Magnetic properties of perovskites with d-orbital degeneracies

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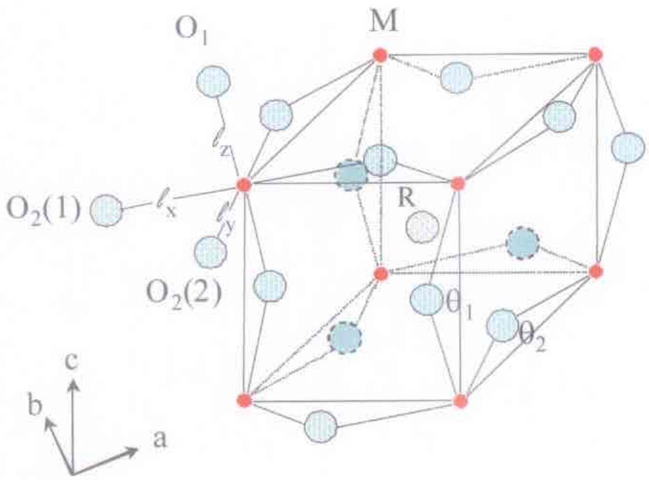
1. Universal octahedral-site distortion in orthorhombic RMO_3 perovskites.
2. $RTiO_3$
3. RVO_3
4. $RMnO_3$
5. $A^{2+}Ru^{4+}O_3$

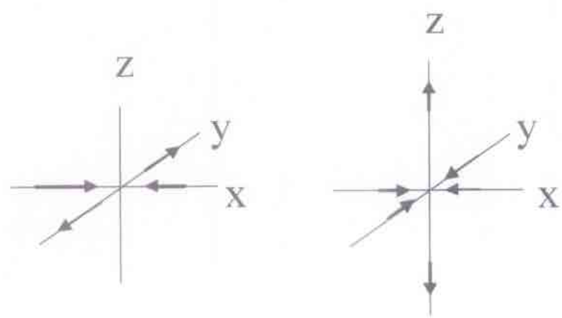
The crystal structure of orthorhombic RMO_3 perovskites



The basic perovskite unit cell with the orthorhombic distortion with Pbnm space group.

Coop. rotation about [110], [001]
→ $a \leq c/\sqrt{2} < b$

Problem: Need $MO_{6/2}$ site distortion to accommodate fixed rotation axis.
O'Keeffe & Hyde (1977)



Q_2 Q_3

$Q_2 = \ell_x - \ell_y$, $Q_3 = (2\ell_z - \ell_x - \ell_y)/\sqrt{3}$,
$\rho_o = (Q_2^2 + Q_3^2)^{1/2}$ and $\phi = \tan^{-1}(Q_3/Q_2)$
IR= R^{3+} -ion radius (9-fold coordination)

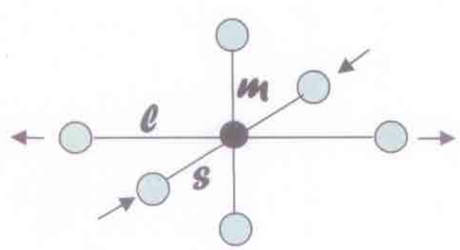
Calculated vs Experimental ω and α

SPuDS program is used for calculating ω vs IR
Lufaso & Woodward, Acta Cryst. B ***57****, 725 (2001)*

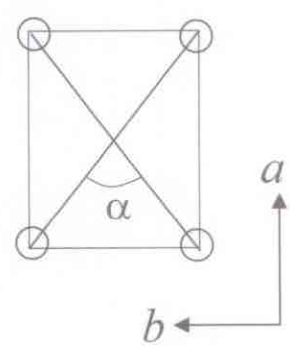
Assumes:
(1) Rigid $MO_{6/2}$ rotations
(2) (M-O) from bond valance sum rule.

Experiments:
$RFeO_3$ (Pbnm for all R), *Marezio et al, Acta Cryst. B 26, 2008 (1970)*
Mat. Res. Bull. 6, 23 (1971).

Apparent octahedral-site distortions:



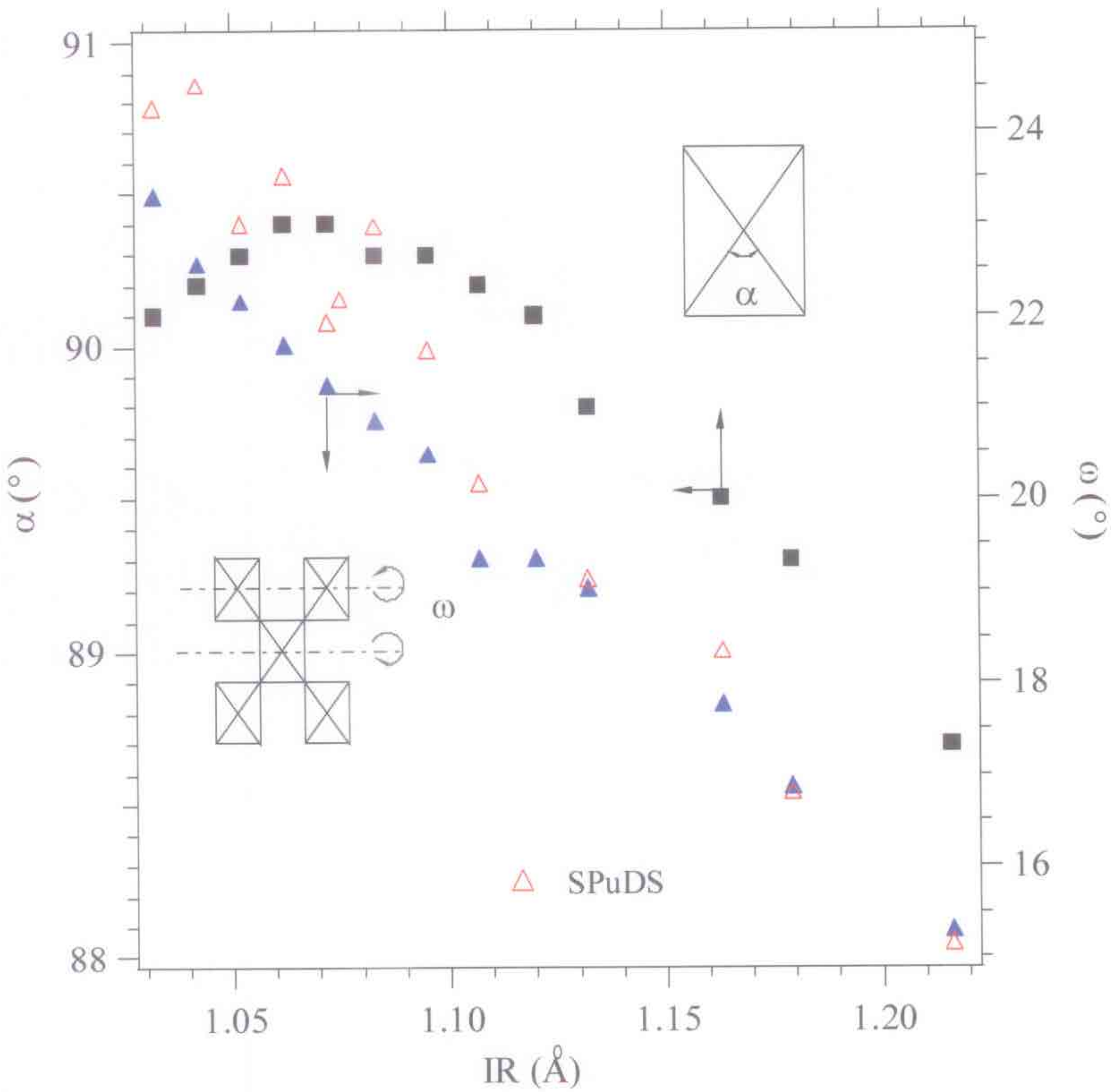
Max. distortion @ IR ≈ 1.11Å

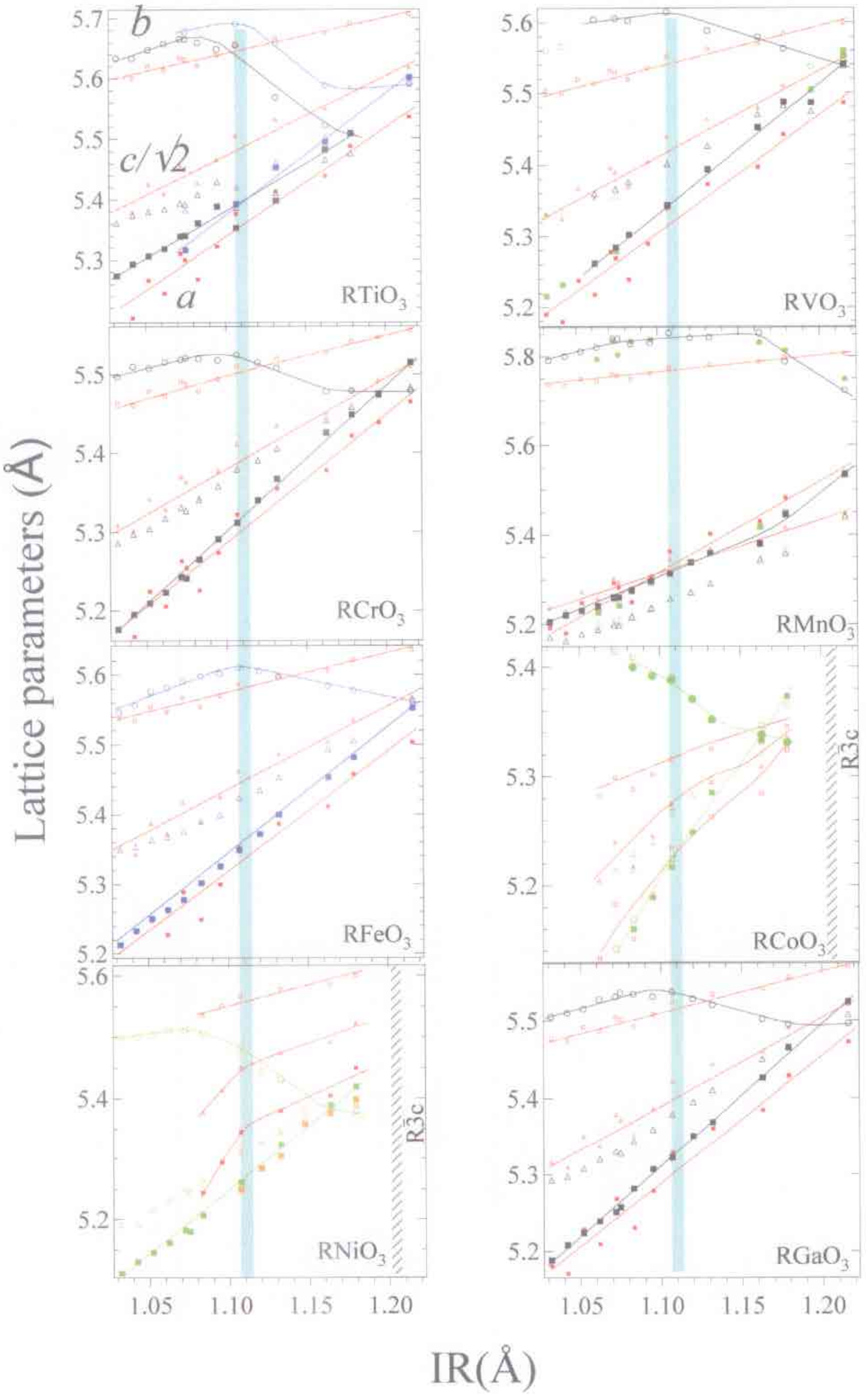


α < 90° for IR > 1.11 Å

Note: With increasing IR,
Ortho (Pbnm) ⟶ Rhomb ($R\bar{3}c$) ⟶ Cubic (Pm3m)
The rhombohedral structure accommodates larger IR.

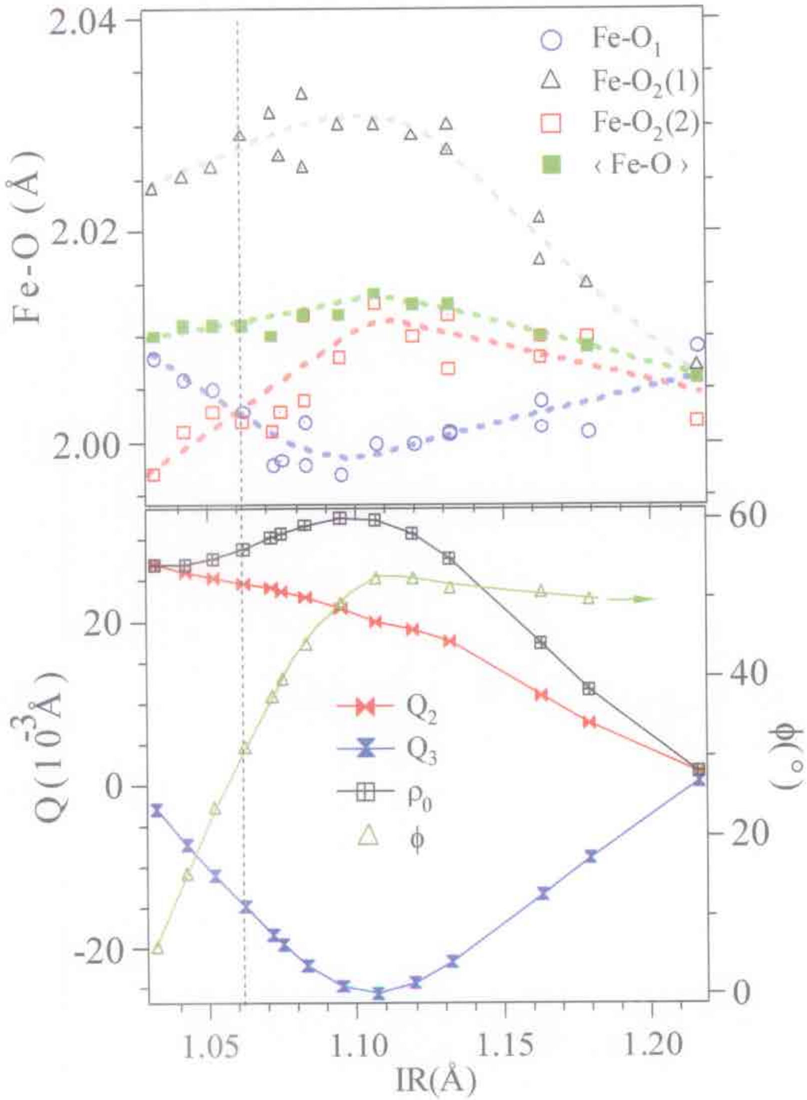
Angles ω and α *vs*. IR for $RFeO_3$ (Data from Marezio et al)



