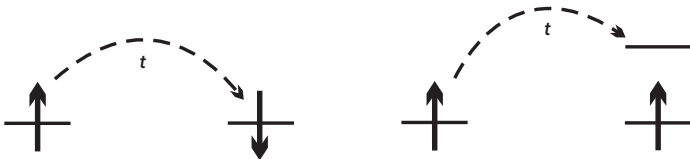


Extending the model approach to magnetic interactions in transition metal compounds

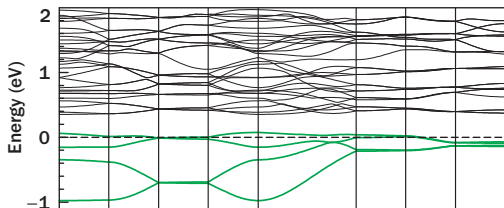
Alexander Tsirlin

Max-Planck Institute for Chemical Physics of Solids, Dresden



Workshop DFT meets Solid State Chemistry
October, 28, 2009

The idea of modeling



(LDA band structure)



$$E(\mathbf{k}) = -\sum_{i,j} t_{ij} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}}$$

(Tight-binding model)



$$\hat{H} = \sum_{i,j} t_{ij} \hat{C}_{i\sigma}^{\dagger} \hat{C}_{j\sigma} + \sum_i U_{\text{eff}} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

(Correlated hamiltonian)

- ▶ Selecting the relevant bands and constructing a minimal model that reproduces essential physics of the system

$$|W_{n\mathbf{R}}\rangle = \frac{V}{(2\pi)^3} \int d\mathbf{k} e^{-i\mathbf{k}\mathbf{R}} |\psi_{n\mathbf{k}}\rangle$$

$$|\psi_{n\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} |W_{n\mathbf{R}}\rangle$$

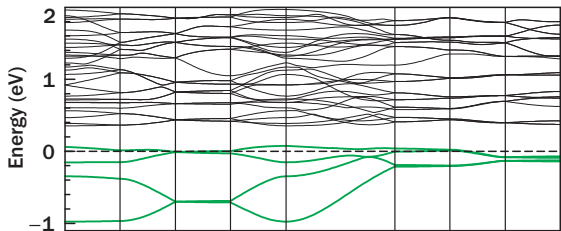
$W_{n\mathbf{R}}(\mathbf{r} - \mathbf{R})$ – Wannier functions, \mathbf{R} denotes the unit cell

$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}}$ – Bloch functions

- The $u_{n\mathbf{k}}$ functions are ambiguous with respect to the phase factor
- To achieve the unique definition of the Wannier functions, one has to introduce an additional condition – e.g., the maximal localization of $W_{n\mathbf{R}}$
- In FPLO, the Wannier functions are based on individual atomic orbitals or their combinations. Then, the high degree of localization and the straight-forward chemical meaning are achieved

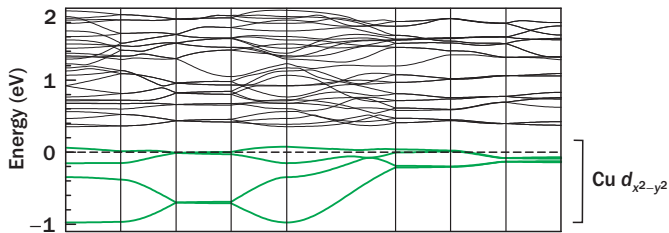
N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997)
H. Eschrig and K. Koepnik, Phys. Rev. B **80**, 104503 (2009)

Constructing models



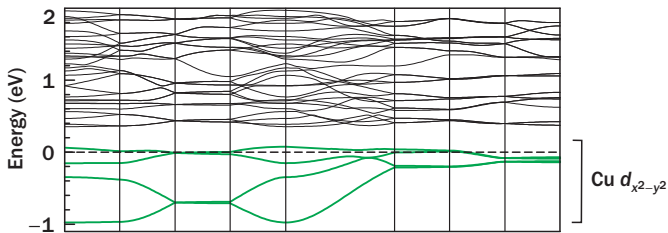
- **Select relevant bands**
- Find their characters
- Construct Wannier functions
- Calculate hopping parameters as overlap integrals of the Wannier functions
- Visualize the Wannier functions – "crystal orbitals"

