# Tight-binding Modelling and generation of first-principles Wannier-like orbitals using the N-MTO Scheme

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## Application to double perovskite $Sr_2FeMoO_6$

Collaboration:
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*Phys. Rev. Lett* **85** *2549 (2000)*

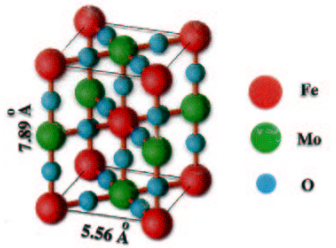
⊙ Discovery of CMR in doped manganites have attracted a great deal of attention due to the technological importance of these materials being used as magnetic devices.

⊙ The strong influence of the low magnetic field on the resistance of these compounds is believed to be caused by the high degree of spin polarization of the charge carriers below the magnetic transition temperature $T_c$.

⊙ However the transition temperatures obtained were low for room-temperature applications. Therefore, the search was on for half-metallic oxides with much higher $T_c$.

⊙ Recent experiment reported CMR effect with a fairly high magnetic transition temperature of 410 - 450$^o$ K in $Sr_2FeMoO_6$, a material belonging to the class of double perovskites ($A_2BB'O_6$).

## CRYSTAL STRUCTURE

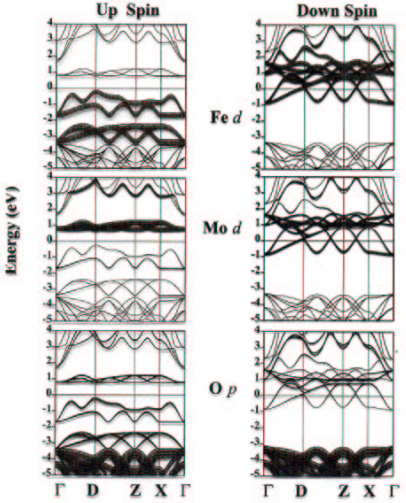



* Occurs in the body-centered tetragonal structure with a space group of I4/mmm and lattice constants $a = b = 5.57$ Å and $c = 7.90$ Å .

* The oxygen atoms surrounding the Fe and Mo sites provide the octahedral environment.

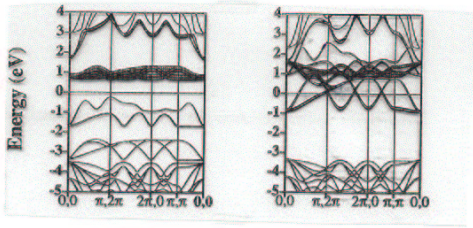
* The $FeO_6$ and $MoO_6$ octahedra alternate along the three cubic axes, while Sr atoms occupy the hollow formed by the corners of $FeO_6$ and $MoO_6$ octahedra at the body-centered positions.

* LDA total energy minimization gives the ground state to be ferrimagnetic : Magn. moment at Fe site is 3.79 $\mu_B$ and -0.29 $\mu_B$ at the Mo site.




* Half Metallic.

* Large hybridization between Fe-d ($t_{2g}$) and Mo-d($t_{2g}$) states for the down spin channel.

