(Xiangang Wan)

Sergej Savrasov, ***UC Davis***

Thomas A. Maier
Oak Ridge National laboratory

Calculate Exchange Interaction J

J in Mott Insulator

J in Kondo System

J in HTC

J in $4f$ Ferromagnetic insulator

DM interaction

Magnetic Exchange interaction

Magnetic materials is very useful

Obtain a **quantitative theory** is important. Open new opportunities in computational design of new magnetic materials.

provide **conclusive theoretical** insights to various contributions to magnetic exchange interactions.

$$H \qquad f\, s_i \qquad \underset{ij}{} \qquad J_{ij} S_i S_j$$

1 1 0 1 2

自旋哈密顿写为：

$$H_S = \sum_{ij} (J_{ij}\vec{S}_i \cdot \vec{S}_j + \vec{D} \cdot (\vec{S}_i \times \vec{S}_j) + S_i^{\alpha}\Gamma_{\alpha\beta}S_j^{\beta})$$

Spin-orbital coupling (SOC)

H ij $t_{ij}c_i\, c_j$ $h.\,c.$ Un_in_i L S

$$\hat{H} = \sum_{ls,l's'} J_{ij}(\vec{R}_l + \vec{\tau}_s, \vec{R}_{l'} + \vec{\tau}_{s'})\hat{S}_i(\vec{R}_l + \vec{\tau}_s)\hat{S}_j(\vec{R}_{l'} + \vec{\tau}_{s'}),$$

$$\{\alpha|\vec{t}\}^+ \hat{H}\{\alpha|\vec{t}\} = \hat{H},$$

$$\{\alpha|\vec{t}\}^+ \hat{H}\{\alpha|\vec{t}\} = \sum_{ls,l's'} J_{ij}(\vec{R}_l + \vec{\tau}_s, \vec{R}_{l'} + \vec{\tau}_{s'})[\{\alpha|\vec{t}\}^+ \hat{S}_i(\vec{R}_l + \vec{\tau}_s)\{\alpha|\vec{t}\}][\{\alpha|\vec{t}\}^+ \hat{S}_j(\vec{R}_{l'} + \vec{\tau}_{s'})\{\alpha|\vec{t}\}]$$

$$\begin{cases} \{\alpha|\vec{t}\}^+ \hat{S}_i(\vec{R}_l + \vec{\tau}_s)\{\alpha|\vec{t}\} = R(\alpha)_{ii'}\hat{S}_{i'}(\{\alpha|\vec{t}\}^{-1}(\vec{R}_l + \vec{\tau}_s)), \\ \{\alpha|\vec{t}\}^+ \hat{S}_j(\vec{R}_{l'} + \vec{\tau}_{s'})\{\alpha|\vec{t}\} = R(\alpha)_{jj'}\hat{S}_{j'}(\{\alpha|\vec{t}\}^{-1}(\vec{R}_l + \vec{\tau}_s)), \end{cases}$$

J

$\{\alpha|\vec{t}\}$ $\hat{H}$ $\hat{S}$

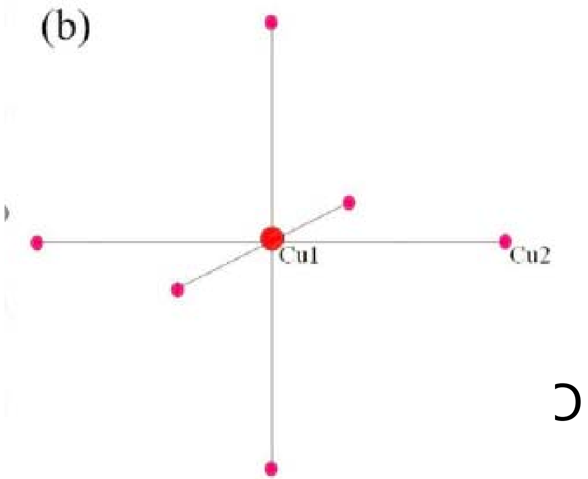
$Sr_8CaRe_3Cu_4O_{24}$ discovered under high pressure and high temperature. (Takayama-Muromachi *et al.*, JSSC175, 366 (2003))

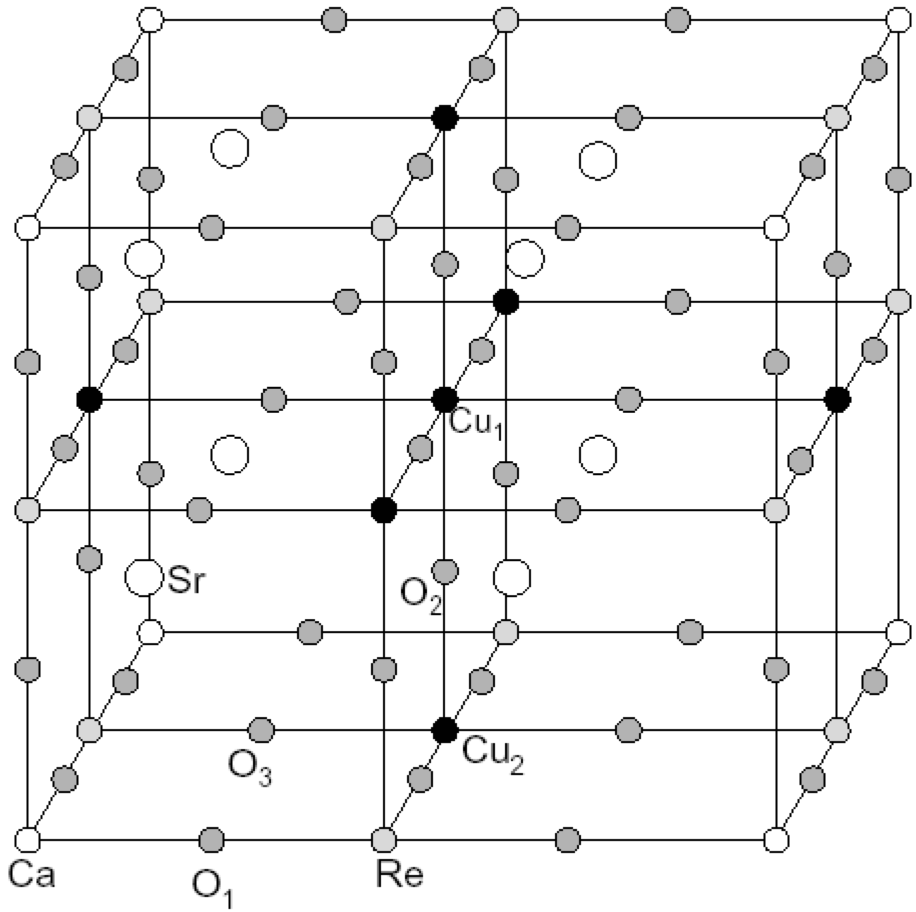
Sr → A site

Ca, Re, Cu → B site

4 Cu atoms → 1 Cu1, 3Cu2

24 O atoms → O1, O2, O3





Experiment

This material is insulator, shows ferromagnetic behavior at room temperature, and the spontaneous magnetization at T=0 is about $0.95\mu_B$/f.u with Tc≈440K.

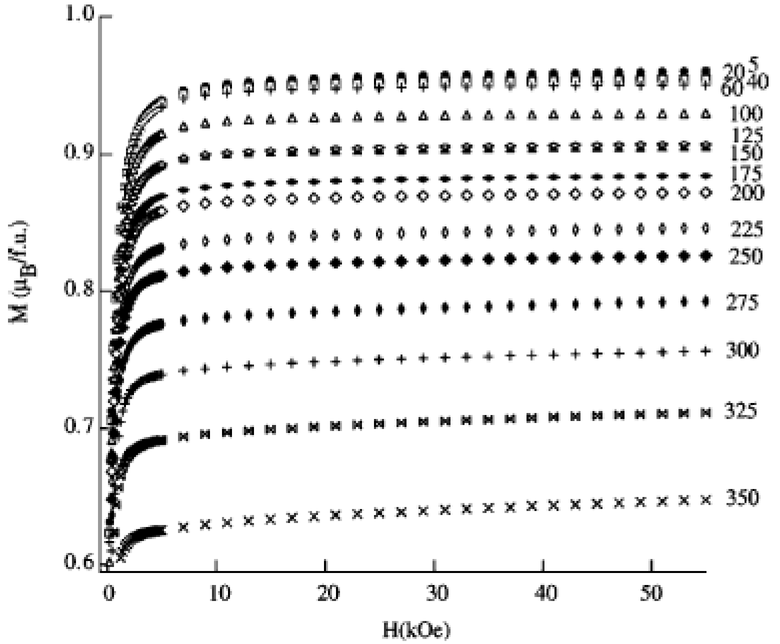


Fig. 6. The magnetization curves at various temperatures of the Ca-containing phase. The numbers shown indicate measuring temperatures in K.

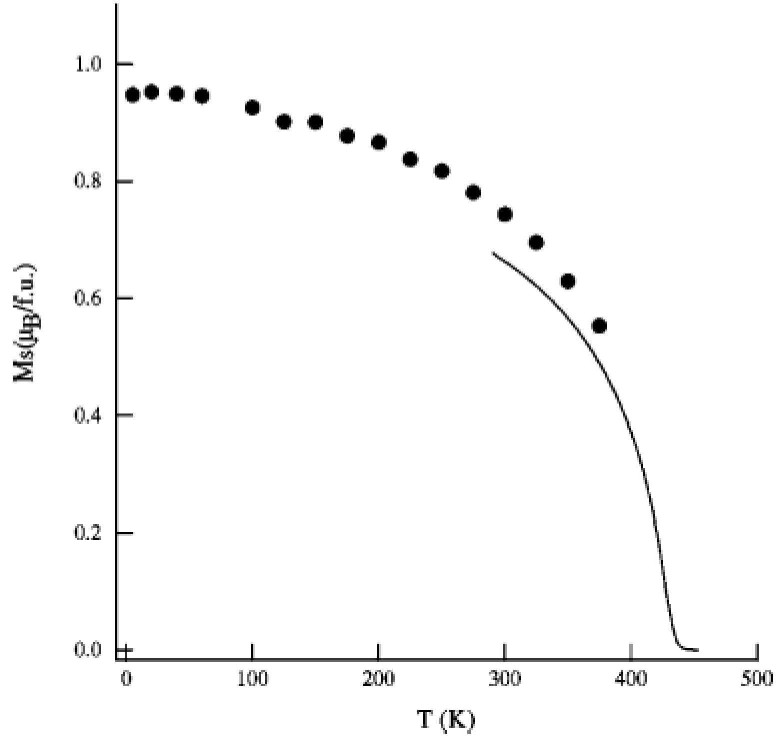


Fig. 7. Spontaneous magnetization M_s of the Ca-containing phase. The solid line indicates high-temperature-magnetization data at 1 kOe measured by VSM.