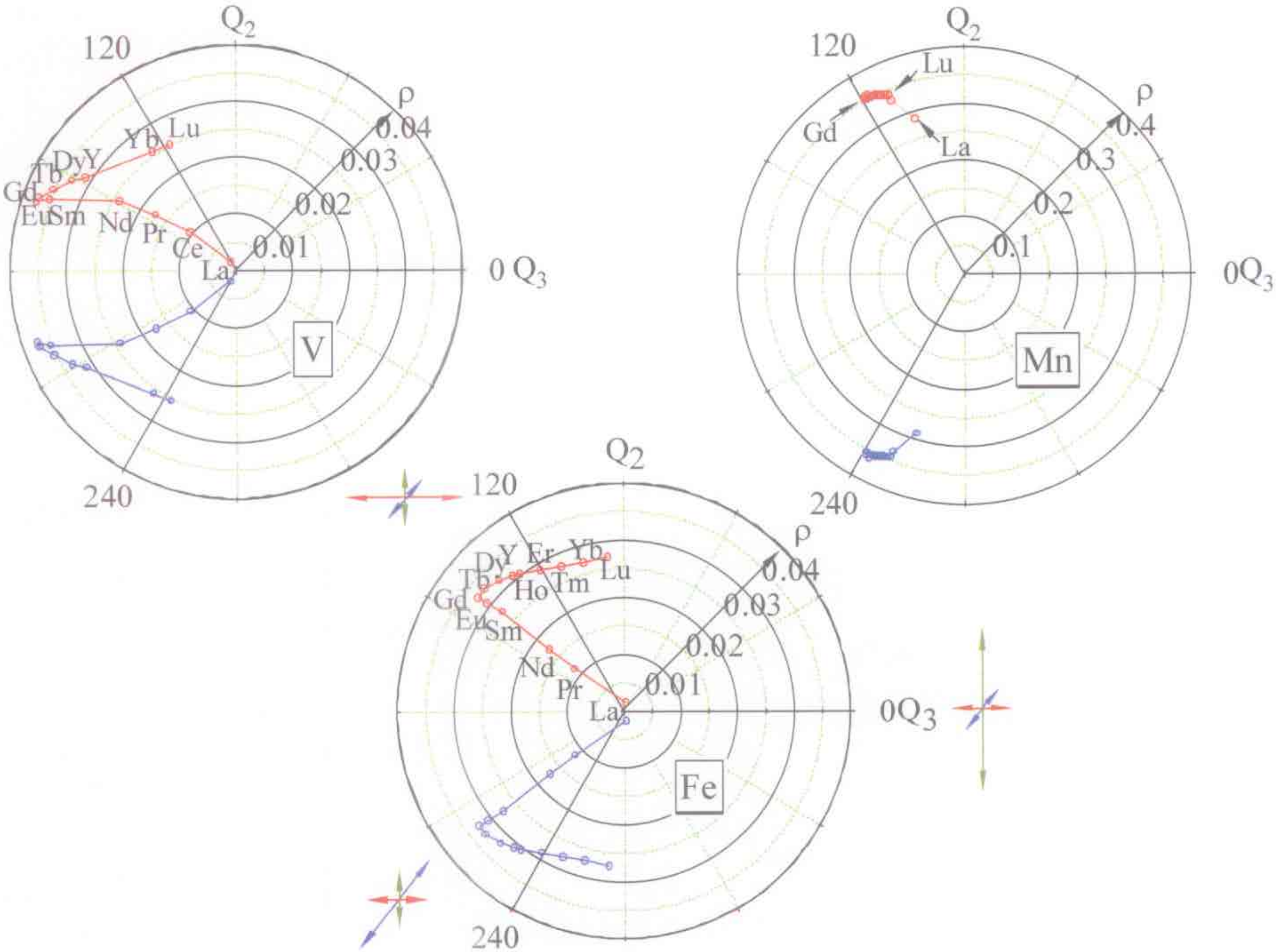


Lattice parameters with red symbols are calculated by SPuDS

Fe-O bond lengths in $RFeO_3$



Note: $\phi = \tan^{-1}(Q_3/Q_2) = 30°$
for the octahedral-site distortion c/a >1

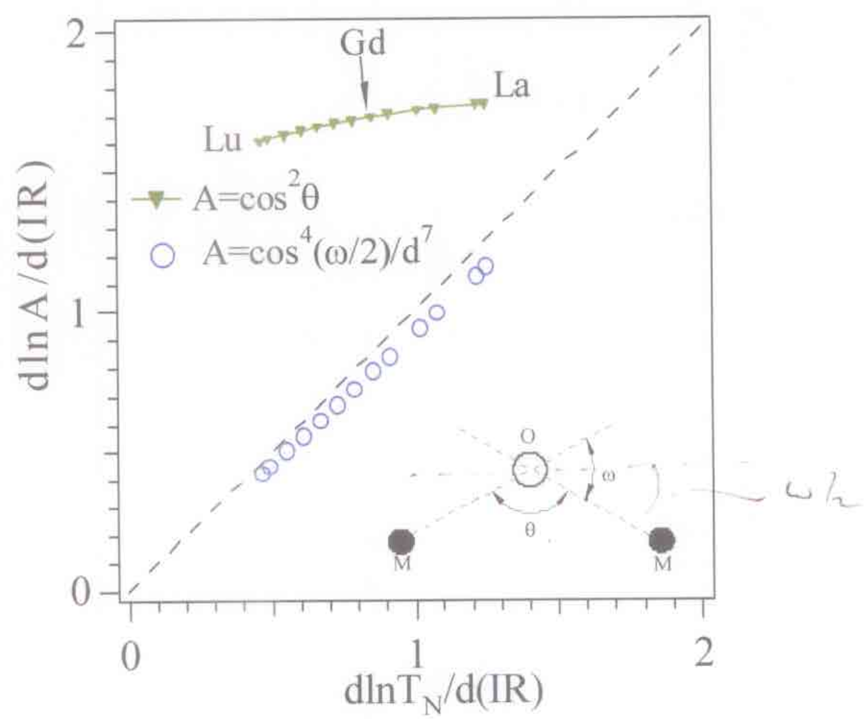


$$Q_2 = \ell_x - \ell_y, \quad Q_3 = (2\ell_z - \ell_x - \ell_y)/\sqrt{3},$$

$$\rho_o = (Q_2^2 + Q_3^2)^{1/2} \text{ and } \phi = \tan^{-1}(Q_3/Q_2)$$

T_N observed *vs* the calculated value from superexchange interaction for $RFeO_3$

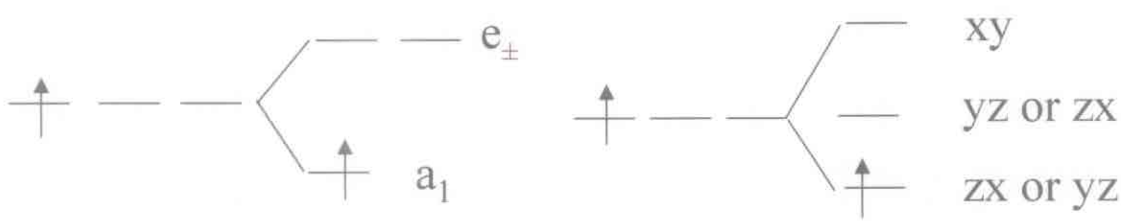
Superexchange: $T_N \sim b^2/U \sim A(\theta,d)$;
θ: Fe-O-Fe bond angle; d: Fe-O bond length.
For fixed U and $A \sim b^2$
→ $d\ln A/d(IR)$ *vs* $d\ln T_N/d(IR)$ is straight line at 45° through origin.
A(IR) from the structural data, T_N(IR) from Mössbauer data.



