Towards a model Hd For V_2O_3

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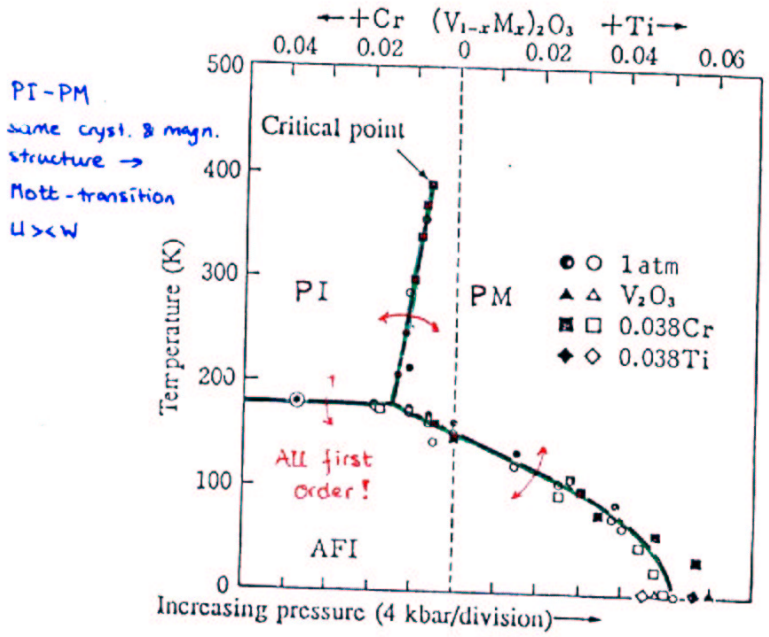
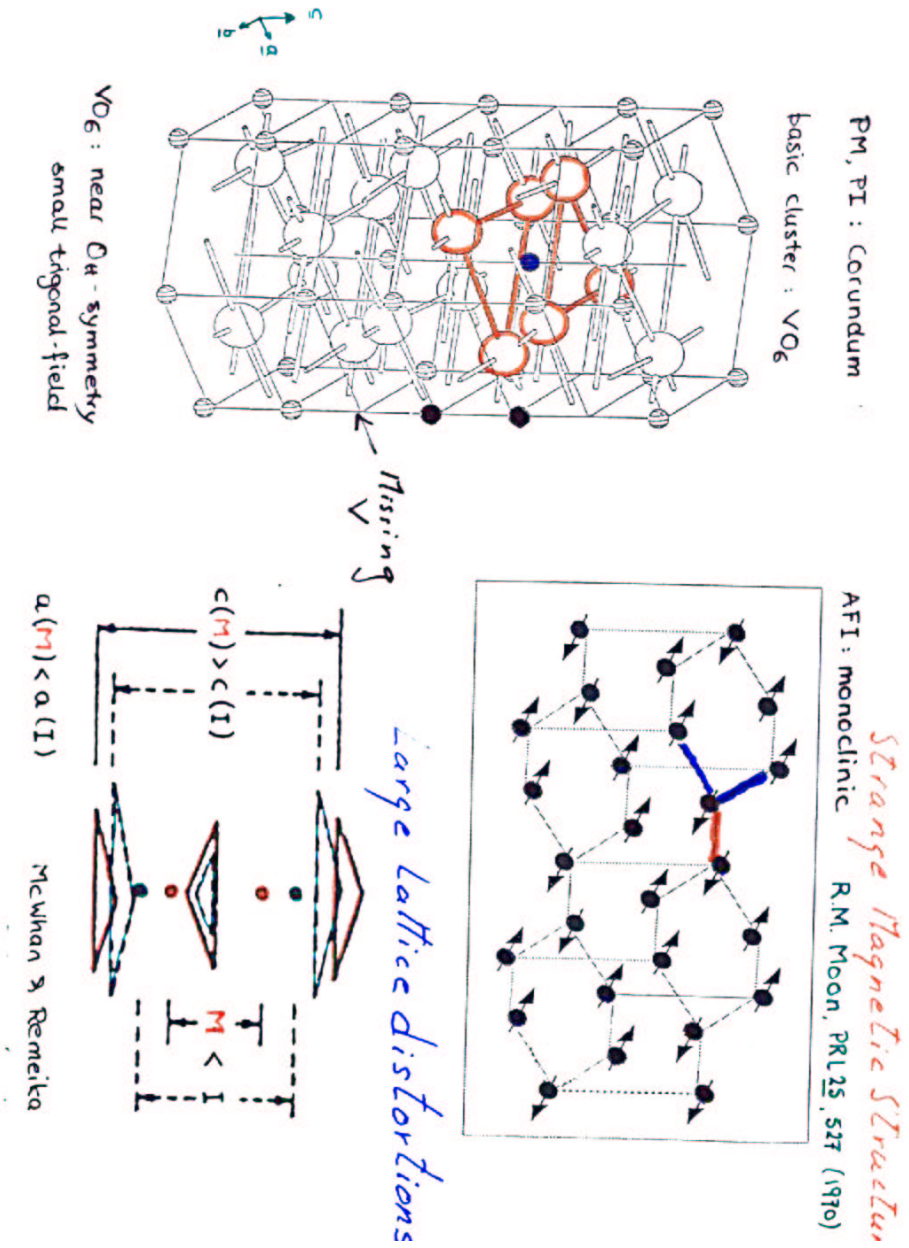
Which states must we include For a minimal Realistic Calculation?