Motivation

1. The FM in cuprate is very rare.
2. The T_c of known FM cuprate is very low

$La_4Ba_2Cu_2O_{10} \longrightarrow$ 5 K

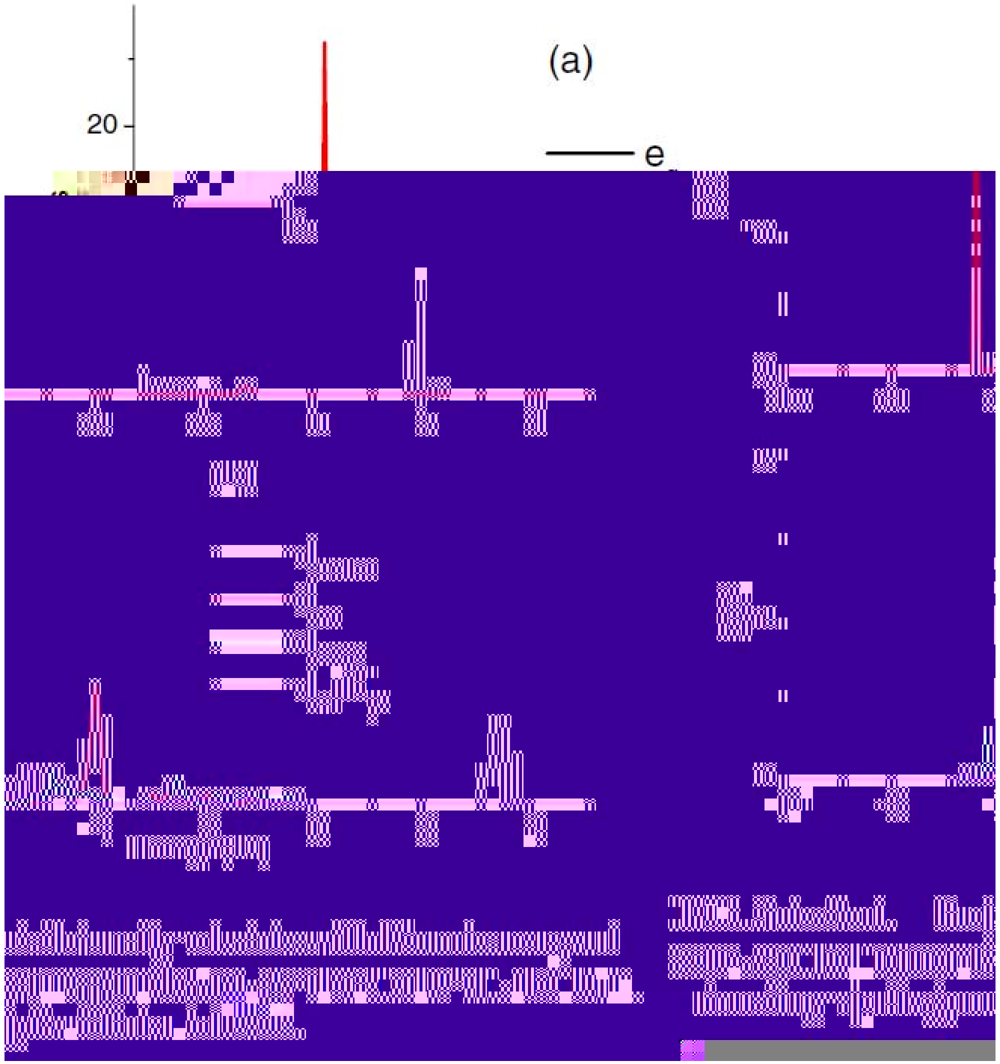
$K_2CuF_4 \longrightarrow$ 6.5K

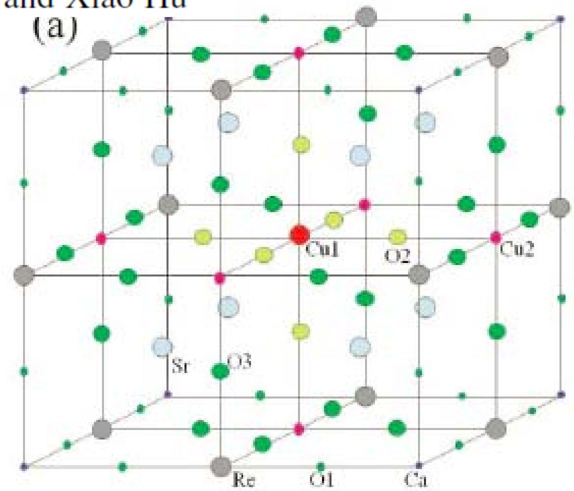
$SeCuO_3 \longrightarrow$ 26K

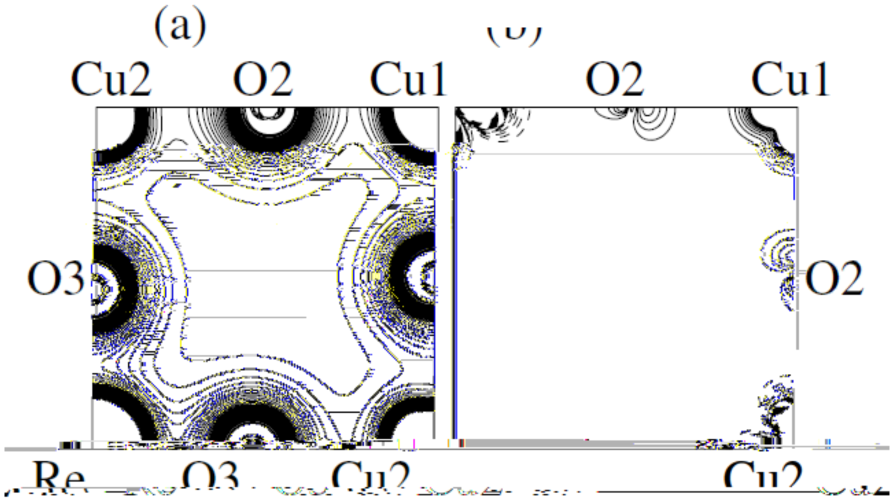
3. Why T_c is so high

Orbital Order and Ferrimagnetic Properties of Sr_8CaR $e_3Cu_4O_{24}$

Xiangang Wan,[1,2] Masanori Kohno,[1] and Xiao Hu[1]







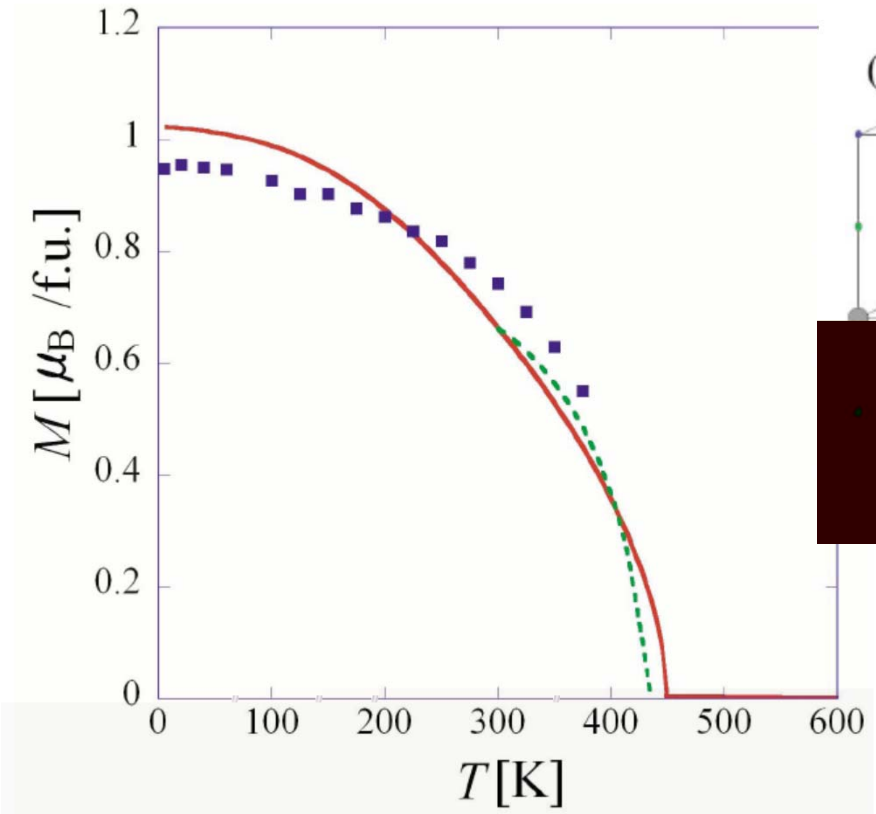
vith FIG. 2. Contours for charge density in the (010) plane v
sity interval $0.03e/\mathrm{bohr}^3$. (a) Total charge density. (b) Spin den
spin-up charge density minus spin-down charge density). The (
lotted lines are negative contours.

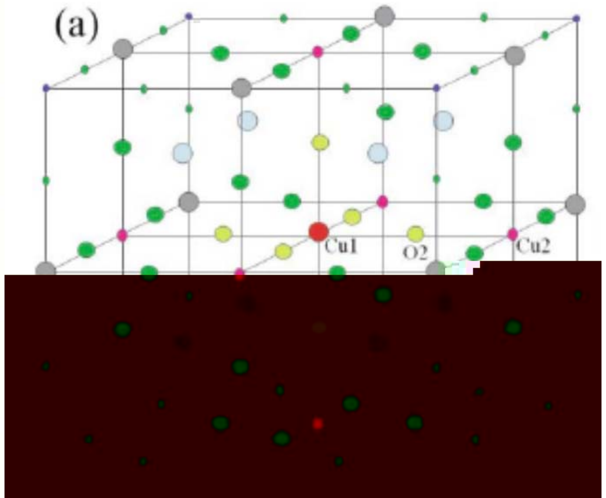
Calculate J by Energy Mapping Scheme

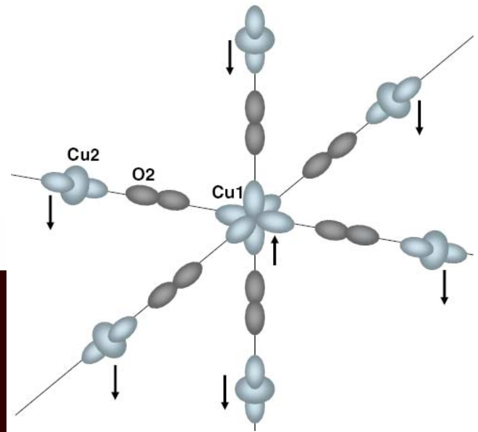
$Sr_8CaRe_3Cu_4O_{24}$

$$\mathcal{H} = J_{\mathrm{eff}} \sum_i \mathbf{S}_i \cdot \sum_p \mathbf{s}_{i+(p/2)}$$