The $RTiO_3$ Perovskites

Ti^{3+}:$t^1\sigma^{*0}$

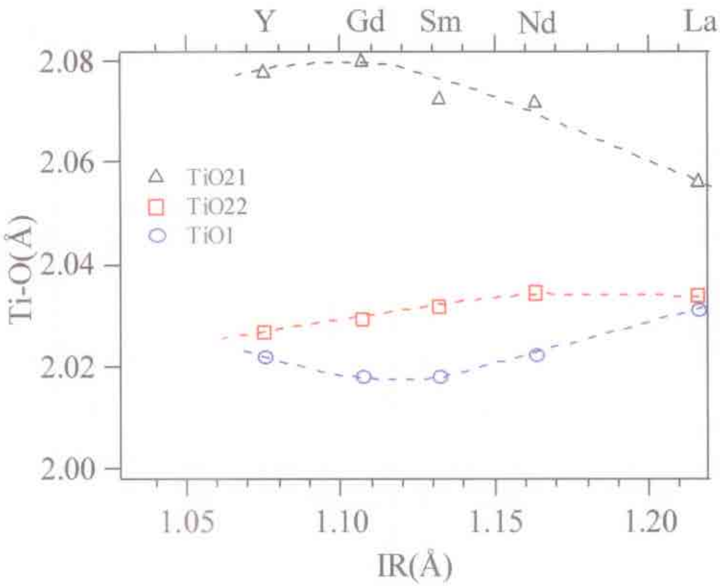
Possible site orbital order

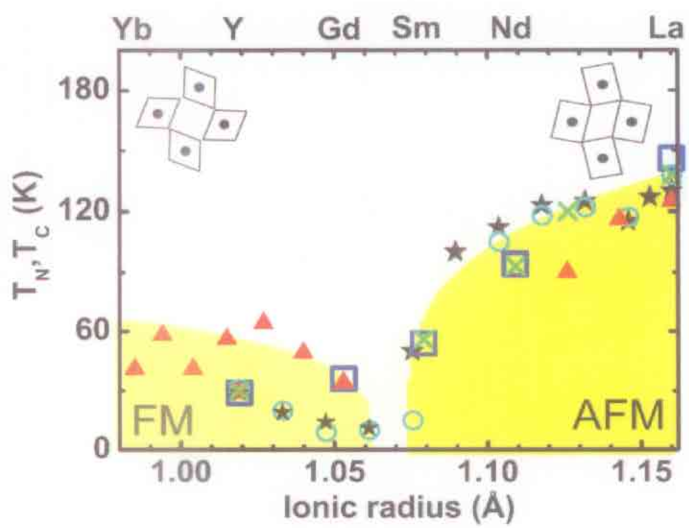


$\alpha < 90°$
AF

$\alpha = 90°$,
orthorhombic, F

$RTiO_3$

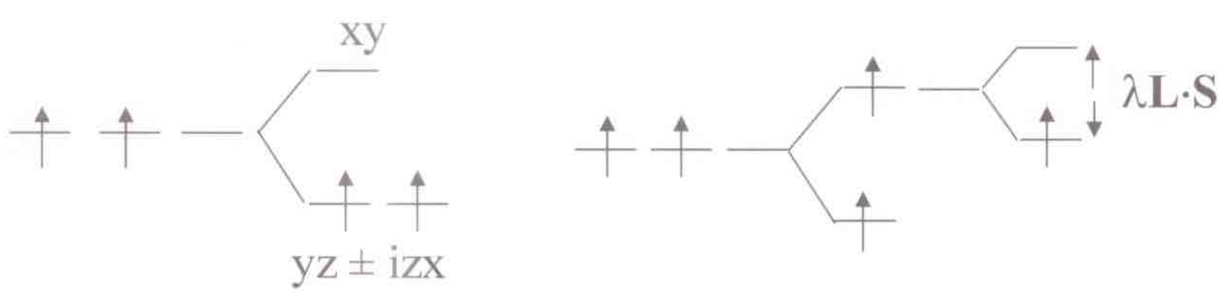




A.C. Komarek *et al* PRB **75**, 224402(2007)

RVO_3 perovskites
V^{3+}:t^2e^0: localized spins

Possible site orbital order



Tetr c/a >1

$T_{OO} > T_N$

Cooperative antiferroic

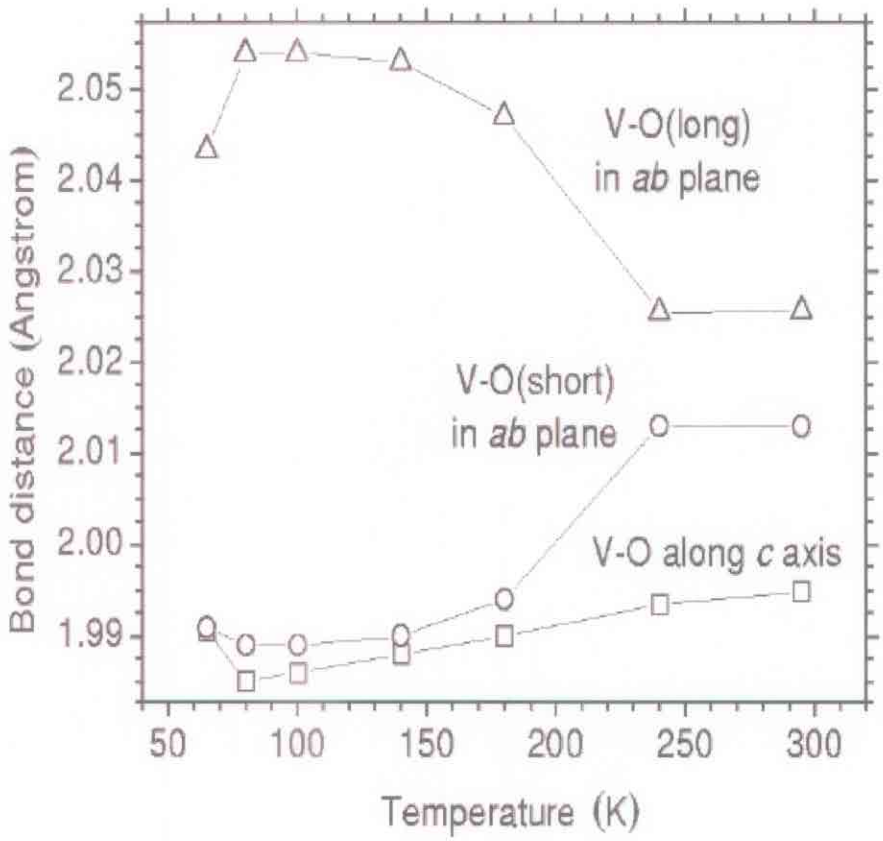
Pseudocubic (c/a ≈ 1)

$T_{OO} \leq T_N$?