Constructing models



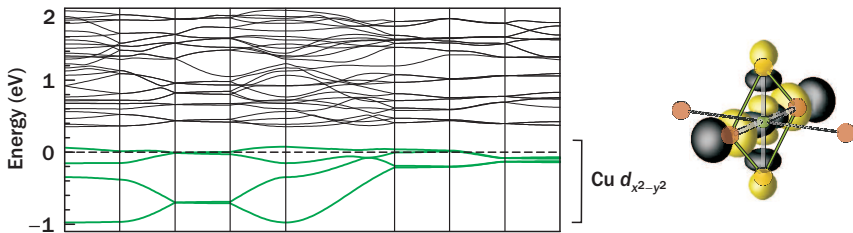
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Constructing models



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Constructing models



- Select relevant bands
- Find their characters
- Construct Wannier functions
- Calculate hopping parameters as overlap integrals of the Wannier functions
- Visualize the Wannier functions – "crystal orbitals"

Multi-orbital Hubbard model

$$\hat{H} = \sum_{i,j,\sigma} t_{ij} \hat{C}_{i\sigma}^+ \hat{C}_{j\sigma} + \sum_i U_{\text{eff}} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

i and *j* label sites

One-orbital model



J^{AFM} at $t \ll U_{\text{eff}}$

Multi-orbital Hubbard model

$$\hat{H} = \sum_{i,j,\sigma} t_{ij} \hat{C}_{i\sigma}^+ \hat{C}_{j\sigma} + \sum_i U_{\text{eff}} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

i and j label sites

One-orbital model



J^{AFM} at $t \ll U_{\text{eff}}$

$$\hat{H} = \sum_{\substack{i,j,\sigma \\ \alpha \neq \beta}} t_{ij}^{\alpha \rightarrow \beta} \hat{C}_{i\alpha\sigma}^+ \hat{C}_{j\beta\sigma} + \sum_{i\alpha} U_{\text{eff}} \hat{n}_{i\uparrow}^{\alpha} \hat{n}_{i\downarrow}^{\alpha} + \\ + \sum_{i,\sigma,\alpha} (\varepsilon_0 + \Delta_{\alpha}) \hat{n}_{i\sigma}^{\alpha} - \sum_{\substack{i,\sigma,\sigma' \\ \alpha \neq \beta}} \frac{J_H}{2} (\hat{C}_{i\alpha\sigma}^+ \hat{C}_{i\alpha\sigma'} \hat{C}_{i\beta\sigma'}^+ \hat{C}_{i\beta\sigma} + \text{H.c.})$$

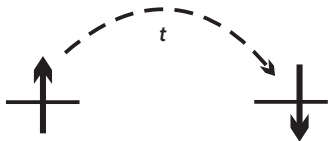
i and j label sites, α and β label orbitals
 Δ_{α} are energy splittings, J_H is the Hund's coupling