	E_{tot}	μ_{tot}	Cu1	Cu2	O2	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
M	0	-1.01	1.09	-0.81	0.07	Fi[illegible]



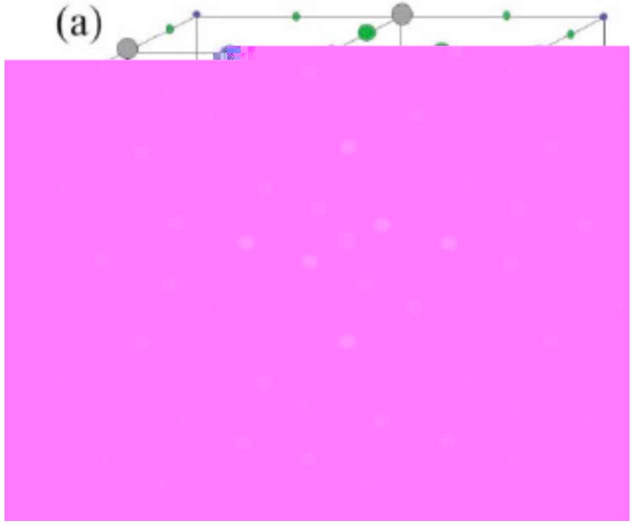


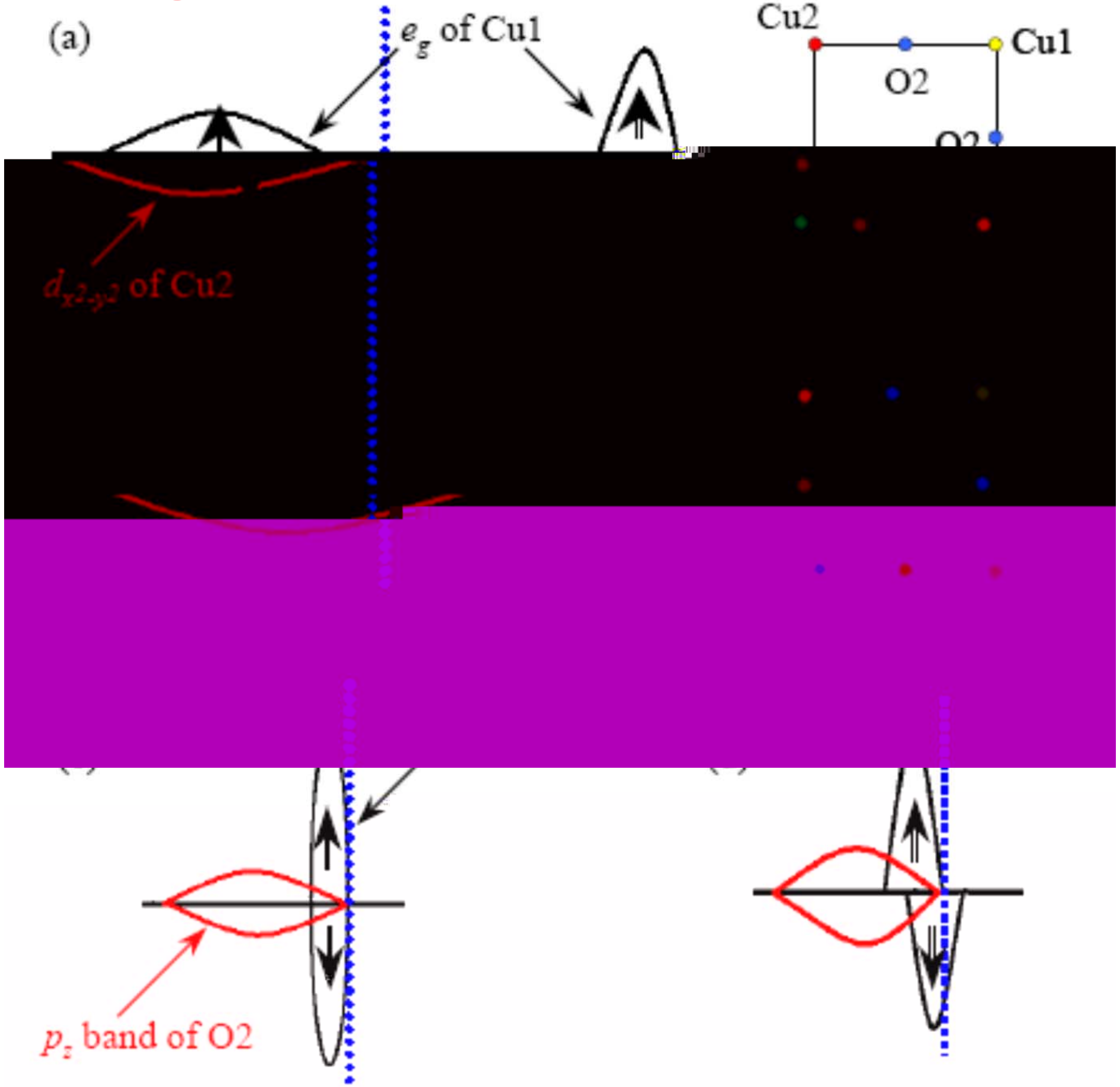


Energy mapping

X. Wan, M. Kohno, X. Hu, PRL 94, 087205 (2005)

Design Magnetic Properties





X. Wan, M. Kohno, X. Hu, PRL 95, 146602 (2005)

Energy Mapping Method

Heisenberg model $H \qquad \underset{ij}{} \qquad J_{ij}S_i \qquad S_j$

In Heisenberg model is fine!

In LDA is NOT OK

only Stoner-excitation is small

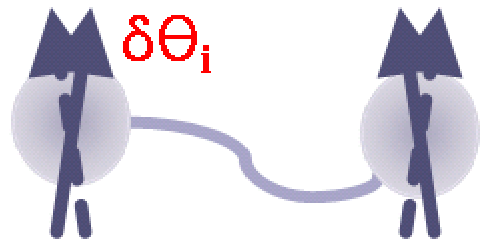
Calculate J

magnetic force theorem

$E \quad V \quad E \quad V$

linear response theory

$B \quad B$



the interatomic exchange constants can give by:

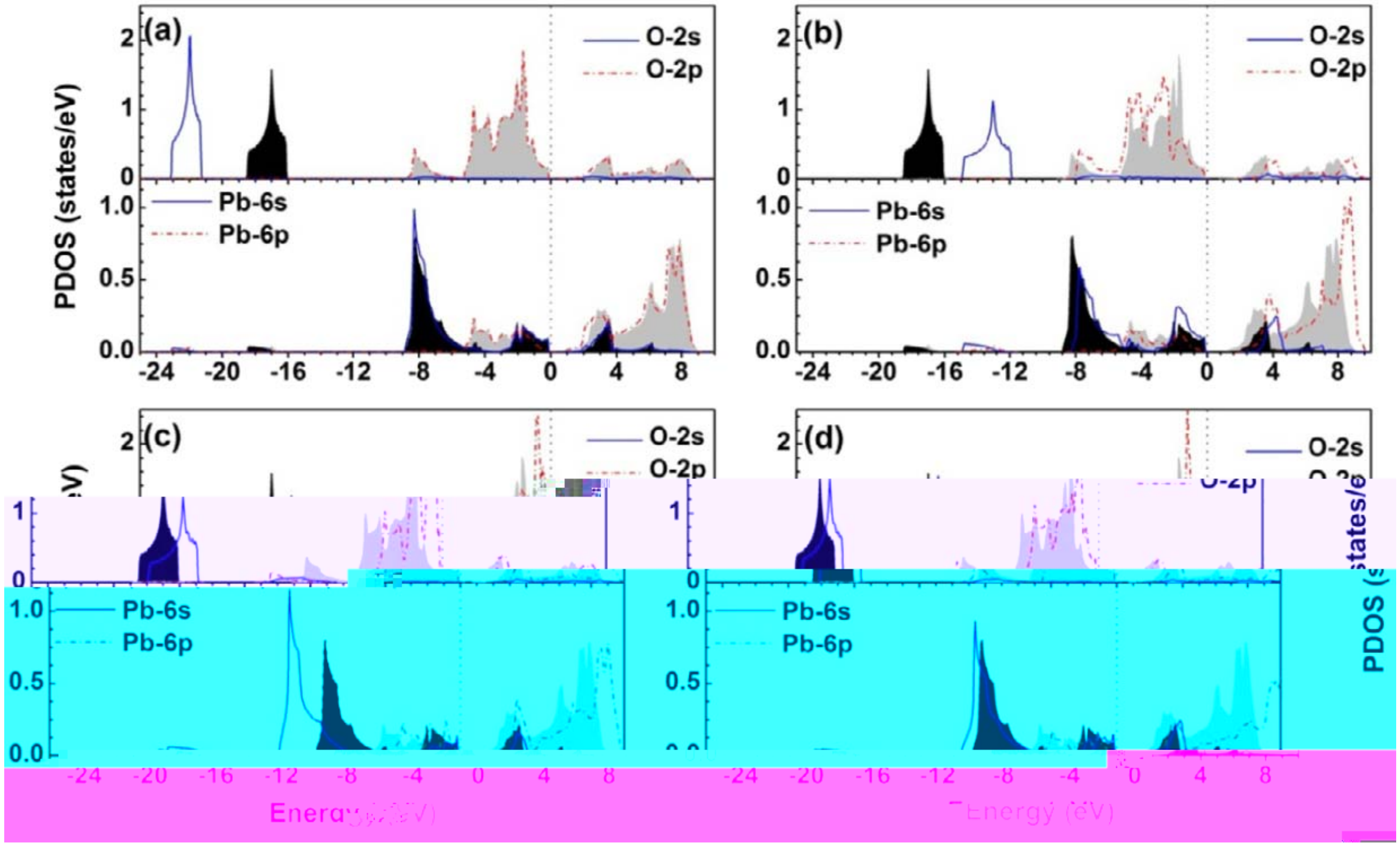
$$J \; R \; R \quad \mathbf{q} \quad \mathbf{k}jj \; \frac{f_{kj} \; f_{k\;qj}}{kj \quad k\;qj} \; kj| \quad \mathbf{B} \quad | \; k\;qj \quad k\;qj| \quad \mathbf{B} \quad | \; kj \; e^{i\mathbf{q}\;\mathbf{R}\;\mathbf{R}}$$

Wan, Yin, Savrasov, PRL 97, 266403 (2006)

Shift Orbital in band structure calculation

$\sigma[V_{ext}^{OSEP}] = E^{\ldots 0} - E^{0}_{KS} + [\ldots]$

PbO



Calculate Exchange Interaction J

J in Mott Insulator

J in Kondo System

J in HTC

J in 4f Ferromagnetic insulator

DM interaction

3*d* Mott Insulator Systems

Magnetic Properties

	LSDA	LDA+U	Hubbard I	Cluster ED	Exp.
MnO	423	240	180	172	122^a
FeO	–	344	297	211	198^a
CoO	–	407	356	300	291^a
NiO	965	603	542	519	523^a
$CaCuO_2$	–	765	698	602	537^b

Neel Temperature

	LSDA	LDA+U	Hubbard I	Cluster ED	Experiment
MnO	178.0	[illegible]	86.3	81.5	40.5^a
FeO	····	94.9	74.5	59.1	51.0^b
CoO	···	152.8	133.5	118.3	112.0^c

Spin Wave velocity (in meV Å) along $(\dot{1}00)$ direction

Why T_N decrease from NiO to MnO

From MnO to NiO, moment increase. So similar interatomic exchange parameters J, will make the T_N decrease instead of increase.