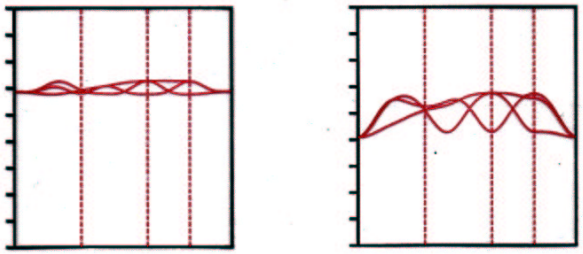


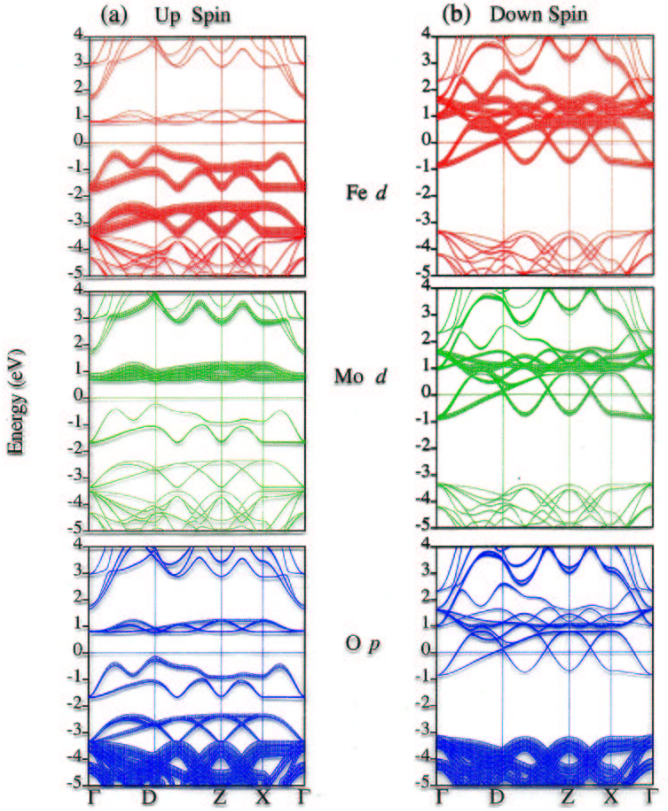

* The large magnetic transition temperature in $Sr_2FeMoO_6$ points to large inter-atomic exchange coupling strength (J), between Fe and Mo.

* However this is counterintuitive considering the fact that Mo is usually non-magnetic with small intra-atomic exchange strength (I) ($\approx$ 0.1-0.2ev) within the 4d manifold.

* We employed the new NMTO downfolding formalism to understand this unusual electronic structure aspect.

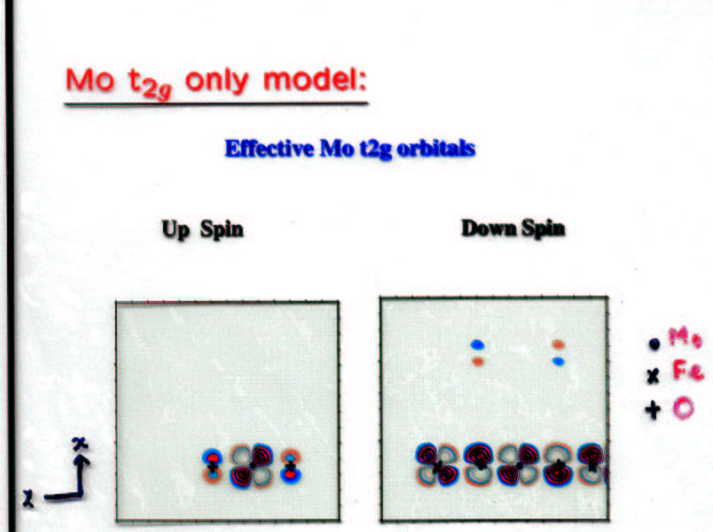
Mo $t_{2g}$ only model:





## Mo $t_{2g}$ only model:

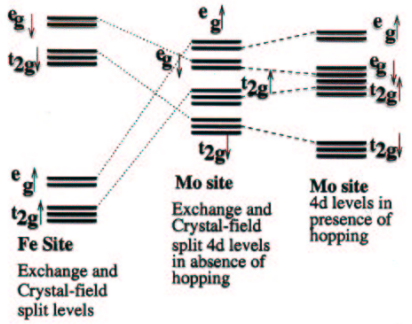
**Effective Mo t2g orbitals**




$\epsilon_{\uparrow}^{eff}(Mo\ \ t_{2g}) - \epsilon_{\downarrow}^{eff}(Mo\ \ t_{2g}) = 0.8eV$

$\Rightarrow I_{eff} = 0.8$ eV (for fully polarized)

$\approx 1.7$eV (using the LMTO estimate)




* The opposite movement of the Mo $t_{2g_\uparrow}$ and Mo $t_{2g_\downarrow}$ makes the effective exchange splitting at the Mo site large.

* The large value of renormalized $I_{eff}$ is driven by the large I at the Fe site and the substantial hopping between the two sites.

* This in turn drives the interatomic exchange interaction J large. (supported by HF calculation)

Sarma, Mahadevan, Saha-Dasgupta, Ray and Kumar, Phys. Rev. Lett. **85** 2549 (2000)

## Application to $\gamma - LiV_2O_5$

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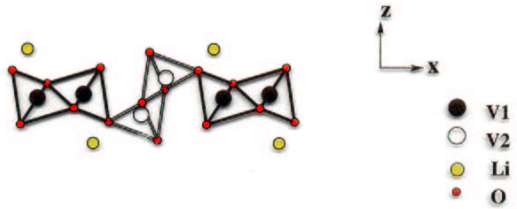
⊙ There is a growing interest in low-dimensional quantum spin systems due to the novel properties exhibited them.