Multi-orbital model



J^{AFM} and J^{FM}
at $t \ll U_{\text{eff}}$

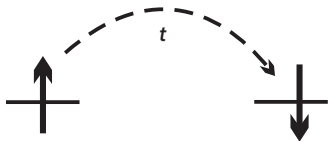
Multi-orbital Hubbard model



Electron hops to the half-filled orbital

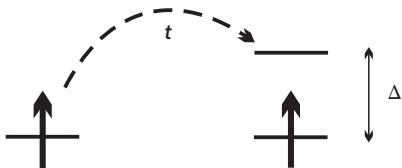
$$J^{\text{AFM}} = 4t^2/U$$

Multi-orbital Hubbard model



Electron hops to the half-filled orbital

$$J^{\text{AFM}} = 4t^2/U$$



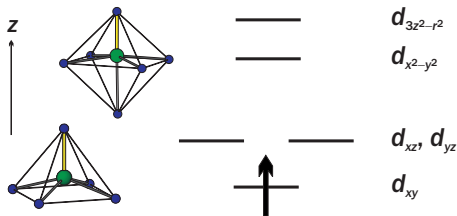
Electron hops to an empty orbital

$$J^{\text{FM}} = -\frac{4t^2}{(U + \Delta)(U + \Delta - J_H)}$$

J_H is the *on-site Hund's coupling*

K. I. Kugel and D. I. Khomskii, *Usp. Phys. Nauk*, **25**, 231 (1982)

The case of V^{+4}



$$V^{+4} = 3d^1$$

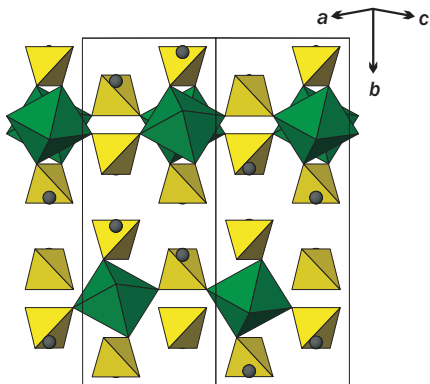
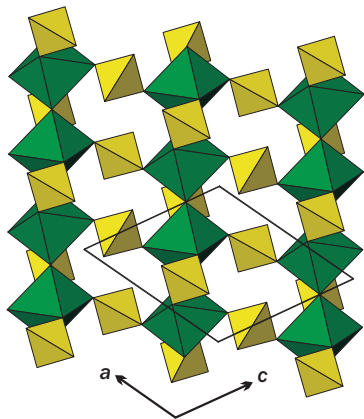
The unpaired electron occupies the d_{xy} orbital

$$J = \frac{4t_{xy \rightarrow xy}^2}{U_{\text{eff}}} - \sum_{\alpha} \frac{4t_{xy \rightarrow \alpha}^2}{(U_{\text{eff}} + \Delta_{\alpha})(U_{\text{eff}} + \Delta_{\alpha} - J_H)}$$

$$\alpha = yz, xz, 3z^2 - r^2, x^2 - y^2$$

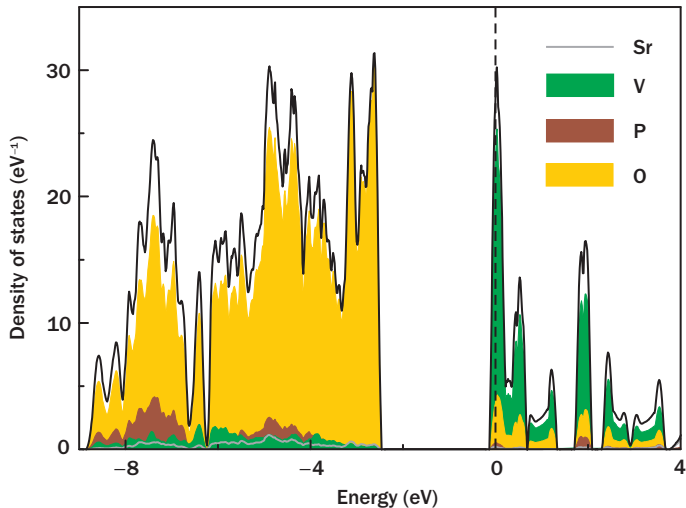
V. V. Mazurenko *et al.* PRB, **73**, 014418 (2006)

$\text{Sr}_2\text{VO}(\text{PO}_4)_2$, crystal structure

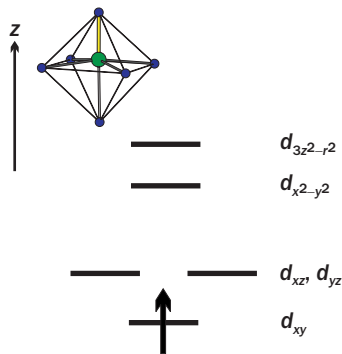
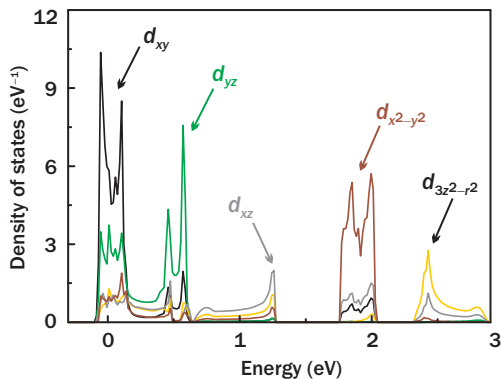


- Chains of corner-sharing V^{4+}O_6 octahedra
- PO_4 tetrahedra couple chains into layers
- 1D or 2D spin system?