We find that

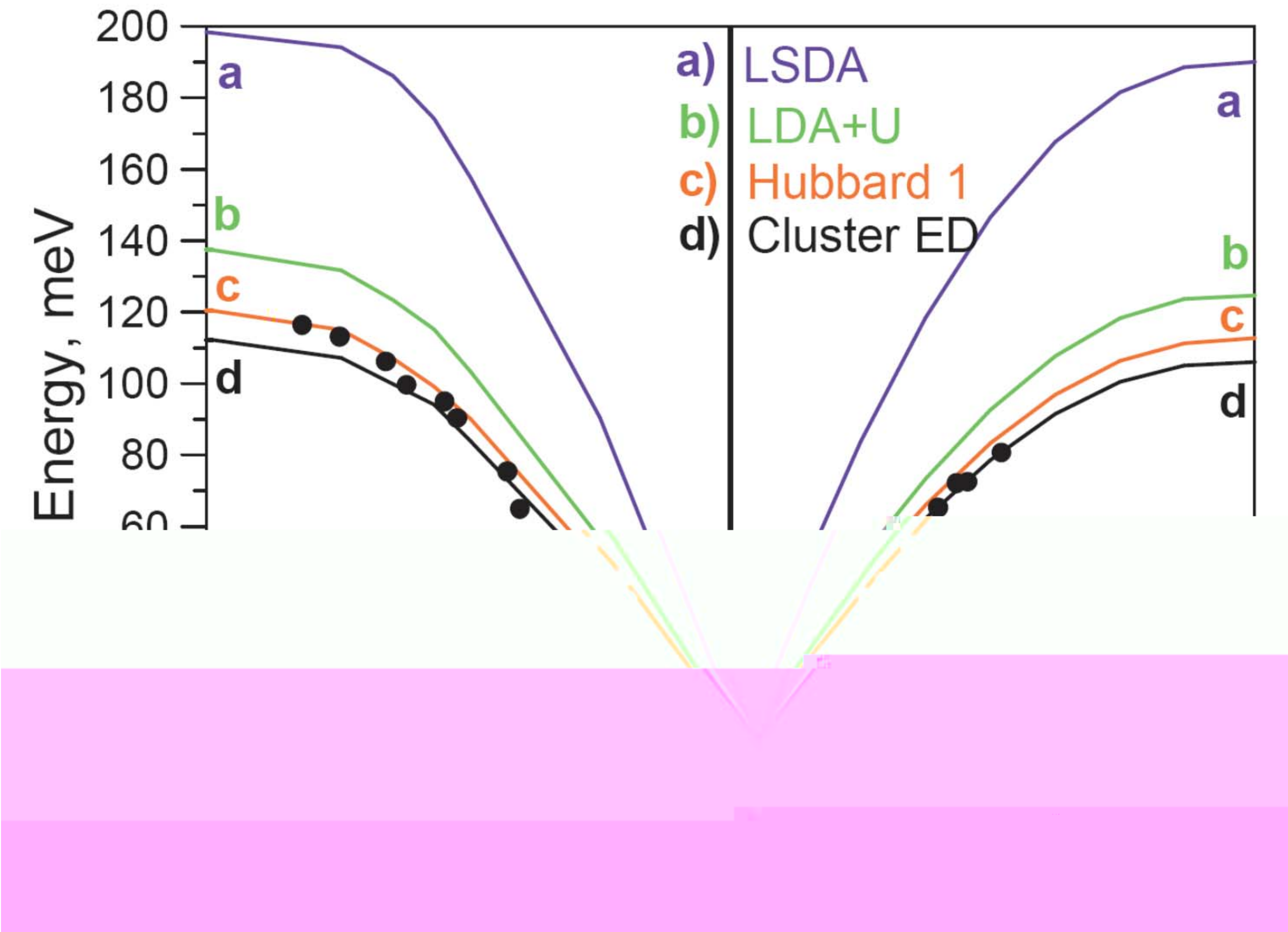
Exp.		LSDA	LDA+U	Hubbard-I	Cluster-ED
122[a]	MnO	423	240	180	172
198[a]	FeO	–	344	297	211
291[a]	CoO	–	407	356	300
523[a]	NiO	965	603	542	519
537[b]	$CaCuO_2$	–	765	698	602

(1) J will change significantly due to the change in lattice parameter. (bond become strong)

(2) Due to the quantum nature of moment, a factor of $S(S+1)/S^2$ will appear. This also have important effect on T_N. (Quantum effect)

(3) Occupation affect. (e_g 180^0, t_{2g} 90^0)

Spin-wave dispersion of NiO



Calculate Exchange Interaction J

J in Mott Insulator

J in Kondo System

J in HTC

J in 4f Ferromagnetic insulator

DM interaction

Magnetic behavior of metallic Plutonium

Naively one expects Pu *f*—shell filled with 5 electrons carries a total (spin+orbital) momentum

LDA, GGA and LDA+U   local magnetic moment

Experimentally   none of the six Pu crystallographic allotropes show local moment formation:

¾. RQGR HIIHFW VFUHHQ WKH PD

6 K LeP al. Nature

¾RQH FDQ WU\ WR LQFUHDVH 3X
RUGHU WR UHGXFH WKH HIIHF
WKXV WR GHFUHDVH WKH YDO
-.

¾'RSLQJ $P

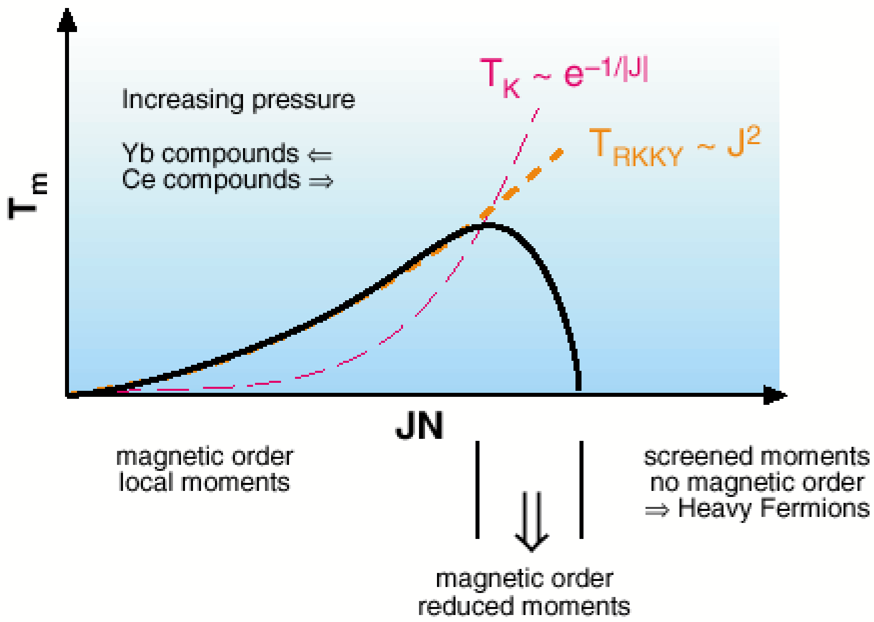
Calculating Kondo Exchange Energy

Minimal Hamiltonian for heavy fermion superconductors – Kondo lattice

$$H = -\sum_{ij\sigma} t_{ij} c_{i\sigma}^{+} c_{j\sigma} + J_K \sum_i S_i \left(\sum c_{i\sigma}^{+} \tau_{\sigma\sigma'} c_{i\sigma'}\right)$$

$CeCoIn_5$, $CeRhIn_5$, $CeIrIn_5$
Antiferromagnetism competes with superconductivity (T_c's~1-4K).
Specific heat values range from 251 to 751 mJ/mol*K^2.

$_5$ has superconducting T_c~18.5K



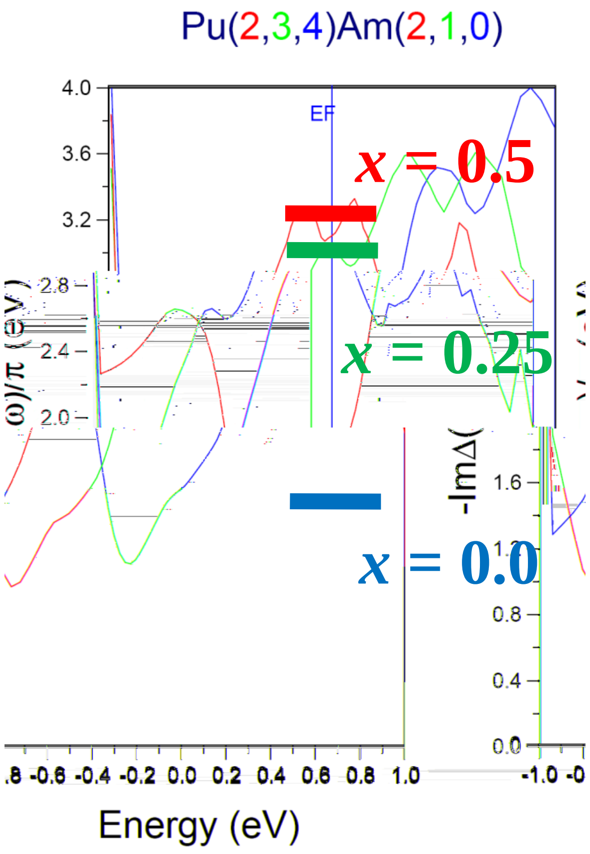
Estimates of T_K J_K can be obtained from LDA+DMFT calculations

