then, the order parameter <u>q</u> exactly represents the surface ratio of the trapped component. On the other hand, fast relaxation rates should mix together the trapped and delocalized components, and prevent from measuring <u>q</u> in such a case.

CONCLUSION

We have shown how this simple model can explain, at least qualitatively, the different behavior of biferrocenium mixed valence salts. A more refined description requieres a vibronic treatement which is under process.

We are indebted to J.Y. Saillard and J.P. Launay for helpful discussions.

REFERENCES

1. D.N. Hendrickson, in *Mixed Valence Systems: Applications in Chemistry, Physics and Biology*, pp 67-90, edited by K. Prassides (NATO ASI Series, Kluwer Acad. Pub., Dordrecht 1991)
2. S.B. Piepho, E.R. Krausz, P.N. Schatz, *J. Amer. Chem. Soc.* <u>100</u>, 2996-3005 (1978)
3. F. Varret, H. Rabah, J. Guillin, D. Talham,in *Mixed Valence Systems: Applications in Chemistry, Physics and Biology* pp. 359-364, edited by K. Prassides (NATO ASI Series, Kluwer Acad. Pub., Dordrecht 1991)
4. M. Blume, V.J. Emery, R.B.Griffiths, *Phys. Rev. A* <u>4</u>, 1071-1077 (1971)
5. S. Nakashima, A. Nishimori, Y. Masuda, H. Sano, M. Sorai, *J. Phys. Chem. Solids* <u>52</u>, 1169-1180 (1991)