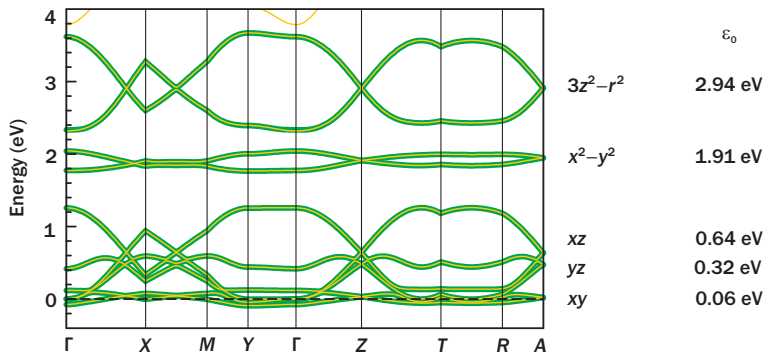
$\text{Sr}_2\text{VO}(\text{PO}_4)_2$, LDA band structure



Sr₂VO(PO₄)₂, LDA band structure



$\text{Sr}_2\text{VO}(\text{PO}_4)_2$, LDA band structure



- At low temperatures, the d_{xy} orbital is half-filled: $\epsilon_{yz} - \epsilon_{xy} = 0.26 \text{ eV} \simeq 3000 \text{ K}$

Sr₂VO(PO₄)₂, microscopic model

t (meV)

$xy \rightarrow xy$	-9
$xy \rightarrow yz$	34, 45
$xy \rightarrow xz$	22, 26
$xy \rightarrow x^2 - y^2$	0
$xy \rightarrow 3z^2 - r^2$	0

$$J_1^{\text{FM}} = -5.5 \text{ K}$$

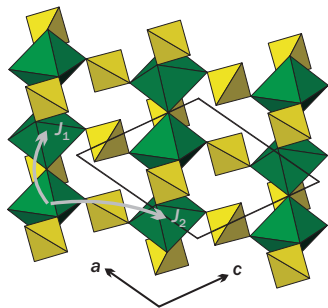
$$J_1^{\text{AFM}} = 0.8 \text{ K}$$

t (meV)

$xy \rightarrow xy$	32
$xy \rightarrow yz$	17, 13
$xy \rightarrow xz$	16, 0
$xy \rightarrow x^2 - y^2$	0
$xy \rightarrow 3z^2 - r^2$	0

$$J_2^{\text{FM}} = -0.9 \text{ K}$$

$$J_2^{\text{AFM}} = 10.6 \text{ K}$$



Sr₂VO(PO₄)₂, microscopic model

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t (meV)

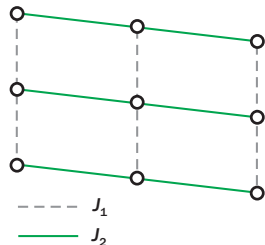
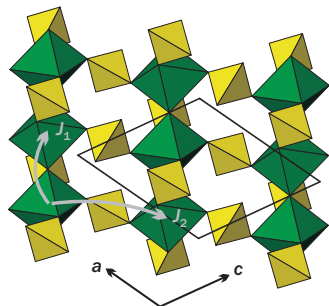
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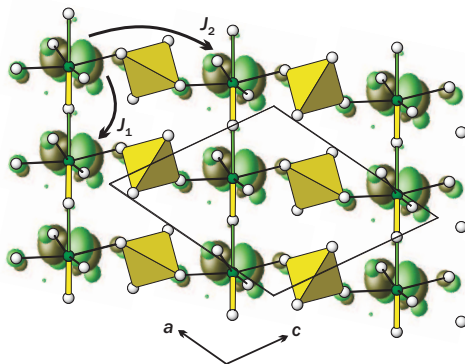
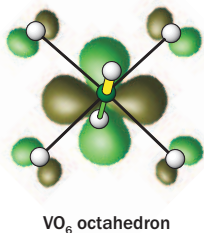
$$J_2^{\text{AFM}} = 10.6 \text{ K}$$

$$J_1 = -4.7 \text{ K}$$

$$J_2 = 9.7 \text{ K}$$

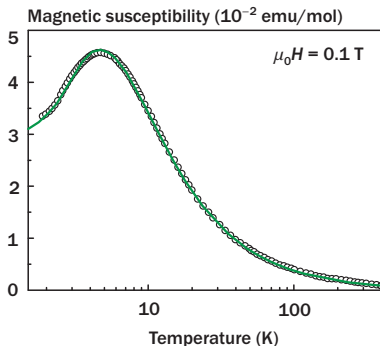


$\text{Sr}_2\text{VO}(\text{PO}_4)_2$, Wannier functions



- Each Wannier function is composed of the V d_{xy} orbital and the O πp orbitals
- Antiferromagnetic J_2 is caused by the overlap of the Wannier functions on the neighboring sites
- There is no overlap of the Wannier functions along the structural chains, hence J_1 is ferromagnetic