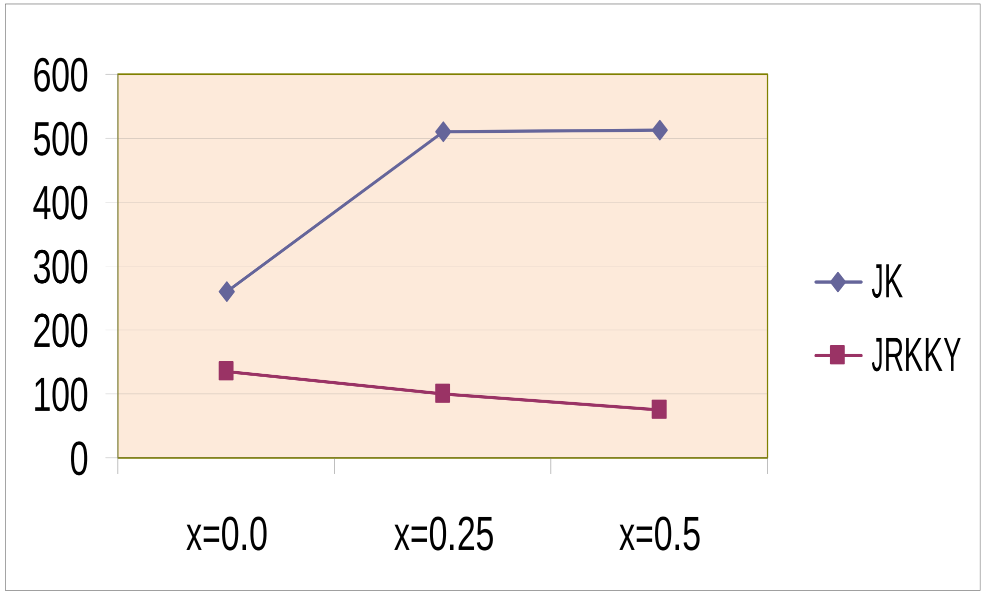
$$\Delta_f(\omega) = \sum_k \frac{|V_f(k)|^2}{\omega - t(k)} \qquad J_K N(0) \approx \operatorname{Im} \Delta_f(0)\left(-\frac{1}{\varepsilon_f} + \frac{1}{\varepsilon_f + U}\right)$$

Material design: Once Kondo exchange J_K and local moment interaction (J_{RKKY}) are computed one can apply pressure or doping.

Am ratio, *x*
($Pu_{1-x}Am_x$)

J_K vs J_{RKKY} in $Pu_{1-x}Am_x$





$J_K > J_{RKKY}$ for $0.0 \le x \le 0.5$

– No moment due to Kondo screening

– No quantum criticality and superconductivity

$Pu_{1-x}Am_x$

J_K increases with x which is attributed to the details in the behavior of the hybridization function near the Fermi level.

J_{RKKY} is found to decrease as interatomic distances get larger with doping.

Robust Kondo effect as the origin of non—magnetic behavior reported in recent experiments on this system.

Kondo effect should be robust against the increase in interatomic spacing of this alloy.

Calculate Exchange Interaction J

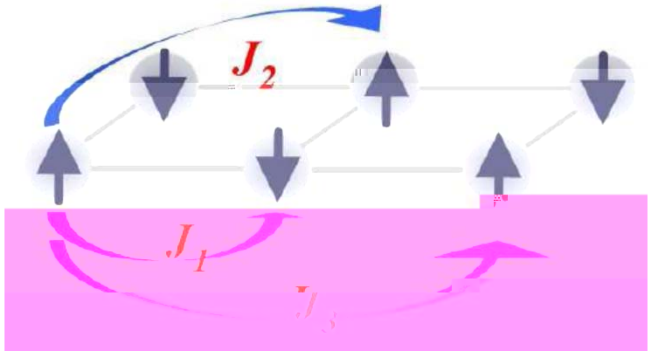
J in Mott Insulator

J in Kondo System

J in HTC

J in 4f Ferromagnetic insulator

DM interaction



LCO (La_2CuO_4

Our numerical result: J1=108.8, J2=-12.0 and J3=-0.2 meV.

Experimental results:

Two-magnon Raman scattering J1=116 meV (Lyons et al., PRB 37, 2353)

Early neutron scattering J1=130 meV.

Other theoretical results:

J1=105 meV (Martin and Illas, PRL 1997)

J1=140 meV (Moreira et al., PRL 2006; Munoz et al., PRL 2000)

Spin Wave

S=1/2, 2D large quantum fluctuation

Renormalization is necessary for the spin-wave excitation

Linear spin-wave theory and consider the quantum renormalization Z_c=1.18.

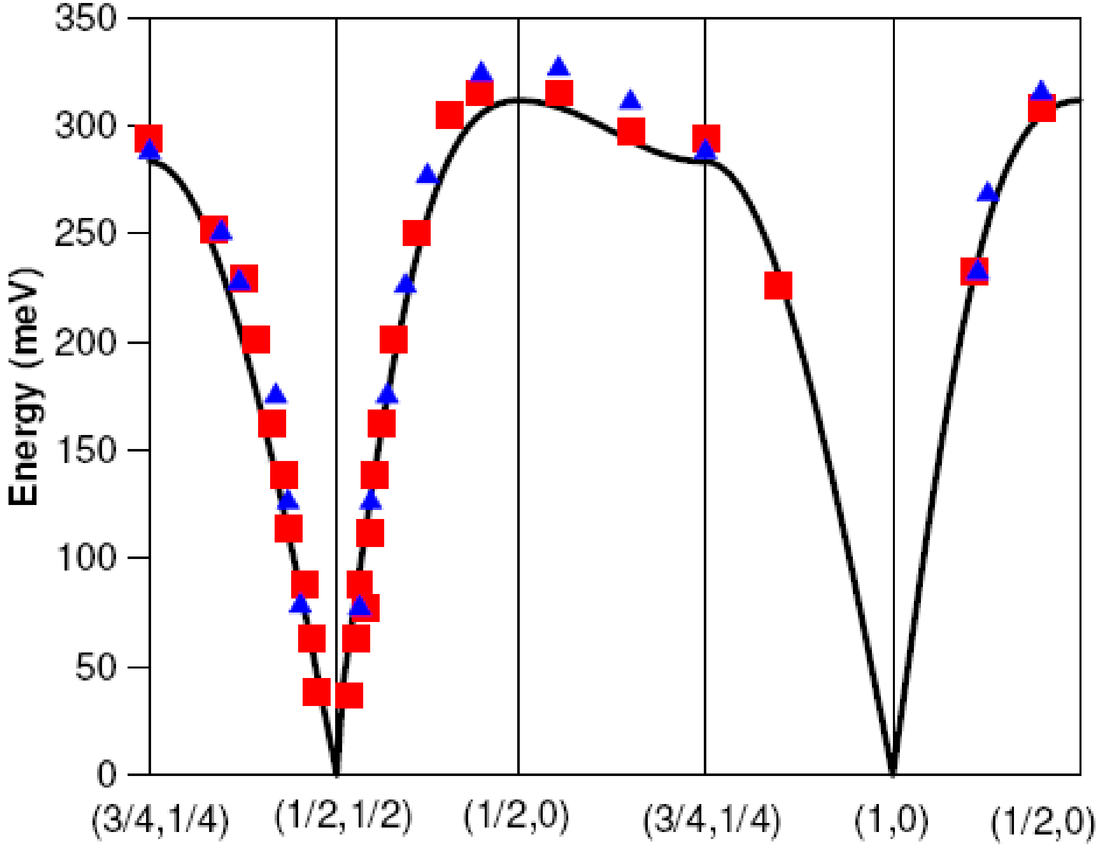
(Igarashi, PRB (1992))

$$E_q = 2Z_c\sqrt{A_q^2 - B_q^2},$$

$$A_q = J_1 - J_2[1-\cos(2\pi q_x)\cos(2\pi q_y)] - J_3\left(1 - \tfrac{1}{2}[\cos(4\pi q_x) + \cos(4\pi q_y)]\right)$$

$$B_q = \tfrac{1}{2}J_1[\cos(2\pi q_x) + \cos(2\pi q_y)]$$

Spin Wave for La_2CuO_4

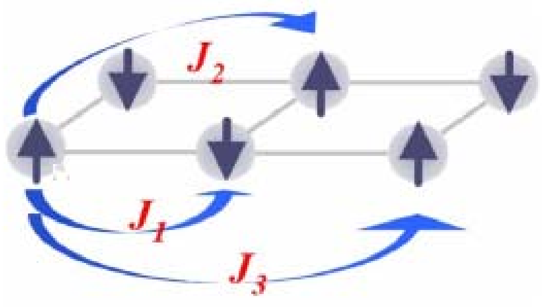


The discrepancy around the zone boundary may be due to the four-particle cyclic exchange interaction.

(Toader et al., PRL 2005; Moreira et al., PRL 2006)

J of Single-layer system

	T_c	J_1	J_2	J_3
$CaCuO_2$	–	110.0	-10.1	3.8
$Tl_2Ba_2CuO_6$	97	109.1	-10.9	3.98
$HgBa_2CuO_4$	94	108.91	-11.1	3.3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]



Experiment shows the J1 in $Sr_2CuO_2Cl_2$ is about 10 meV smaller than that of La_2CuO_4.

We reproduce this experimental trend.

J1, J2 is almost not material-dependent. J3 is too weak to explain the T_c-difference.

	T_c	J_1	J_2	J_3
$HgBa_2CaCu_2O_6$	128	110.4	-11.9	2.9
$Tl_2Ba_2Cu_2O_8$	125	108.7	-10.7	2.5
$YBa_2Cu_3O_6$	90	93.0	-4.7	2.4

We reproduce the experimental trend for La_2CuO_4, $Sr_2CuO_2Cl_2$ and $YBa_2Cu_3O_6$.

Undoped HTC have similar J1, although their T_c vary from 28 K to 128 K.

J2 is also similar for different compounds, show FM behavior do not induce the spin fluctuation.

J3 induce a weak spin-fluctuation but may not response for the difference of Tc.

Effect of Apical Oxygen

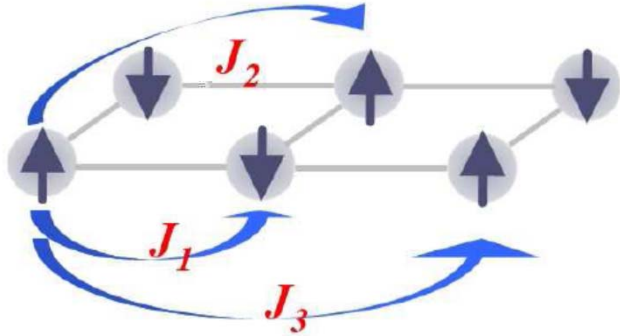
Apical oxygen has significantly effect on Tc.