Depends on the energy scale we are trying to describe

McWhan et al., PRB 7, 1920 (1973)





PHYSICAL REVIEW B VOLUME 18, NUMBER 9 1 NOVEMBER 19

Magnetic structure of V_2O_3 in the insulating phase

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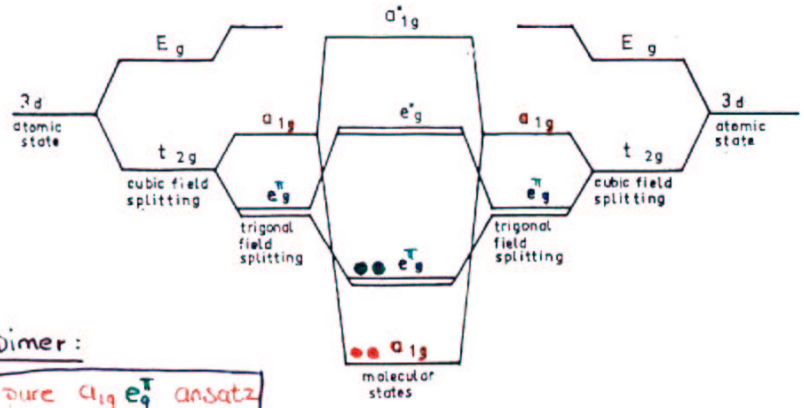
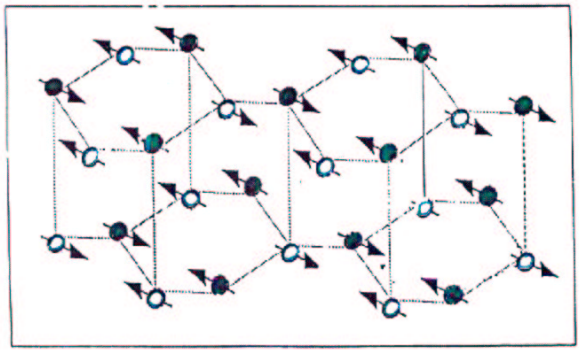
A phase diagram for all the possible collinear spin arrangements for V_2O_3 is derived within the atomic limit. Due to the fact that the a_{1g} electrons of the V atoms form a diamagnetic bond for the vertical pairs of V atoms, the magnetic structure of V_2O_3 can be considered to be essentially determined by the remaining one electron per V atom in a twofold degenerate e_g level. Depending on only two parameters: t_{ij}^{11}/t_{ij}^{22}, the ratio of the hopping integrals within the two orbital states 1 and 2 and between a certain pair (i,j) of V atoms in the basal plane, and J/U, the ratio of the exchange constant to Hubbard's U, the regions of stability for a particular magnetic and orbital order are determined. The experimentally observed magnetic order falls into a region of values of these parameters which are expected for V_2O.

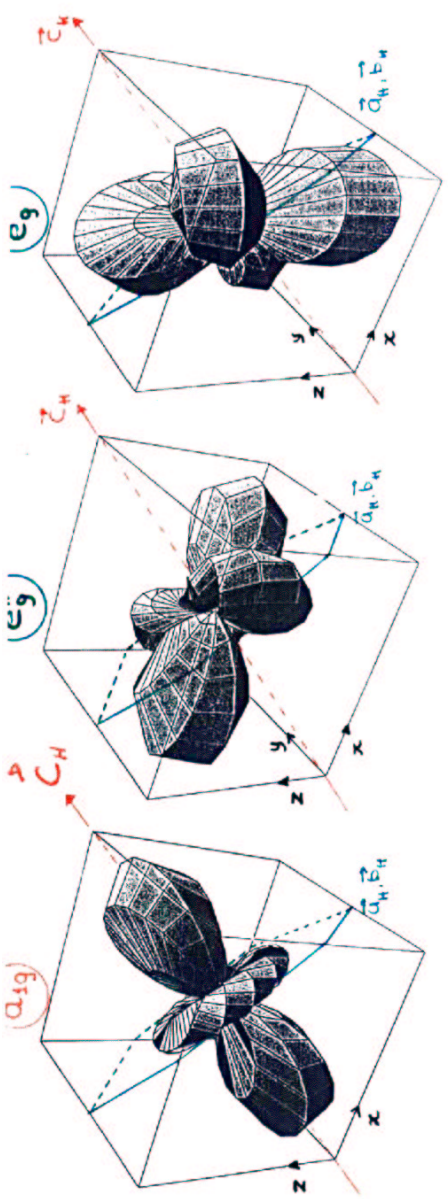


Dimer:

* pure $a_{1g}\, e_g^\pi$ ansatz
* a_{1g} molecular orbital = doubly occupied → singlet state a_{1g} project out a_{1g}



$S = \frac{1}{2}$ system with doubly degenerate e_g^π orbitals. → orbital ordering "AO-RS"