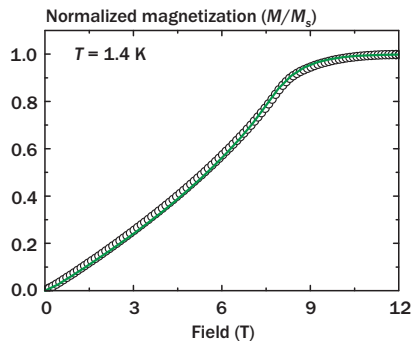
$\text{Sr}_2\text{VO}(\text{PO}_4)_2$, experimental data



Experiment

$$J_1 = -8.3 \text{ K}$$

$$J_2 = 5.9 \text{ K}$$



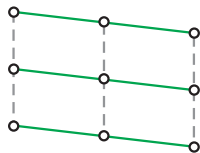
LDA-based model

$$J_1 = -4.7 \text{ K}$$

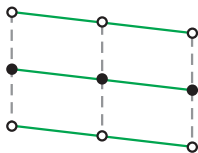
$$J_2 = 9.7 \text{ K}$$

Experimental data:
in collaboration with Enrique Kaul and Christoph Geibel (MPI CPfS)

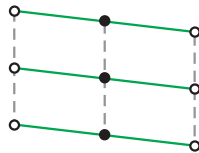
Sr₂VO(PO₄)₂, model approach vs. LSDA+U



$$E = E_0 + J_1 + J_2$$



$$E = E_0 - J_1 + J_2$$

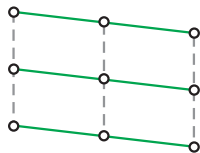


$$E = E_0 + J_1 - J_2$$

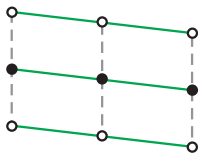
- spin-up
- spin-down

	J_1 (K)	J_2 (K)
LDA-based model	-4.7	9.7
LSDA+U, $U_d = 4$ eV	2.5	15.7
LSDA+U, $U_d = 6$ eV	-8.1	13.2
Experiment	-8.3	5.9

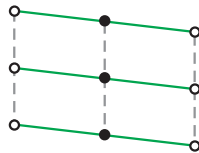
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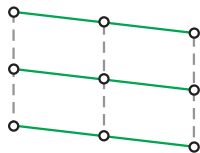


$$E = E_0 + J_1 - J_2$$

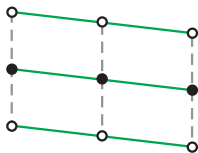
- spin-up
- spin-down

	J_1 (K)	J_2 (K)	
LDA-based model	-4.7	9.7	28 atoms, less than 1 day
LSDA+U, $U_d = 4$ eV	2.5	15.7	56 atoms, three configurations, ~ one week for each U_d value
LSDA+U, $U_d = 6$ eV	-8.1	13.2	
Experiment	-8.3	5.9	

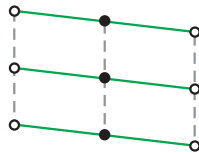
Sr₂VO(PO₄)₂, model approach vs. LSDA+U



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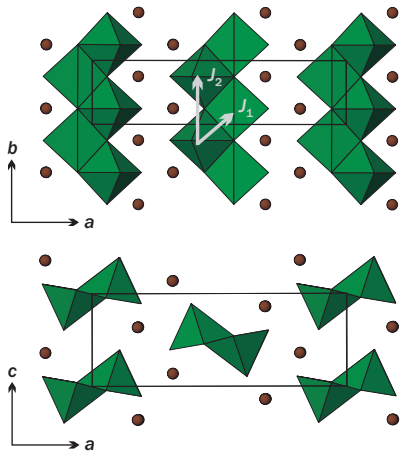


$$E = E_0 + J_1 - J_2$$

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- spin-down

	J_1 (K)	J_2 (K)	
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LSDA+U, $U_d = 6$ eV	-8.1	13.2	
Experiment	-8.3	5.9	years...

CdVO₃, crystal structure

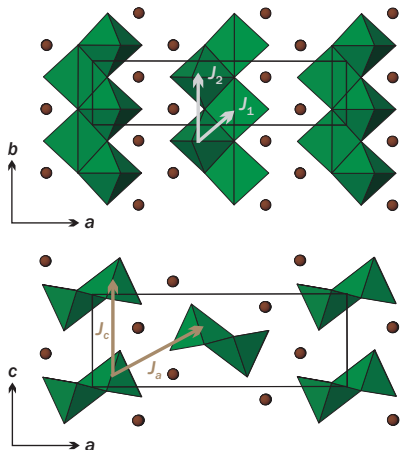


Zigzag chains of VO₅ square pyramids

Competing interactions J_1 and J_2 ?