Cooperative ferroic

YVO_3 site distortion

Note: Distortion at $T > T_{OO}$ largest for IR ≈ 1.11 Å



Temperature dependence of V-O bond lengths determined by using neutron powder diffraction.
Blake et al *Phys. Rev. B* 65, 174112 (2002)

Orbital & Spin ordering in YVO_3

Orbital ordering and spin-spin interactions:

G_{OO}: $T_{CG} < T < T_{OO}$

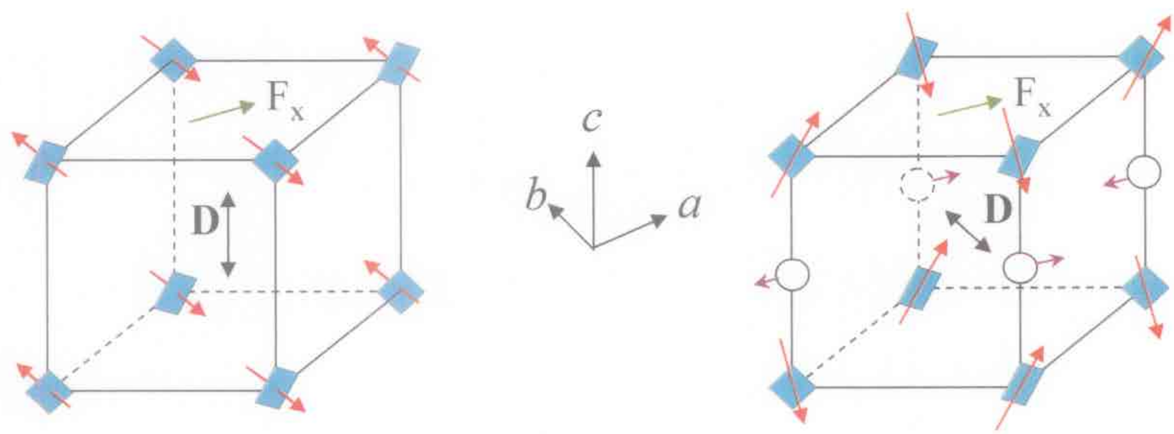
C_{OO}: $T < T_{CG}$

AF: xy^1- xy^1, yz^1-yz^1, zx^1-zx^1

F: yz^1-yz^0, zx^1-zx^0

$G_{OO}C_{SO}$: $T_{CG} < T < T_N$

$C_{OO}\ G_{SO}$: $T < T_{CG}$



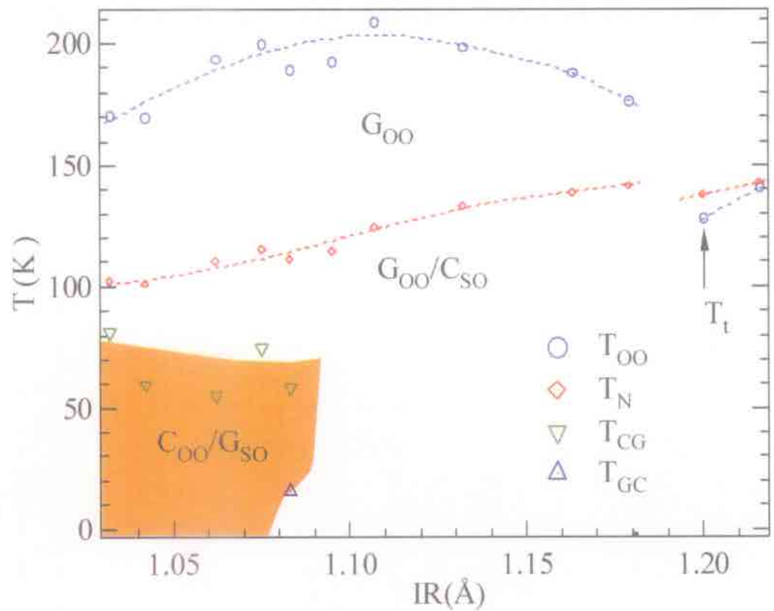
$T_{CG} < T < T_N$
C_yF_x

$T < T_{CG}$
G_zF_x

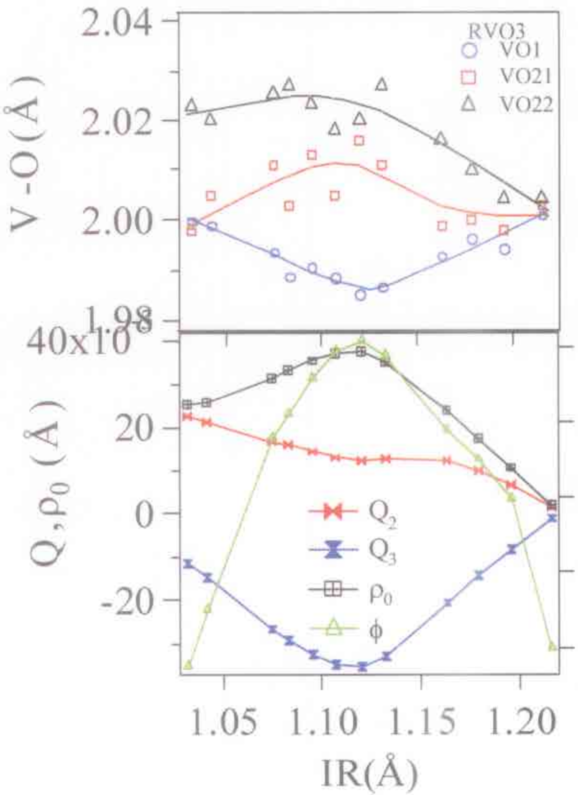
$\mathbf{D}_{ij}\cdot\mathbf{S}_i\times\mathbf{S}_j$ gives F_x