(Pavarini et al, PRL (2001))

TABLE II. The calculated exchange interaction in La_2CuO_4, with different d_A, where d_A is the distance between apical oxygen and Cu atom. d_A is in Å and J is in meV.

d_A	J_1	J_2	J_3
2.5	111.1	−12.4	−0.4
2.6	112.9	−13.1	0.1
2.7	114.2	−13.8	1.2
2.8	116.0	−14.6	2.1

	N_{layers}	T_c	J_1	J_2	J_3
$CaCuO_2$	1	–	110.0	-10.1	3.8
$Tl_2Ba_2CuO_6$	1	97	109.1	-10.9	4.0
$HgBa_2CuO_4$	1	94	108.9	-11.1	3.3
La_2CuO_4	1	42	108.8	-12.0	0.[illegible]
$Sr_2CuO_2Cl_2$	1	28	99.2	-8.2	1.6
$HgBa_2CaCu_2O_6$	2	128	110.4	-11.9	2.9
$Tl_2Ba_2Cu_2O_8$	2	125	108.7	-10.7	2.5
$YBa_2Cu_3O_6$	2	90	93.0	-4.7	2.4
$HgBa_2Ca_2Cu_3O_8$	3	135	109.9	-10.1	2.8



undoped HTC compounds have similar J1

J2 is FM, one order magnitude smaller than J1

J3 is AFM and induce spin fluctuation

Calculate Exchange Interaction J

J in Mott Insulator

J in Kondo System

J in HTC

J in 4*f* Ferromagnetic insulator

DM interaction

Continue attention more than 50 years

EuX– **the only know example of FM Heisenberg model in nature**

Doping resulting in 100% conduction spin polarization even stronger colossal magnetoresistance than the manganites (*Steeneken et al., PRL 2002)*

Can been integrated with silicon and GaN

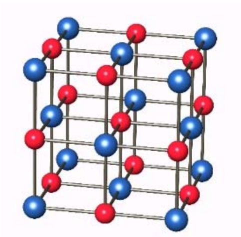
(*Schmehl et al., Nature Materials 2007*)

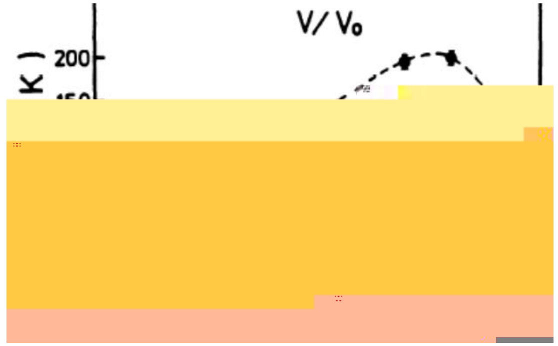
Very recently strain-induced ferroelectricity had been predicted (*Spaldin et al., PRL 2010*)

Debate about the exchange mechanism

- Despite tremendous amount of efforts have been devoted to these FM semiconductor, there still is several controversy about the magnetic properties

1) The effect of p-electron in anion





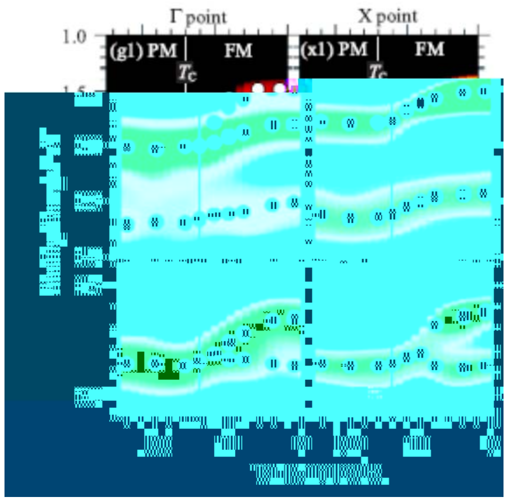
2) Pressure and epitaxial strain can vary the T_c of EuX significantly.

3) T_C can be enhanced by electronic doping. But the exact reason is still unknown

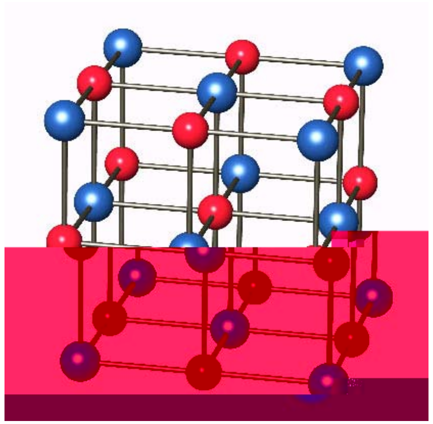
Debate about effect of p-electron in anion

4*f* is localized 4*f*-*p* hybridization is small the superexchange via the p orbital of anion is negligible (*Kasuya 1970*)

Recently, Wannier function analysis considerable *4f-p* hybridization, suggest *4f-p-4f* superexchange (*Kunes, Ku, Pickett, 2005*)



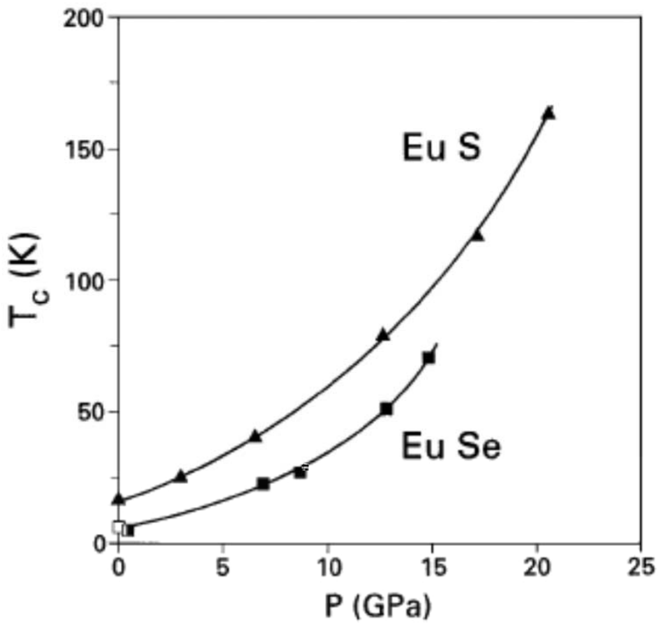
Miyazaki et al., PRL 2009



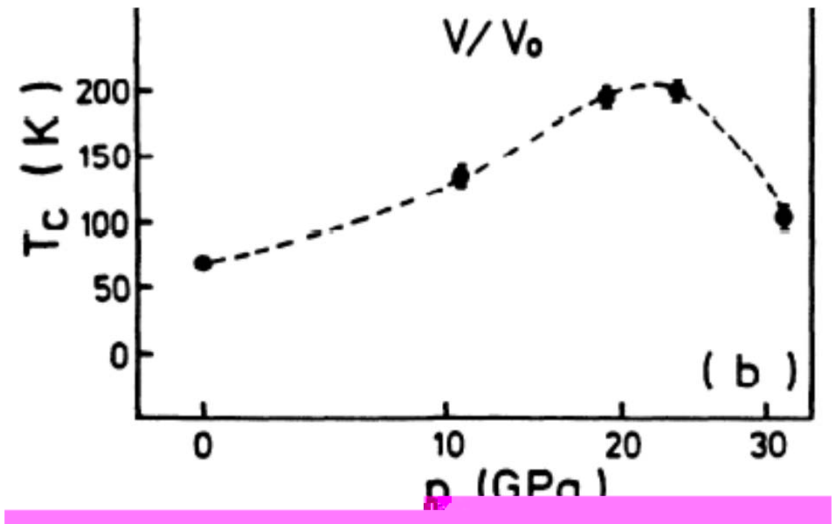
x-ray absorption spectroscopy indicates that the anion p states plays only minor role

N.M. Souza-Neto, PRL 2009

Debate about pressure affect



Goncharenko, PRL 1998



Abd-Elmeguid, PRB 1990

electronic collapse?

High pressure $4f^7$ $4f^6$, f^6—J=0 ?

Results

Reproduce the band structure and the magnetic moment.

Reproduce the conduction band exchange splitting (about 0.6 eV).

Murnaghan equation of state

Enthalpy   pressure-induced phase transition

TABLE I: Theoretical and experimental B_0, B' and P_c. The experimental value is in the parentheses.

	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Exchange interaction

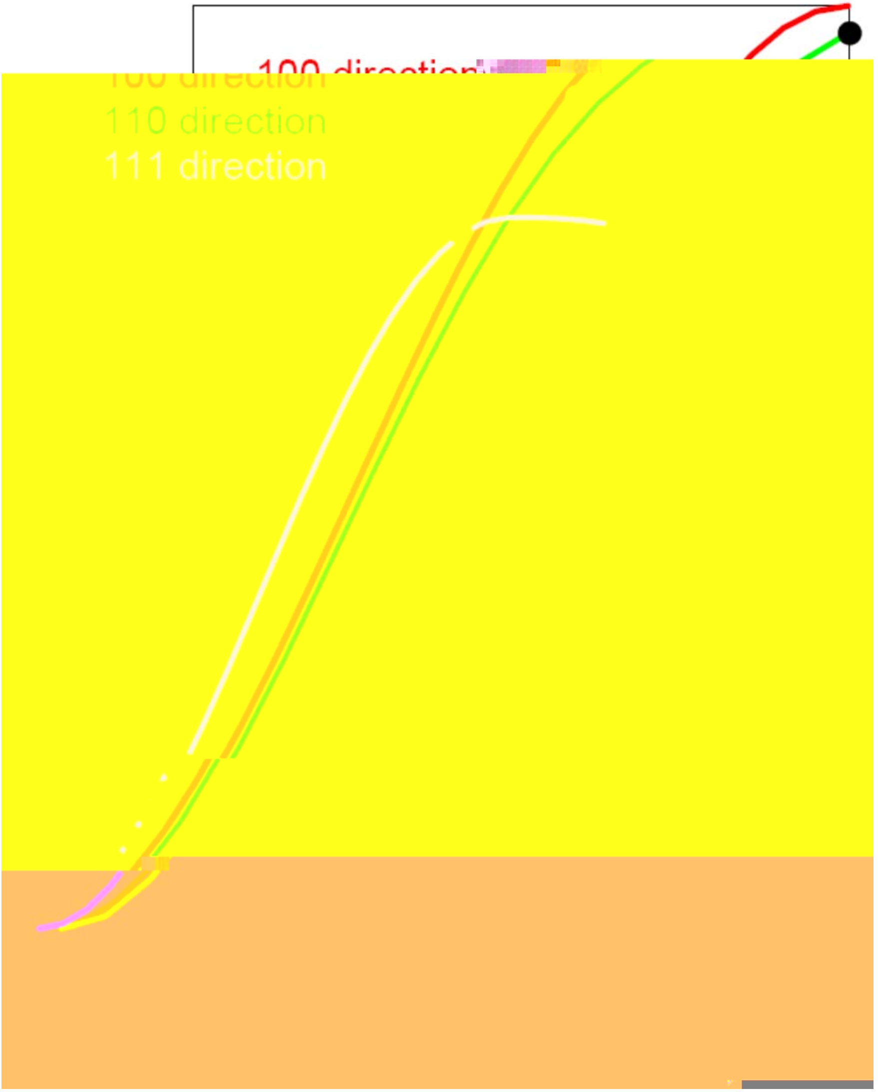
J is short range. Mean-field approximation T_c

TABLE II: Exchange interactions and magnetic transition temperature for EuX (X=O, S, Se and Te). J_1 and J_2 are the nearest neighbor and second nearest neighbor exchange coupling. The negative sign denotes the Neel temperature The unit is K.