Frustrated spin chains?

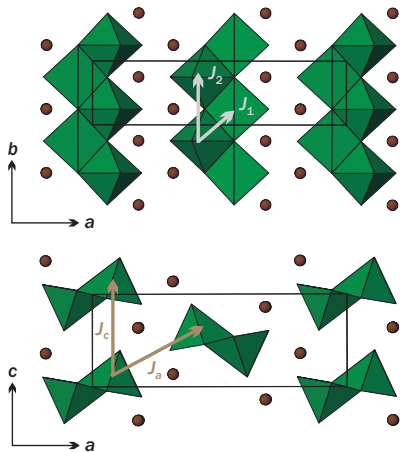
Spiral ground state?



J_1	J_2	J_a	LSDA+ <i>U</i> double counting
-18	18	3	Around the mean field

$$U_d = 3 \text{ eV}$$

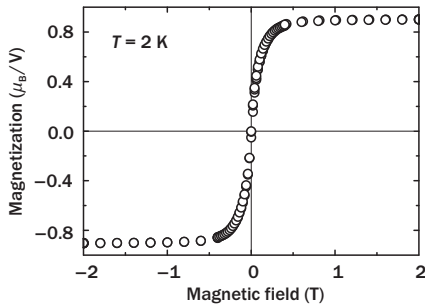
CdVO₃, LSDA+U



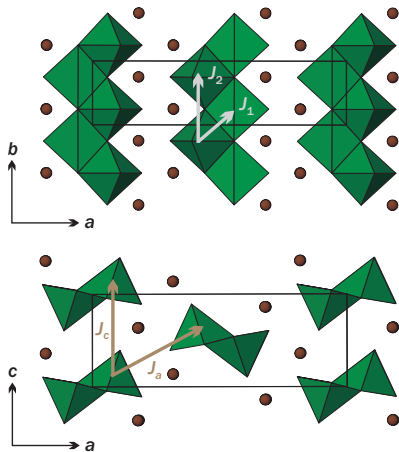
J_1	J_2	J_a	LSDA+U double counting
-18	18	3	Around the mean field

$$U_d = 3 \text{ eV}$$

► Ferromagnetic ground state



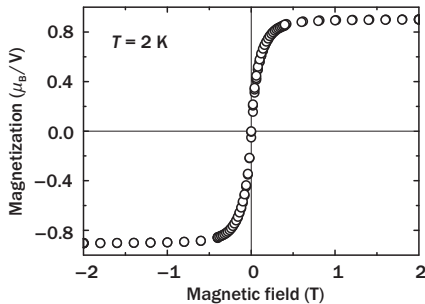
CdVO₃, LSDA+U



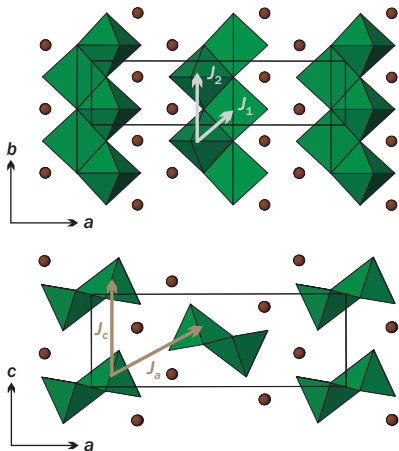
J_1	J_2	J_a	LSDA+U double counting
-18	18	3	Around the mean field
-130	11	-4	Atomic limit