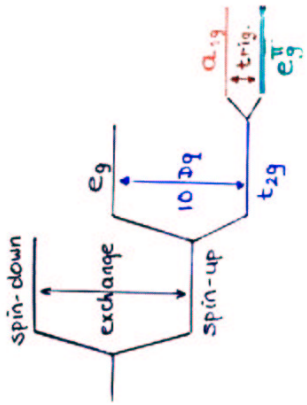


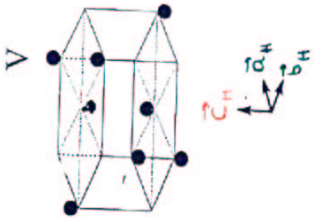
V_2O_3 : $3d^2 \Rightarrow$ in O_H : $(t_{2g}^1)^2 \Rightarrow$ trig. : $(a_{1g}^\uparrow e_g^{\pi\uparrow})$, $(e_g^{\pi\uparrow} e_g^{\pi\uparrow})$

t_{2g} : xy, yz, zx

a_{1g} : $\frac{1}{\sqrt{3}}(xy+yz+zx)$

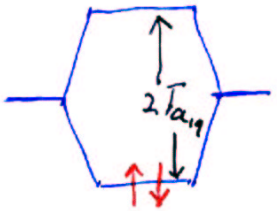
e_g^π : $\frac{1}{\sqrt{6}}(2xy-yz-zx)$, $\frac{1}{\sqrt{2}}(yz-zx)$





the generally accepted idea was

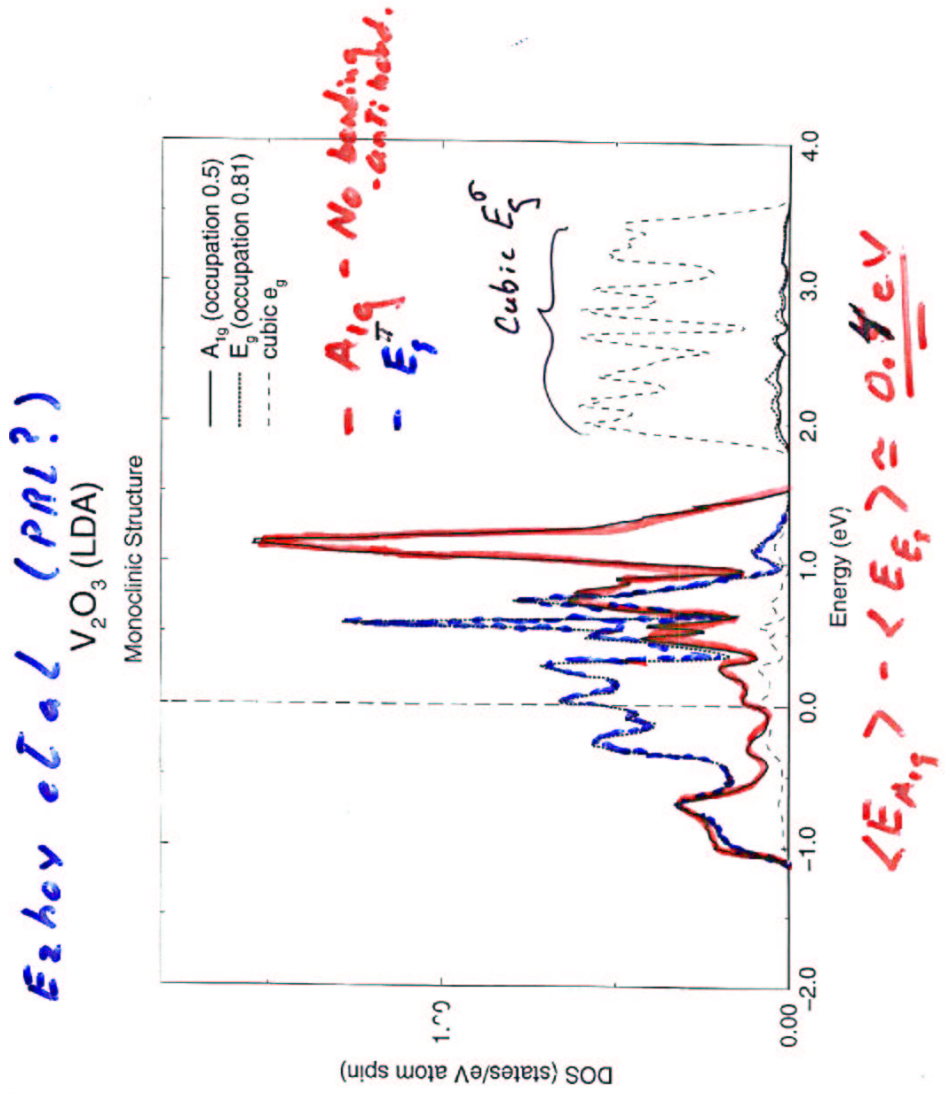
1. a_{1g} orbitals for c axis pair form MO's with 2 electrons in the bonding MO