		EuO	EuS	EuSe	EuTe
Our results	J1	0.60	0.12	0.10	-0.03
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]		
	[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Spin wave dispersion of EuO

Circle is experimental (polycrystalline)



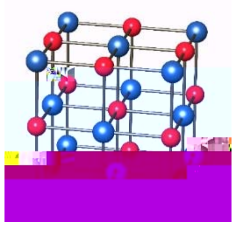
Linear spin-wave theory

Magnetic Mechanism Effect of p Band

LSDA+Hub1 vs LDA+Hub1

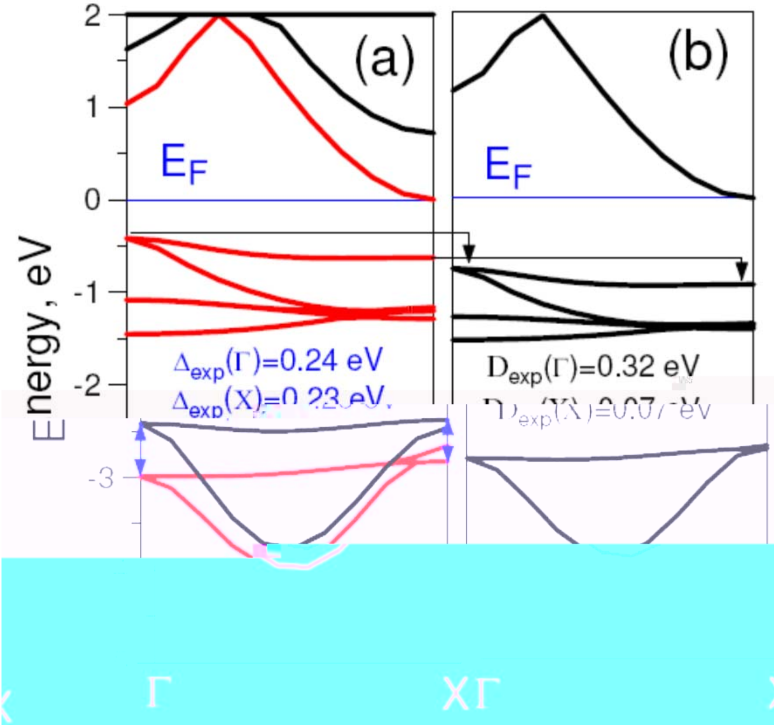
Main different in LDA+H and LSDA+H is the spin-splitting in the conduction band (ie. 5*d* and 6*s* band of Eu).

LDA+H can reproduce the spin-splitting of p-band of anion **overlap between Eu-4f and p-anion is not omitable**.



Numerical J from LDA+Hub1 is very small ***4f-p-4f*** **super-exchange can be ignored**.

Temperature dependent band EuO



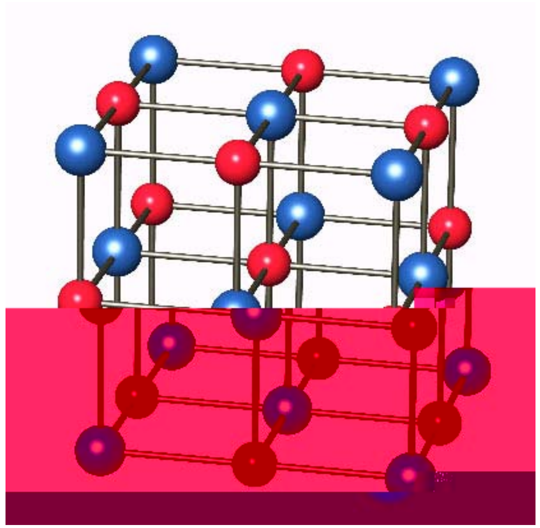
Experimental spin splitting of O-2p is about 0.25 eV at 5K

Temperature induced 4f shift at Gamma-point and X-point is different.

We reproduce the experimental Momentum-Dependent band shift

1) **Spin-splitting reduced with increasing temperature**
2) **4f band has a different temperature-induced band-shift**

We shift the orbital level to see the effect

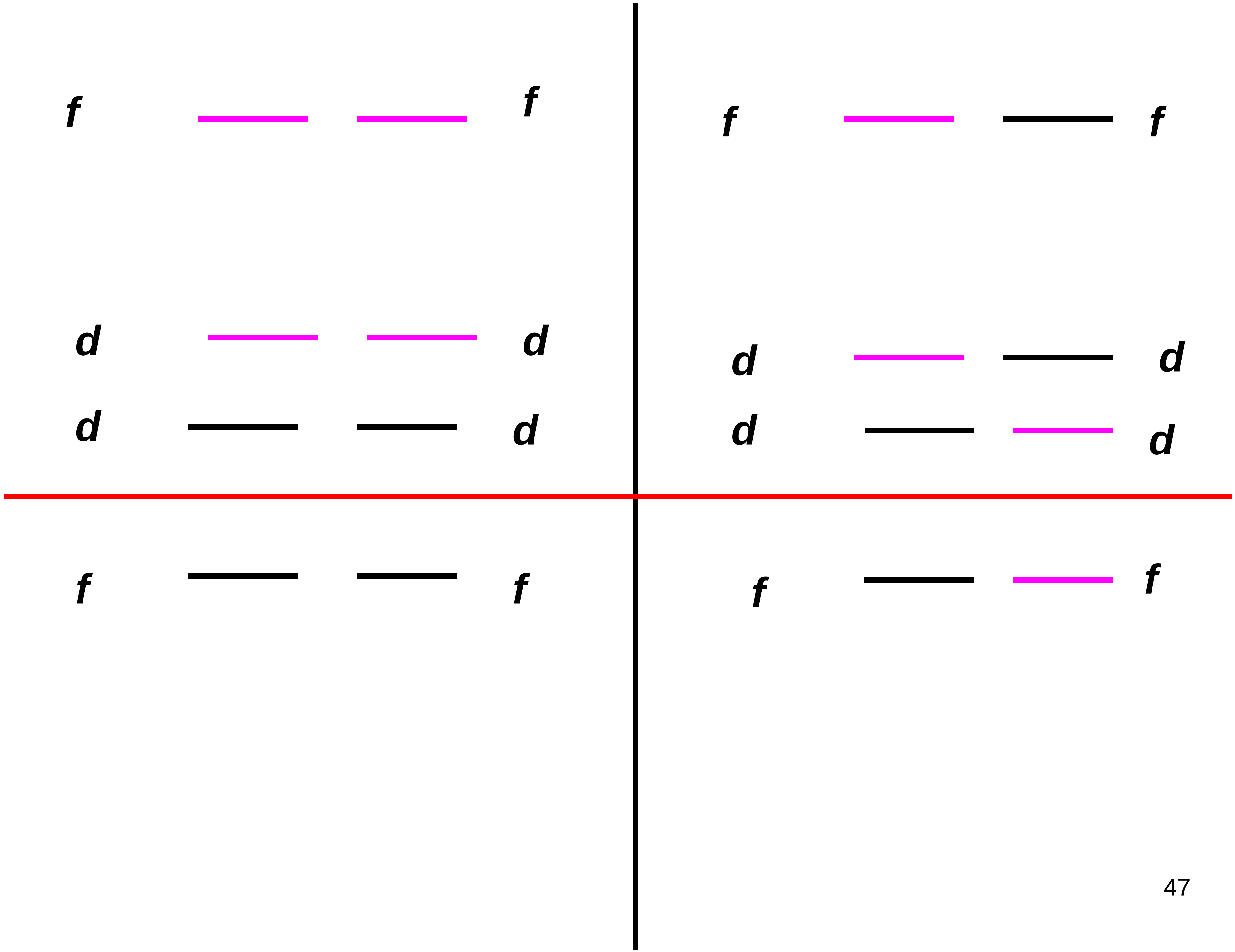


J is very sensitive to the 5d-shift

J is also dependent on the 6s-shift

J is almost not depend on p-band shift, **NO 4*f*-5*d*-2*p***

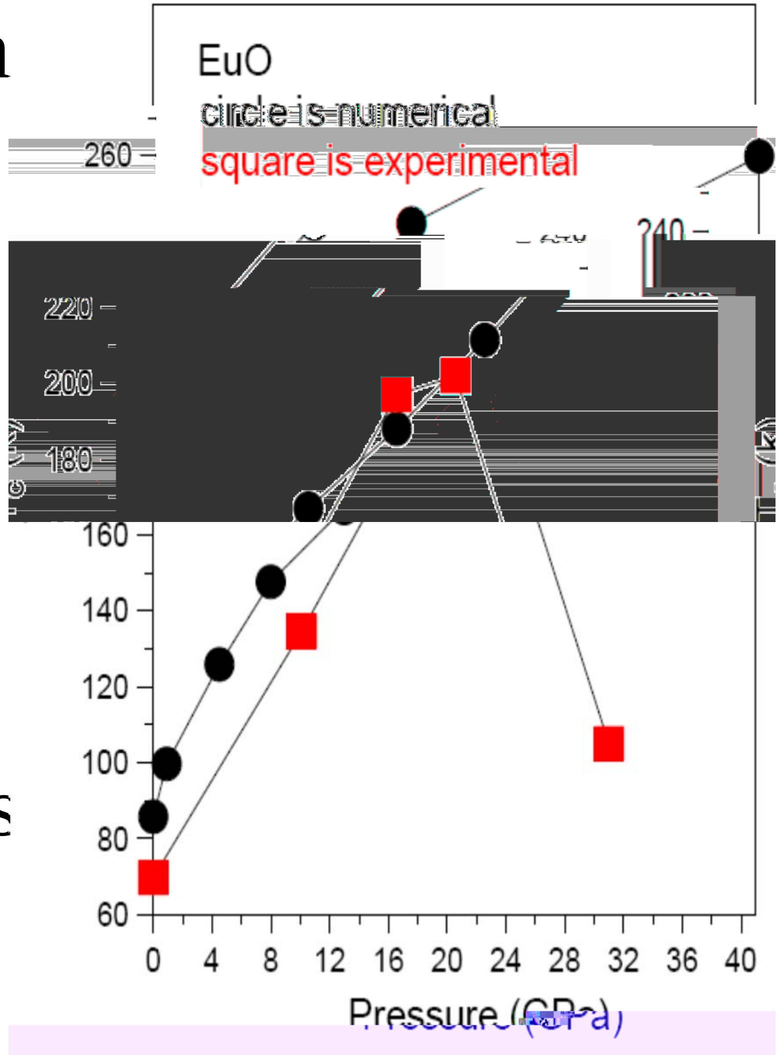
J is mainly due to 4f-5d and 4f-6s indirect exchange. p-band of anion is not participate in, despite the considerable 4f-2p hybridization.


f
f
f
f
d
d
d
d
d
d
d
d
f
f
f
f

The affect of pressure

Enhance the hopping between *5d-4f*, enlarge the crystal splitting of 5*d* enlarge the exchange interaction J

Pressure band-gap close, but the J is still short, so RKKY is not response for this decreasing



The affect of pressure

The 4f occupation from LDA+H is not change too much, therefore $f^7 \quad f^6$ transition is not like.