$VO_{6/2}$ rotations also give F_x for $T < T_{CG}$

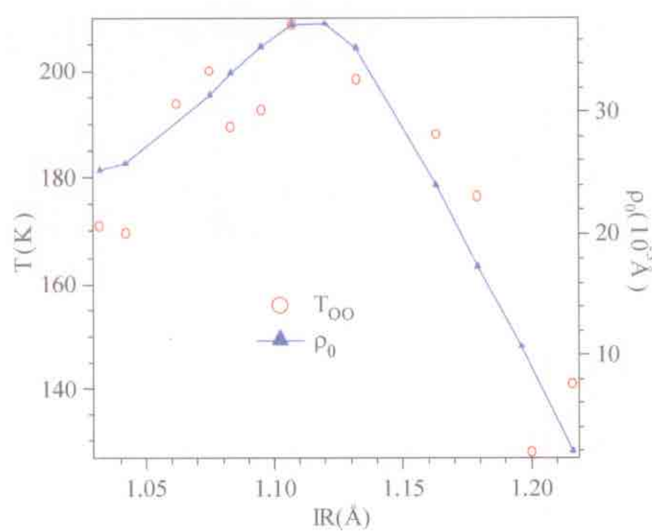
RVO_3



T(K)
IR(Å)
G_OO
G_OO/C_SO
C_OO/G_SO
T_t
T_OO
T_N
T_CG
T_GC

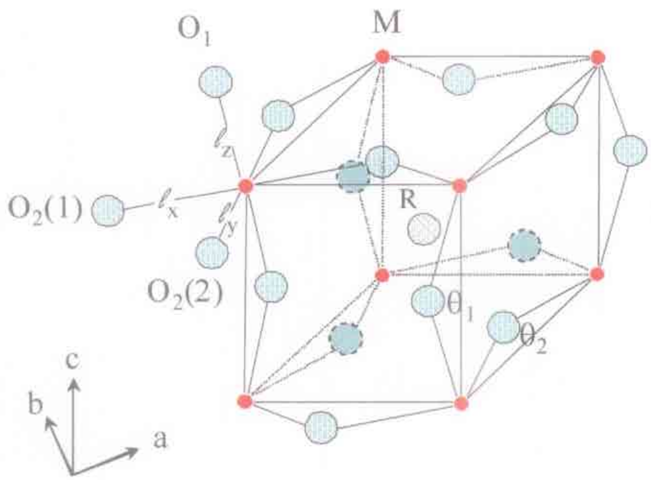


V-O(Å)
RVO3
VO1
VO21
VO22
Q, ρ0 (Å)
ϕ(°)
Q2
Q3
ρ0
ϕ
IR(Å)

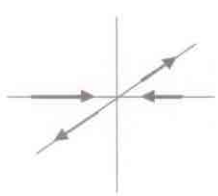


T(K)
ρ0(10^-3 Å)
T_OO
ρ0
IR(Å)