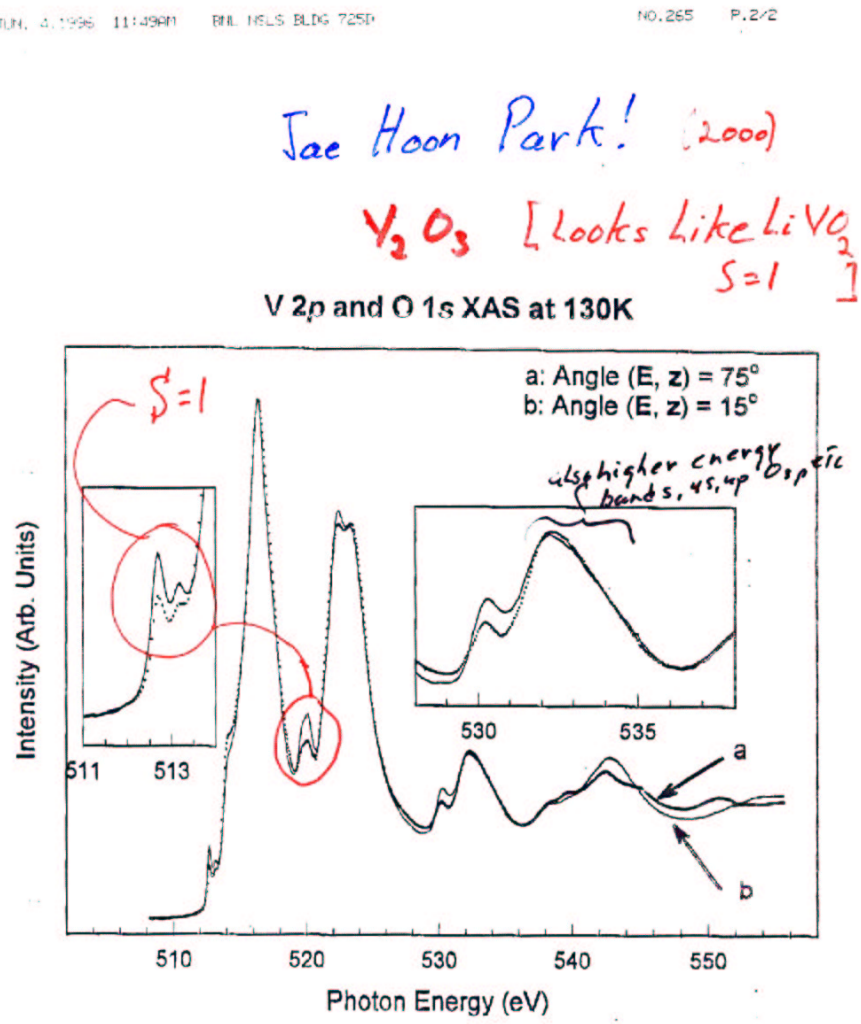


Valid for $2T_{a_{1g}} >> U$

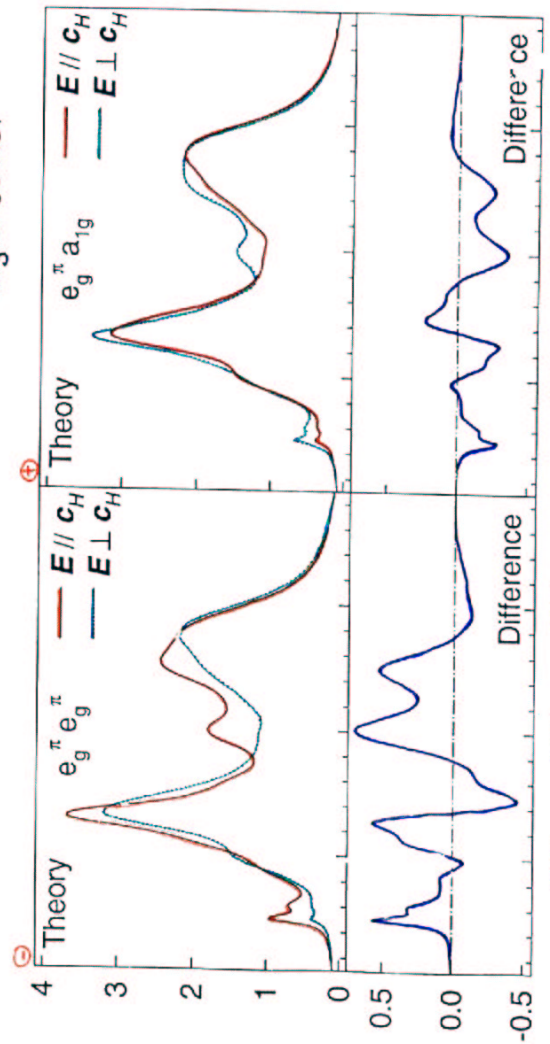
2. the e_g^π orbitals in the basal plane's are in the Heitler London Limit $2T_{e_g^\pi} << U$