$$U_d = 3 \text{ eV}$$

► Ferromagnetic ground state



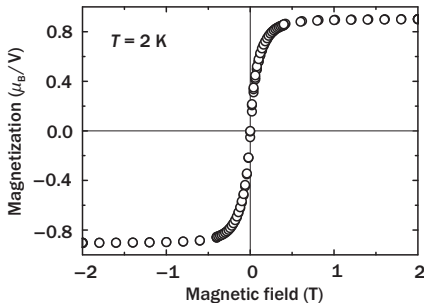
CdVO₃, LDA-based model



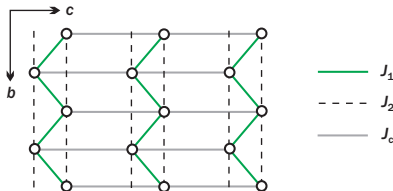
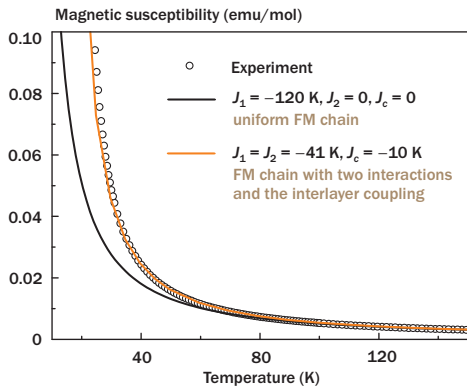
(in K):

	J_1	J_2	J_a	J_c
J^{AFM}	0	1	0.5	2
J^{FM}	-84	-69	-3	-17
J	-84	-68	-2.5	-15

► Consistent with the experiment



CdVO₃: comparison to the experiment



(in K):	J_1	J_2	J_a	J_c
Model	-84	-68	-2.5	-15
Experiment	-41	-41	0	-10

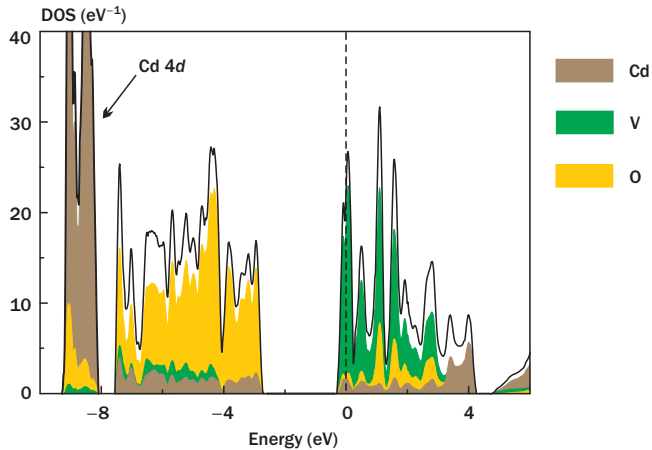
- ▶ LDA-based model predicts the ordering temperature of 30 K
- ▶ Good agreement with the experimental $T_C = 24$ K

- **LDA-based modeling** is an effective approach to magnetic interactions in transition metal compounds:
 - **One-orbital model** helps to establish the range of the interactions and to get quantitative estimates of the antiferromagnetic contributions
 - **Multi-orbital models** yield ferromagnetic contributions to the exchange and provide a microscopic insight into the mechanism of the interaction
- **LSDA+ U** is another option to estimate the exchange couplings. But:
 - No insight into the mechanism
 - U dependence
 - Severe failures for certain materials

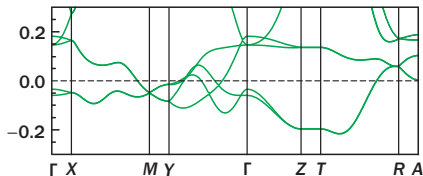
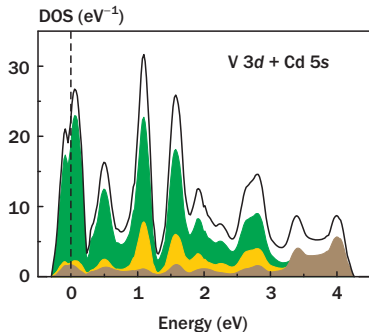
Take-home messages:

- ▶ Always try the model approach while dealing with magnetic interactions in insulators
- ▶ Structure-properties relationships become simple: look for the interplay between chemical/structural features and hopping parameters of the LDA band structure

LDA band structure



LDA band structure



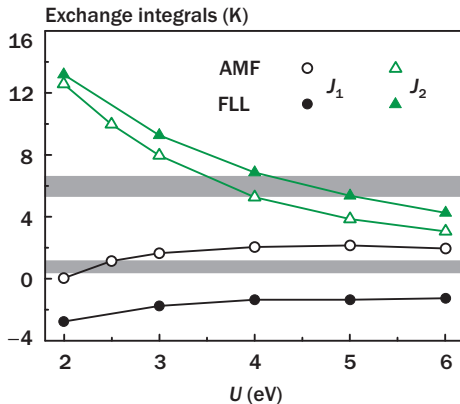
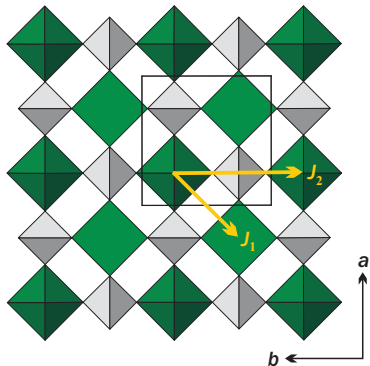
At the Fermi level:

- Four narrow d_{xy} bands
- Nearly equal contributions of O 2p and Cd 5s orbitals

E_{dc} vs. exchange couplings: $\text{Li}_2\text{VO}_2\text{SiO}_4$

E_{LSDA+U} depends on the occupancies on each site
and does not depend on the mutual orientation of neighboring spins.

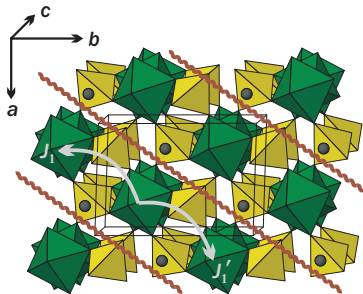
Should E_{dc} have any influence on the exchange integrals?



E_{dc} vs. exchange couplings: AgVOAsO_4

E_{LSDA+U} depends on the occupancies on each site
and does not depend on the mutual orientation of neighboring spins.

Should E_{dc} have any influence on the exchange integrals?

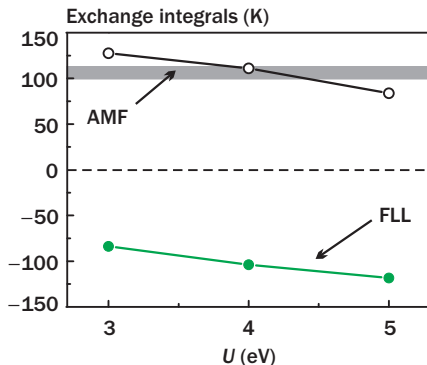
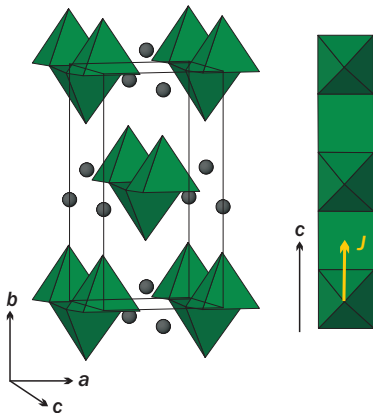


	J_1	J'_1	J_{ic1}	J_{ic2}	J_{ic3}	J_{ic4}
AMF	47	47	-9	6	-4	1
FLL	41	36	-8	4	0	-1

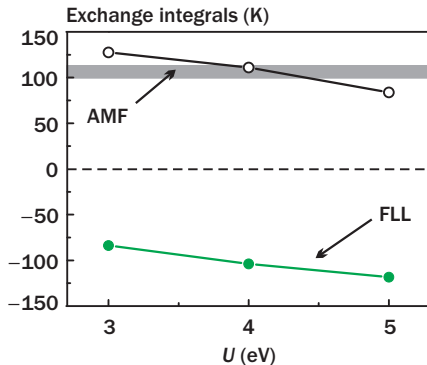
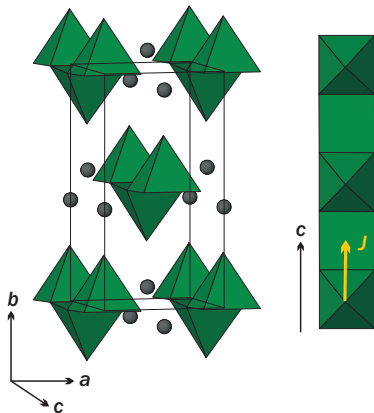
$$U_d = 4 \text{ eV}$$

E_{dc} vs. exchange couplings: MgVO_3

E_{LSDA+U} depends on the occupancies on each site
and does not depend on the mutual orientation of neighboring spins.
Should E_{dc} have any influence on the exchange integrals? It has...



E_{dc} vs. exchange couplings: MgVO_3



$E_{\text{FM}} - E_{\text{AFM}}$ (meV)	Kinetic energy	Potential energy	Exchange-correlation energy	LSDA+U	Total
AMF	113.4	-58.5	-43.2	-2.2	9.5
FLL	99.0	-72.6	-36.2	1.1	-9.0