⊙ Examples include Haldane chains, Heisenberg chains, Alternating chains, Ladder compounds. Synthesis of new materials appropriate to these systems, has bought new insights in the study of these low-dimensional systems.

⊙ An important family of low-dimensional compounds are the layered vanadates $AV_2O_5$ (A≡Na, Cs, Ca, Mg ...). Among these quarter-filled ladder compound, $NaV_2O_5$ is a highly discussed material in recent time showing charge ordering transition $2V^{4.5+} \rightarrow V^{4+} + V^{5+}$, with simultaneous opening of spin-gap.

⊙ A much less studied, though not less intriguing system belonging to same vanadium oxide family is γ-LiV2O5.

## Crystal Structure:

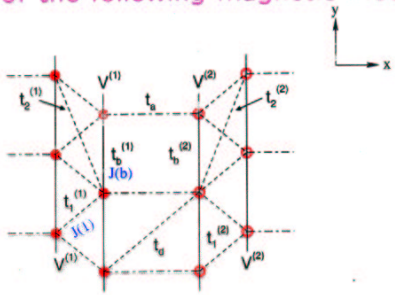



* $\gamma$-LiV2O5 has a layered structure of $VO_5$ square pyramids with lithium ions between the layers.

* It crystallizes in the orthorhomic *Pnma* structure and has two crystallographic inequivalent vanadium sites, V(1) and V(2), which form two different zig-zag chains running along the y axis.

* Within the layers $V(1)O_5$ zig-zag chains are linked to $V(2)O_5$ zig-zag chains by corner sharing via the bridging O(1).

* The temperature dependence of the measured susceptibility data suggests a low-dimensional nature of the spin system.
* The experimental susceptibility is compatible with any of the following magnetic model:

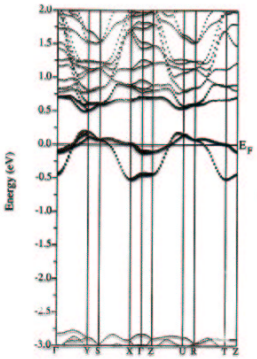



(i) Heisenberg zig-zag chain → J(1) ≫ J(b)

(ii) Heisenberg double chain → J(b) ≫ J(1)

(iii) A model of asymmetric ladder with one electron per V(1)-O-V(2) rung would then describe the system in analogy with $NaV_2O_5$

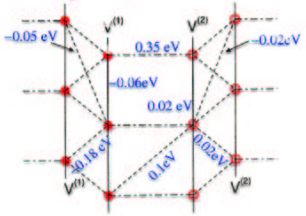
## LDA bands:




* The V-3d$_{xy}$ states have the predominant contribution to the bands at $E_F$
* The 4 low lying bands at $E_F$ are half-filled and made up of V(1)-3d and of V(2)-3d in the ratio of $p(1)/p(2) \approx 2.3 : 1$.
* The O-2p states lye low separated by a gap of $\approx$ 2.2 eV from the bottom of V-3d bands.

Microscopic parameters: Tight-binding model with one orbital per vanadium sites

NMTO downfolding procedure to derive an effective V-d$_{xy}$ only model shows:




* Substantial on-site energy splitting for V(1) and V(2) d-orbitals.
* Rung hopping, $t_a$ is quite close to that obtained for $NaV_2O_5$
* Diagonal hopping, $t_d$ is significant
* 2NN inter-ladder hopping, $t_2^1$ and $t_2^2$ are needed to describe the crossing along $\Gamma - Y$ and $Z - U$.
* The NN hopping $t_1^1$ is much larger than $t_2^1$

The microscopic parameters associated with V(1) and V(2) differ substantially

In absence of any contribution of V(2) (i.e. $p(2) = 0.$), the microscopic model could be considered as that of zig-zag chain with $J \approx 4(t_1^1)^2/U$ as $t_b^1 < t_1^1$.