Result $S = 1/2$ Mott-Hubbard

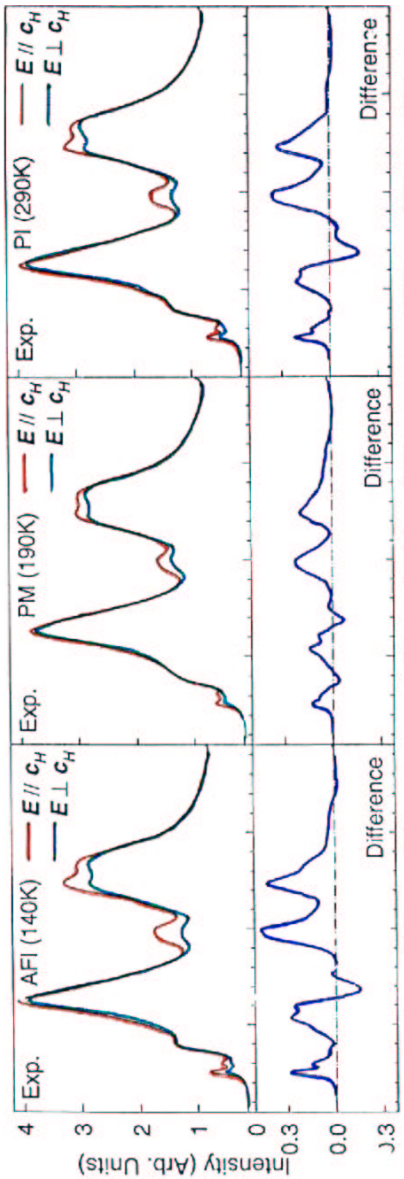

E_2 hov et al (PRL?)
V_2O_3 (LDA)
Monoclinic Structure
A_{1g} (occupation 0.5)
E_g (occupation 0.81)
cubic e_g
A_{1g} - No binding. anti bond.
E_g^π
Cubic E_g^σ
$\langle E_{M,I} \rangle - \langle E_{E_F} \rangle \simeq 0.4$ eV
Energy (eV)
DOS (states/eV atom spin)


TUN. 4.1996 11:49AM BNL NSLS BLDG 725D NO.265 P.2/2
Jae Hoon Park! (2000)
V_2O_3 [Looks Like LiVO$_2$ S=1]
V 2p and O 1s XAS at 130K
S=1
a: Angle (E, z) = 75°
b: Angle (E, z) = 15°
also higher energy magnetic bands, 4s, 4p
Intensity (Arb. Units)
511
513
530
535
a
b
510
520
530
540
550
Photon Energy (eV)