Jahn-Teller deformation in $RMnO_3$

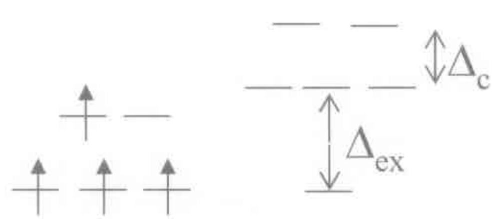


$\ell_x = \ell$
$\ell_z = m$
$\ell_y = s$



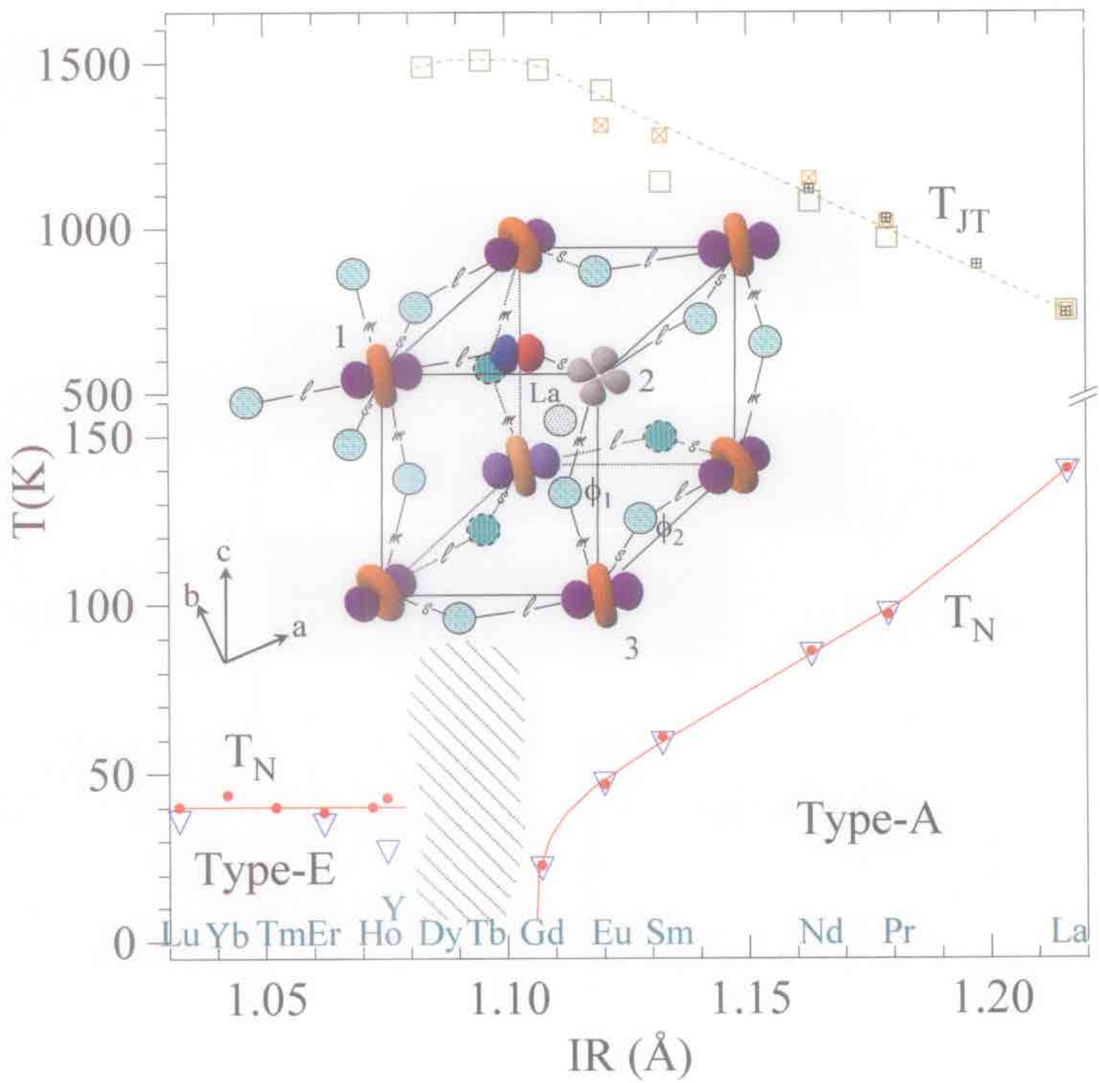
Q_2

Q_3



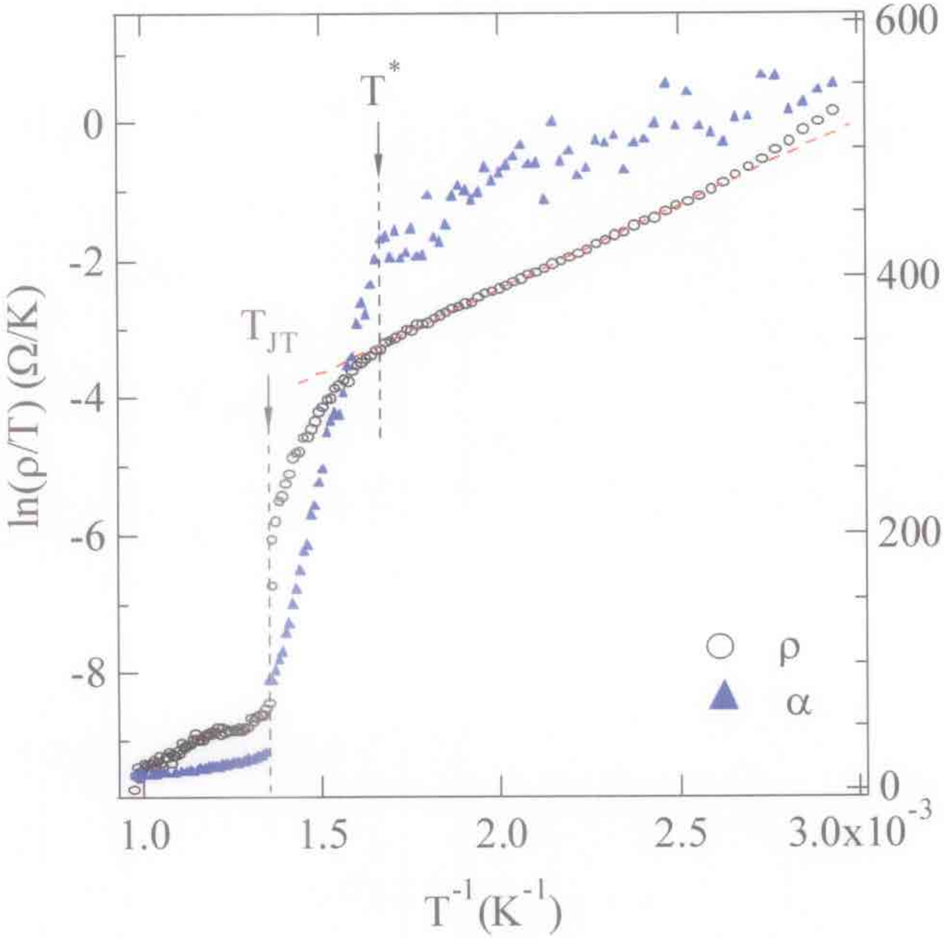
α-spin β-spin

RMnO$_3$



1500
1000
500
150
100
50
0
T(K)
T_{JT}
T_N
T_N
Type-A
Type-E
1
2
3
La
ϕ_1
ϕ_2
c
b
a
Lu Yb Tm Er Ho Dy Tb Gd Eu Sm Nd Pr La
Y
1.05
1.10
1.15
1.20
IR (Å)

$LaMnO_3$



(Measured in vacuum)

$T > T_{JT}$: Orbital disorder
Partial $2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$

$T^* < T < T_{JT}$: short-range orbital disorder

Mn-O-Mn Superexchange

c axis: e^0-O-e^0 (AF) & t^3-O-t^3 (AF)

a-b plane: t^3-O-t^3 (AF) & e^1-O-e^0 (F)

For type-A magnetic order
$T_N \sim b_\sigma^2/\Delta_\sigma$

Where
$b_\sigma^2 \sim \cos^4(\gamma/2)\cos^4(\omega/2)|(3x^2-r^2)\,|H'\,|(x^2-z^2)\,|^2$

$\Delta_\sigma \approx \Delta_{JT} \sim kT_{JT}$

$\gamma \;\; = 30° - \tan^{-1}(Q_3/Q_2)$

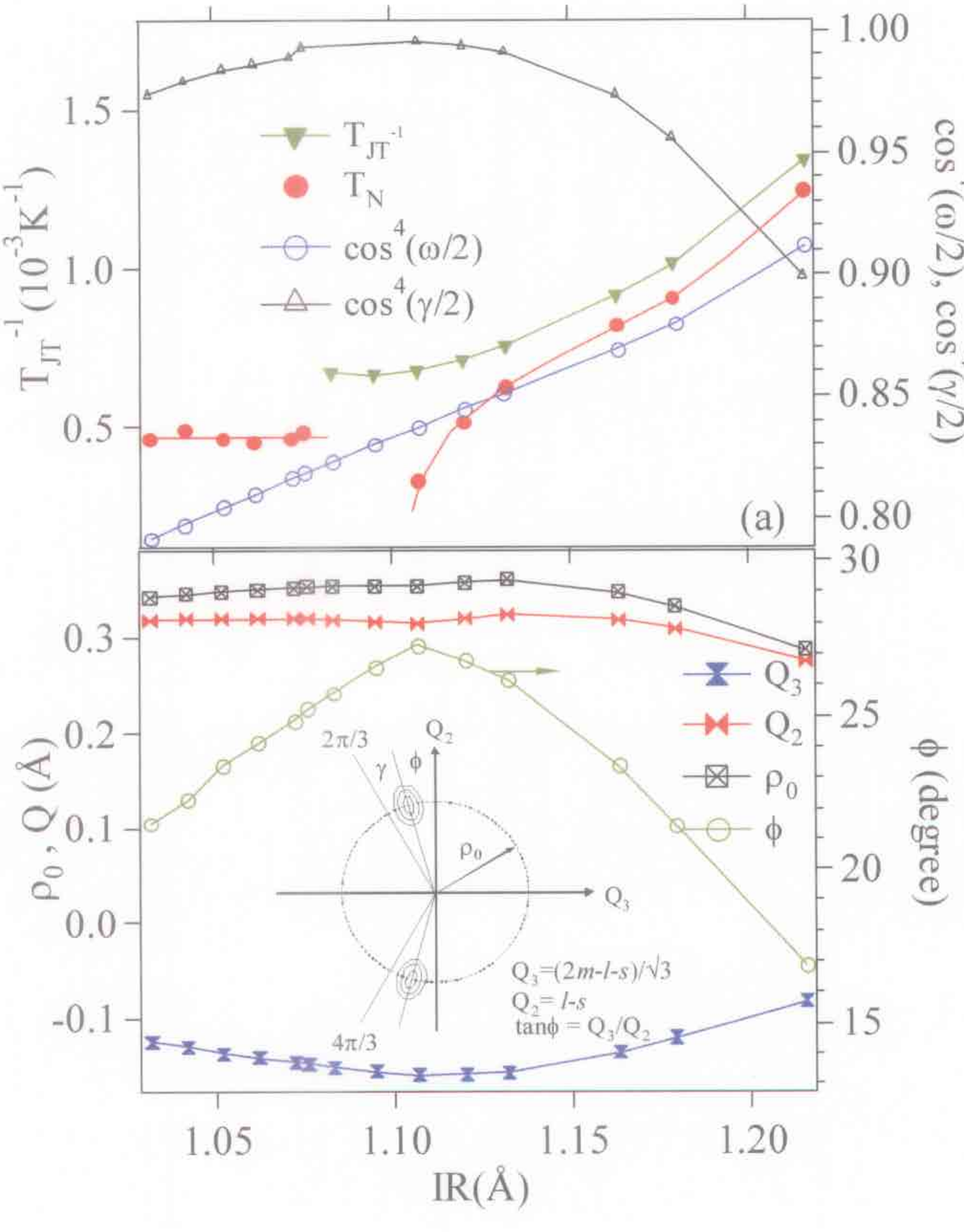
Note:

(1) $d[\ln\cos^4(\omega/2)]/d(IR) : d\ln T_N/d(IR) = 0.8 : 9$

(2) $d[\ln\cos^4(\gamma/2)]/d(IR)$ is negative, whereas $d\ln T_N/d(IR)$ is positive.