Pressure will enhance J_k this is the reason.

Competition between J and J_k

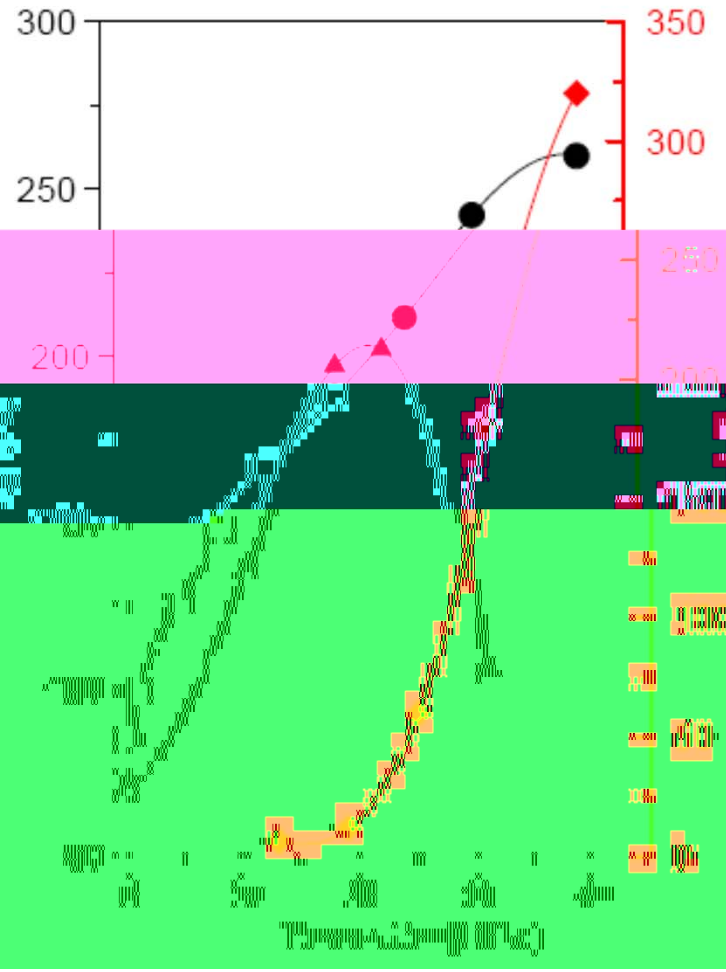


FIG. 3: Pressure dependence of magnetic transition temperature of EuO experimental (triangle)[30], theoretical(circles) as well as Pressure dependence of Kondo coupling J_K.

Calculate Exchange Interaction J

J in Mott Insulator

J in Kondo System

J in HTC

J in 4f Ferromagnetic insulator

DM interaction

PHYSICAL REVIEW B VOLUME 39, NUMBER 7 1 MARCH 1989

Metamagnetism in La_2CuO_4

S-W. Cheong, J. D. Thompson, and Z. Fisk
Los Alamos National Laboratory, Los Alamos, New Mexico 87545
(Received 19 September 1988)

$$\theta = \frac{D}{2J} = \frac{M_s(0)}{g\mu_B S} \qquad \theta = 3.9 \times 10^{-3}$$

θ

$$\theta = \frac{\left|\sum_j \vec{D}_{1j}\right|}{2\sum_j J_{1j}} = 1.1\times10^{-3}$$

$$J^{\alpha\beta}_{\tau R \tau' R'} = \sum_{q} \sum_{kjj'} \frac{f_{kj} - f_{k+qj'}}{\epsilon_{kj} - \epsilon_{k+qj'}} \langle \psi_{kj} | [\sigma \times \mathbf{B}_{\tau}]_{\alpha} | \psi_{k+qj'} \rangle$$

$$\times \langle \psi_{k+qj'} | [\sigma \times \mathbf{B}_{\tau'}]_{\beta} | \psi_{kj} \rangle e^{iq\cdot(R-R')},$$

SO small   Dzyaloshinsky-Moriya

SO large   B. Coqblin and J.R. Schrieffer, Phys. Rev. 185, 847 (1969).

PHYSICAL REVIEW B, VOLUME 63, 195104

2001

Continuous metal-insulator transition in the pyrochlore $Cd_2Os_2O_7$

D. Mandrus,[1,2,*] J. R. Thompson,[2,1] R. Gaal,[3] L. Forro,[3] J. C. Bryan,[4] B. C. Chakoumakos,[1] L. M. Woods,[2,1] B. C. Sales,[1] R. S. Fishman,[1] and V. Keppens[1,†]

PHYSICAL REVIEW B, VOLUME 65, 155109

2002

Electronic structure of the pyrochlore metals $Cd_2Os_2O_7$ and $Cd_2Re_2O_7$

D. J. Singh
Code 6391, Naval Research Laboratory, Washington, DC 20375

P. Blaha and K. Schwarz
Institut für Physik und Theoretische Chemie, TU Wien, A-1060 Wien, Austria

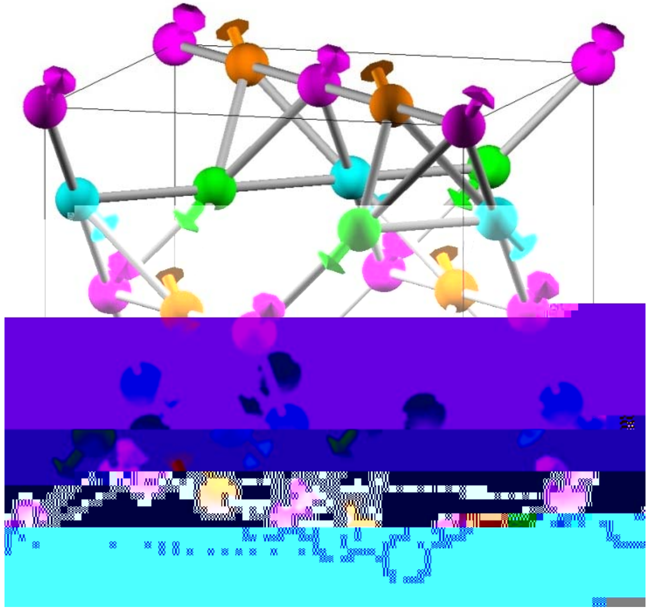
J. O. Sofo

Magnetic ground state for 5*d* Pyrochlore Iridates

$A_2Ir_2O_7$ (A=Y,   )

All-in/all-out nonlinear

tetrahedron



moment will rotation to 111 direction

It is the only stable configuration in calcul

J(q) is max at q=0

no Fermi surface nesting

•烧绿石结构Ir氧化物实验进展

RESEARCH | REPORTS

$Nd_2Ir_2O_7$,

MAGNETISM

Mobile metallic domain walls in an all-in-all-out magnetic insulator

[redacted]

538 30 OCTOBER 2015 • VOL 350 ISSUE 6260

sciencemag.org SCIENCE

All-in/all-out ($Cd_2Os_2O_7$)

PRL 108, 247204 (2012) PHYSICAL REVIEW LETTERS week ending 15 JUNE 2012

Noncollinear Magnetism and Spin-Orbit Coupling in 5*d* Py...

We investigate the electronic and magnetic properties of the pyrochlore oxide $Cd_2Os_2O_7$ using the density functional theory plus on-site repulsion (U) method, and depict the ground state phase diag... We conclude that the all-in–all-out noncollinear magnetic order is stable in a wide r...

PRL 108, 247205 (2012) PHYSICAL REVIEW LETTERS week ending 15 JUNE 2012

Tetrahedral Magnetic Order and the Metal-Insulator Transition in the Pyrochlore Lattice of $Cd_2Os_2O_7$

accompanied with any spatial symmetry breaking. We propose a noncollinear all-in–all-out spin arrangement on the tetrahedral network made of Os atoms. Based on this we suggest that the transition is not caused by the Slater mechanism as believed earlier but by an alternative mechanism related to the

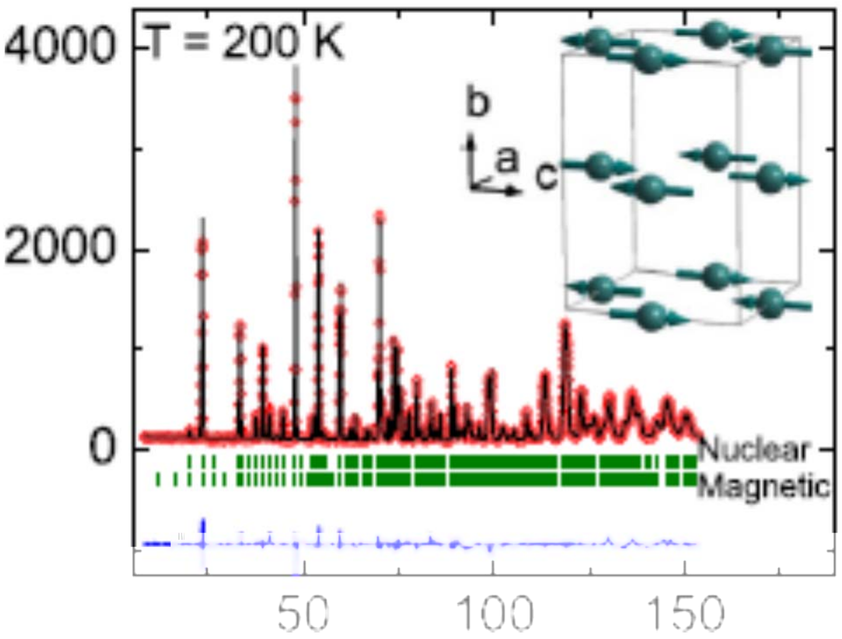
Slater insulator? $NaOsO_3$

1) Despite its big value the SOC has only weak effect on the band structure and magnetic moment.
2) The electronic correlations alone cannot open the band gap, and the low-temperature phase of $NaOsO_3$ is not a Mott-type insulator.
3) The magnetic configuration has an important effect on the conductivity, and the ground state is a G-type AFM insulator.
4) magnetic ordering   insulating behavior of $NaOsO_3$.
5)

Du et al., PRB 85, 174424 (2012)

PRL 108, 257209 (2012) PHYSICAL REVIEW LETTERS week ending 22 JUNE 2012

Magnetically Driven Metal-Insulator Transition in $NaOsO_3$



-
- SOC

Thank you for your attention