Multiplet calculation : V $3d^2$ high-spin 10 Dq = 1.5 eV trig. = 50 meV

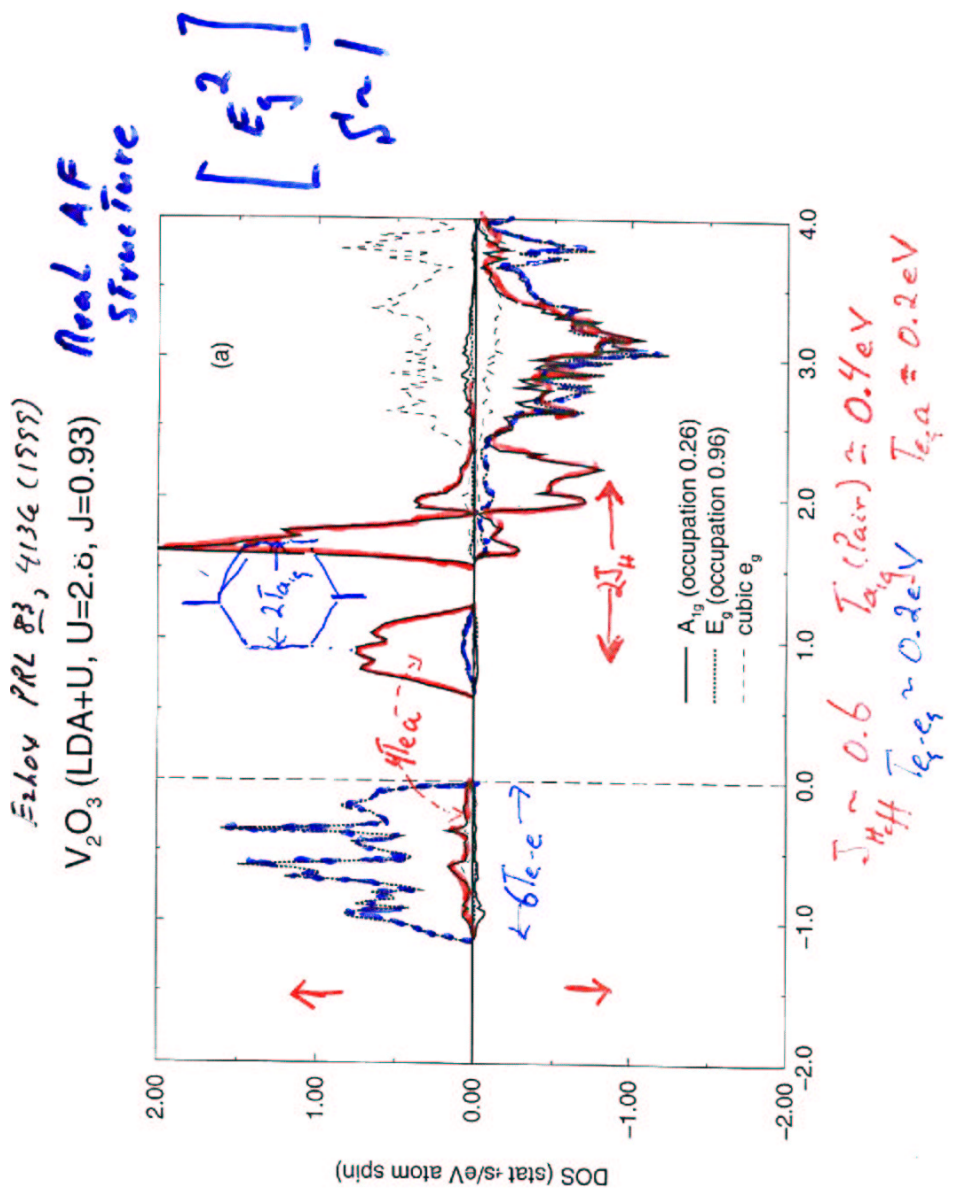


Exp. spectra show that V^{3+} - $3d^2$ is high spin : S=1



Difference spectra indicate that V^{3+} - $3d^2$ occupation is :

* certainly not $c_{g}^{T}a_{1g}$: wrong sign !
* also not pure $e_{g}^{T}e_{g}^{T}$: not large enough amplitude



$J_{H_{eff}} \sim 0.6$ $T_{a_{1g}}(\text{pair}) \simeq 0.4eV$ $T_{e_g a} \simeq 0.2eV$ $T_{e_g e_g} \sim 0.2eV$

Effective U

U_0 (Same orbital) $\simeq$ 3eV

U_1 (different orbital) $\simeq$ 1eV

J_H $\simeq$ 0.7eV

$T_{a\text{-}a}$ (pair) $\simeq$ 0.4eV

$T_{e\text{-}e}$ $\simeq$ 0.2eV

$T_{e\text{-}a}$ $\simeq$ 0.2eV

3 band model

Strong electron phonon

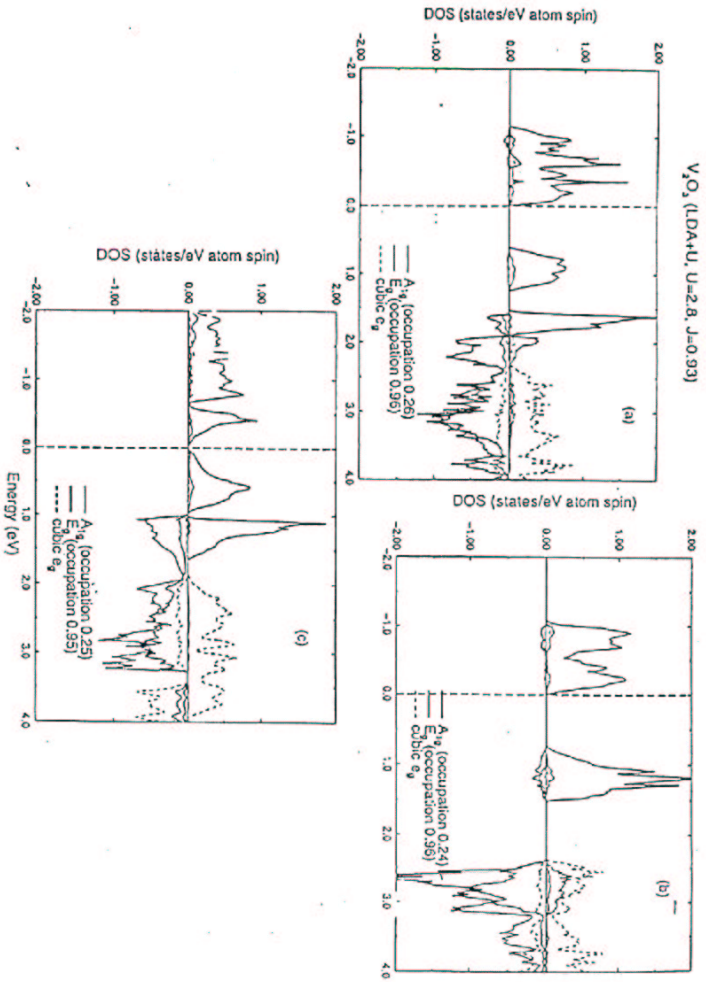


FIG. 3. Partial densities of states for d states of V obtained in the LDA + U calculation. (a) Real antiferromagnetic structure; (b) simple antiferromagnetic structure; (c) ferromagnetic structure

IF we want to describe the electron addition spectral function up to 4eV above E_F a lot of the weight comes from e_g^σ and higher bands Especially for Okedge XAS!!