BUT:

The contribution of about $p(2) \approx 0.3$ of the V(2) has important consequences for the underlying microscopic model:

The effective hopping matrix element $t_b^{eff}$ in between two asymmetric rung states along b is:

$$t_b^{eff} = p(1)t_b^1 + p(2)t_b^2 - 2\sqrt{p(1)p(2)}t_d \approx -0.13eV$$

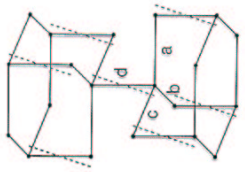
⇓

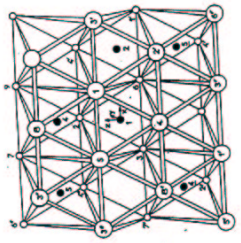
Asymmetric Ladder Model

Degree of charge ordering has a substantial influence on the nature of the magnetic state

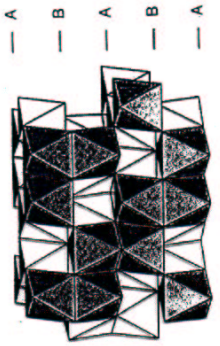
* Supported by recent numerical study of optical conductivity data *(cond-mat/0106213)*

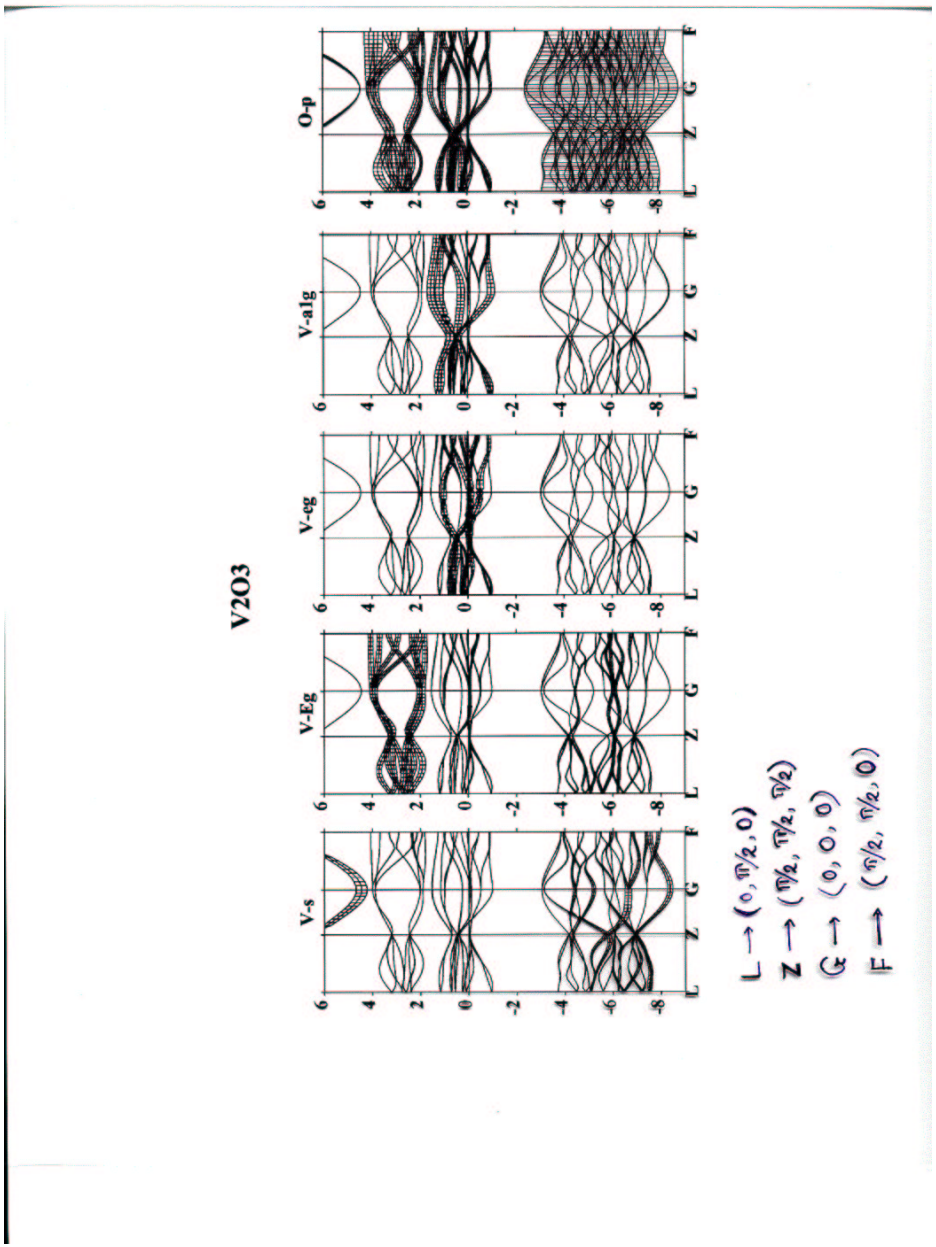
* In accordance with Inelastic neutron scattering