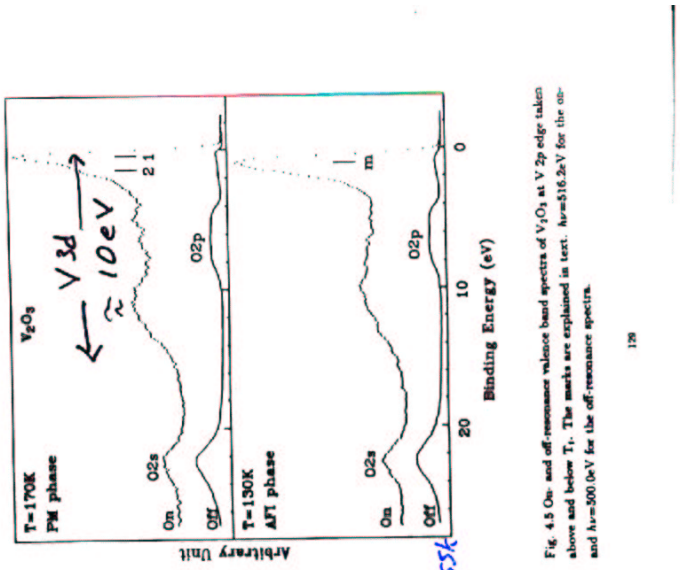


Fig. 4.5 On- and off-resonance valence band spectra of V_2O_3 at V 2p edge taken above and below T_t. The marks are explained in text. $h\nu$=516.2eV for the on- and $h\nu$=500.0eV for the off-resonance spectra.

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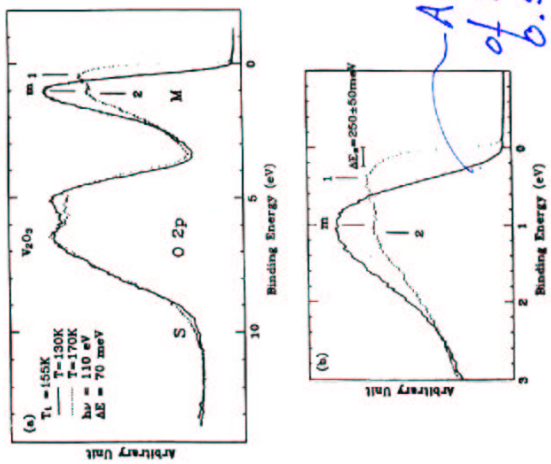
UPS / XPS

Park, Allen Tjeng



Agap opens of more than 0.5eV at T_t=155K

Fig. 4.4 Valence band spectra of V_2O_3 above and below T_t. The marks are explained in text. (a) Broad spectrum. (b) Near E_F spectrum.

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V 3d N-1 Spectral weight extending to 10eV below E_F!!

IF we want to describe this must go back to "Bare" U include e_g^σ and the strong hybridization with O2p!!

For the low energy Scale Effective U is reduced by $O2p \rightarrow V_{3d e_g^\sigma}$ charge fluctuations. i.e Treat t_{2g} Like core state in electron removal screening by Transfer of on electron from O2p to e_g^σ

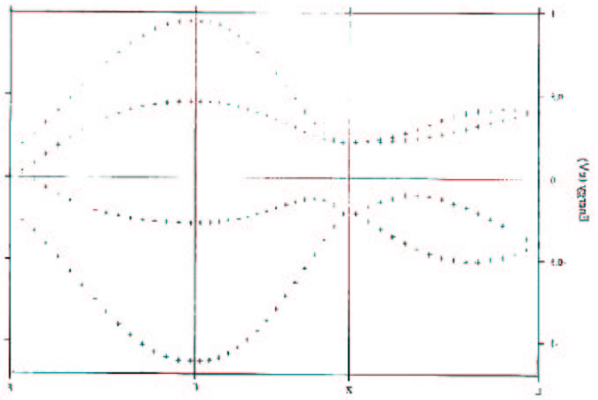


Fig. 6. Tight binding a_{1g} bands for t_1=-0.03eV, t_2=-0.25eV, t_3=-0.15eV, t_4=-0.0355eV. To obtain the very evident asymmetry between the upper and lower pairs of bands we need a small t_1 of the negative sign. This is now close to the LDA+U band structure.

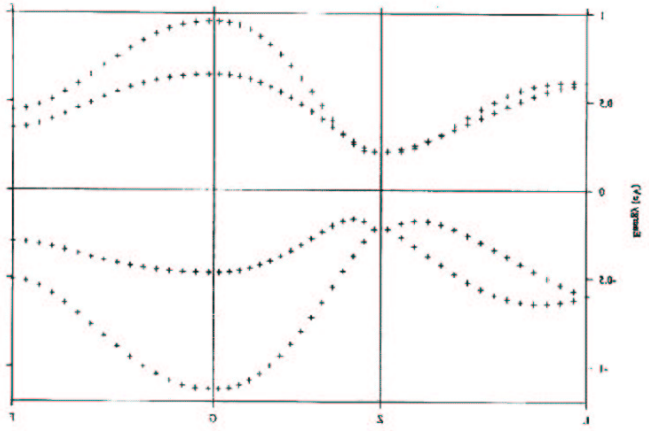


Fig. 7. Tight binding a_{1g} bands for t_1=-0.03eV, t_2=-0.5eV, t_3=-0.1eV, t_4=-0.04eV.

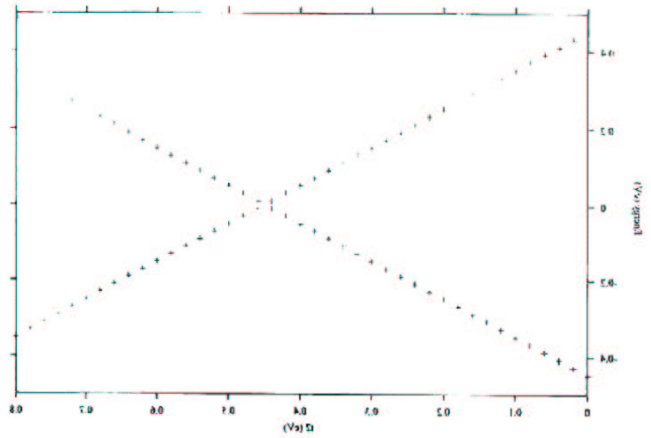


Fig. 8. Tight binding a_{1g} bands at Z-point for t_1=0, t_3=-0.1eV, t_4=-0.0355eV as a function of t_2. Note, that the band structure at this point of the Brillouin zone does not depend on the value of t_2.

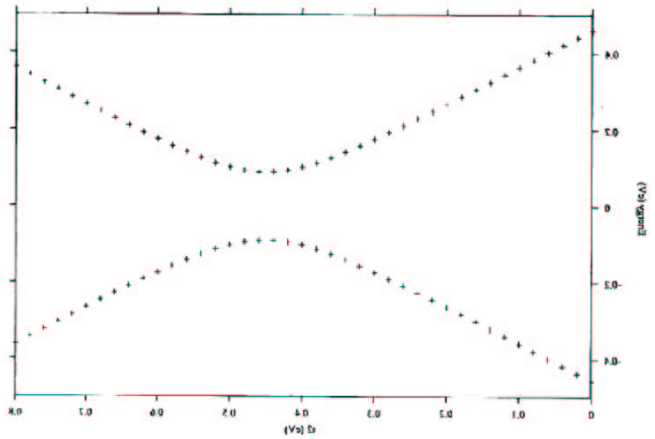
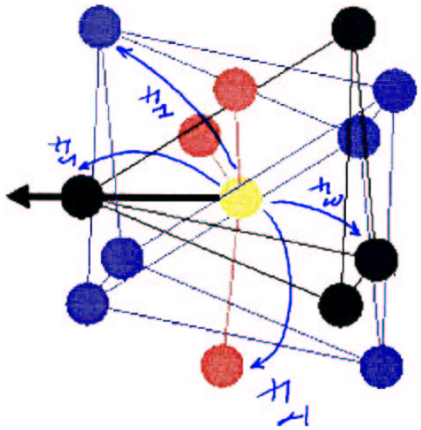


Fig. 9. Tight binding a_{1g} bands at Z-point for t_1=-0.03, t_3=-0.1eV, t_4=-0.0355eV as a function of t_2. Note, that the band structure at this point of the Brillouin zone does not depend on the value of t_2.

Fig. 5. Tight binding a_{1g} bands for t_1=0, t_2=-0.25eV, t_3=-0.15eV, t_4=-0.055eV. A small t_4 but with 6 nearest neighbors is sufficient to case the large splitting into 4 bands seen in the band structure from LDA+U. Note again the splitting at Z stays nearly the same.

Fig. 3. Tight binding a_{1g} bands for t_1=0, t_2=-0.25eV, t_3=0, t_4=0. The splitting is 2*t_2 and there is no dispersion if we take only t_2 as finite. Note the zero of energy now is at the center of the gap between the split bands. This is also the case for the following figures.

Fig. 4. Tight binding a_{1g} bands for t_1=0, t_2=-0.25eV, t_3=-0.15eV, t_4=0. Note that the large splitting at Γ is dominated by t_3 and not t_2.



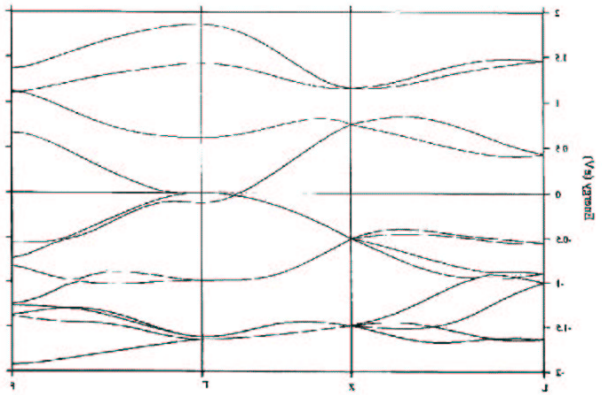


Fig. 1. LDA+U spin up band structure of ferromagnetic V_2O_3 in corundum crystal structure for U=3eV and J=0.8eV. Here the Γ-Z direction is along the c-axis and the a_{1g} bands are the ones above the Fermi energy at zero energy.

Parameters for d_{xy} bands.

$t_1 = -.03$

$t_2 = .25$

$t_3 = .15$

$t_4 = .055$