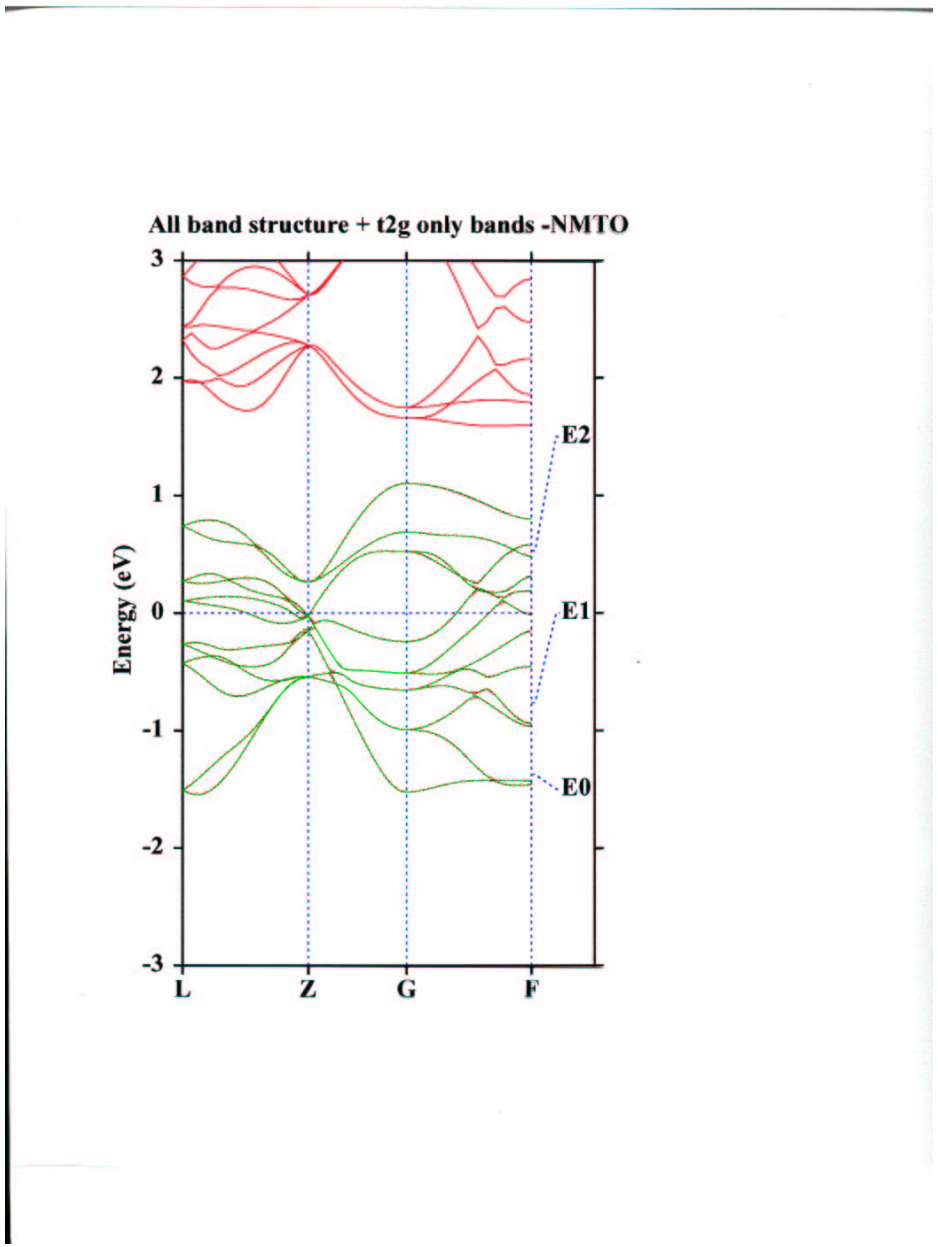


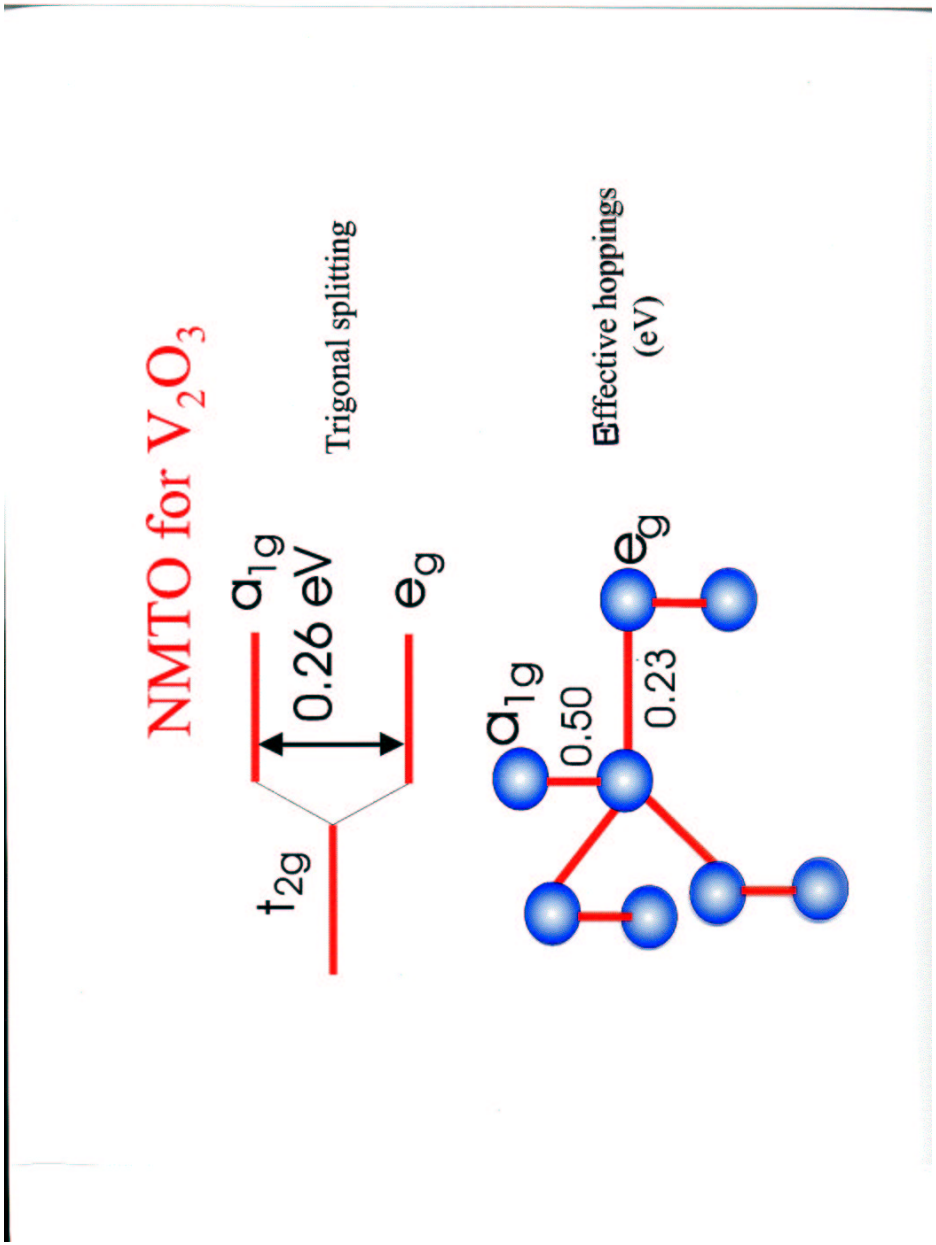



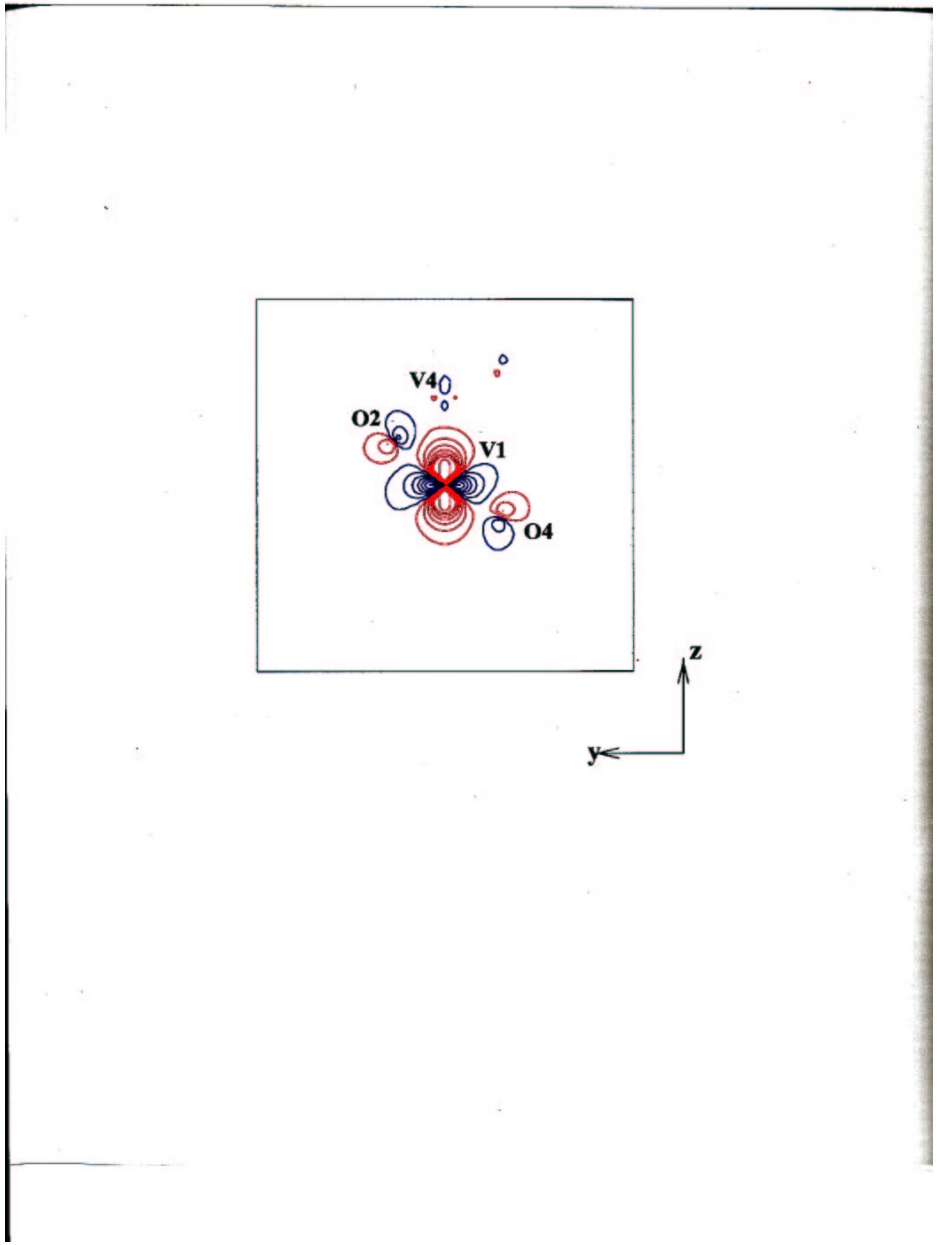
$V_2O_3$




V2O3
O-p
V-a1g
V-eg
V-Eg
V-s
6 4 2 0 -2 -4 -6 -8
L Z G F
L → (0, π/2, 0)
Z → (π/2, π/2, π/2)
G → (0, 0, 0)
F → (π/2, π/2, 0)


All band structure + t2g only bands -NMTO
Energy (eV)
3
2
1
0
-1
-2
-3
E2
E1
E0
L
Z
G
F


NMTO for $V_2O_3$
Trigonal splitting
$a_{1g}$
0.26 eV
$e_g$
$t_{2g}$
Effective hoppings (eV)
$e_g$
$a_{1g}$
0.50
0.23


V4
O2
V1
O4
z
y