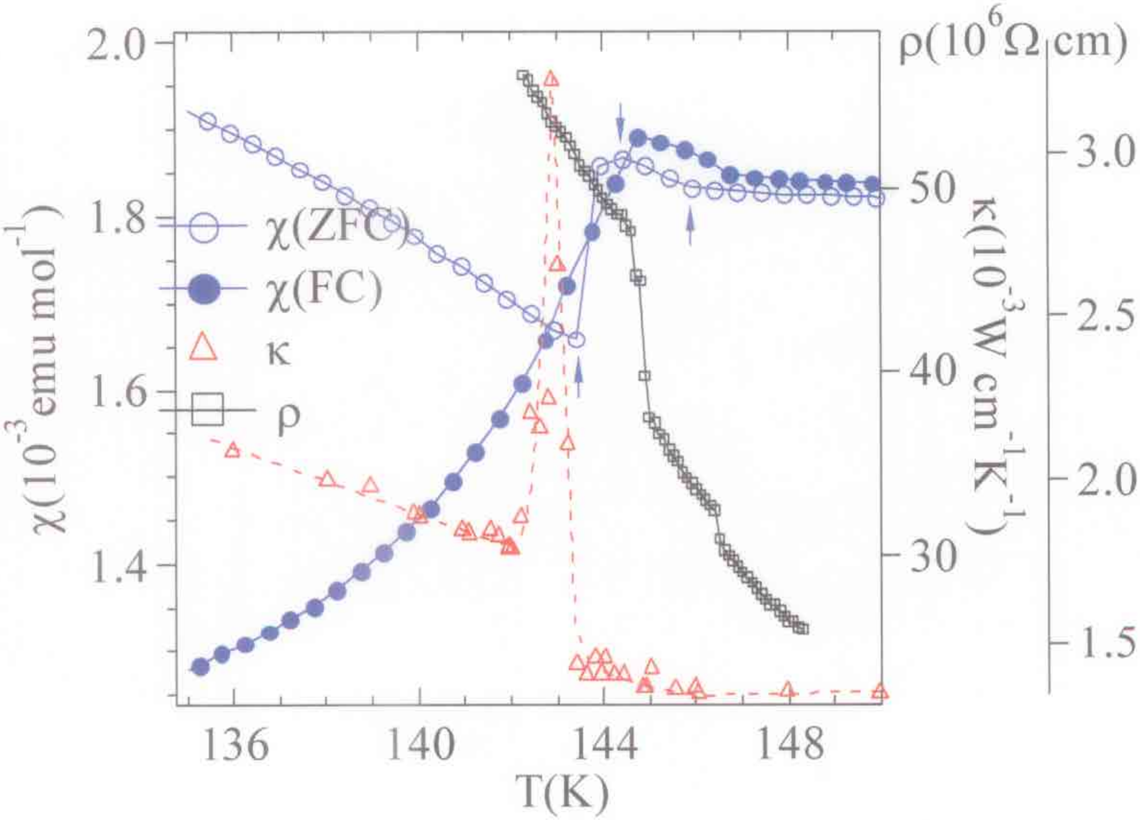
(3) $d[\ln(1/T_{JT})]/d(IR) : d\ln T_N/d(IR) = 7 : 9$

RMnO$_3$

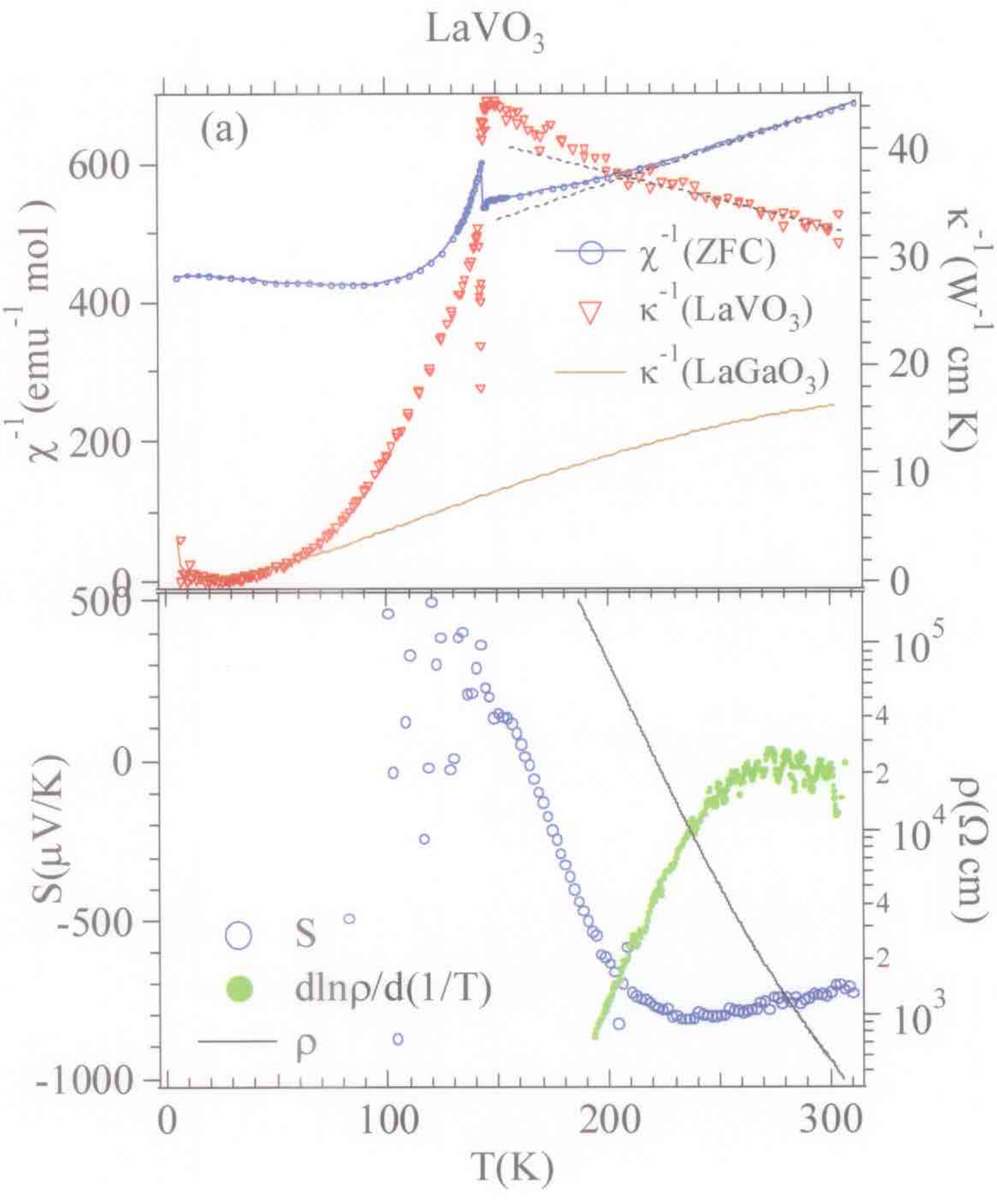


T_JT^-1
T_N
cos^4(ω/2)
cos^4(γ/2)
T_JT^-1 (10^-3 K^-1)
cos^4(ω/2), cos^4(γ/2)
(a)
1.5
1.0
0.5
1.00
0.95
0.90
0.85
0.80
Q_3
Q_2
ρ_0
ϕ
ρ_0 , Q (Å)
ϕ (degree)
0.3
0.2
0.1
0.0
-0.1
30
25
20
15
2π/3
γ
ϕ
4π/3
Q_3=(2m-l-s)/√3
Q_2= l-s
tanϕ = Q_3/Q_2
1.05
1.10
1.15
1.20
IR(Å)

$LaVO_3$

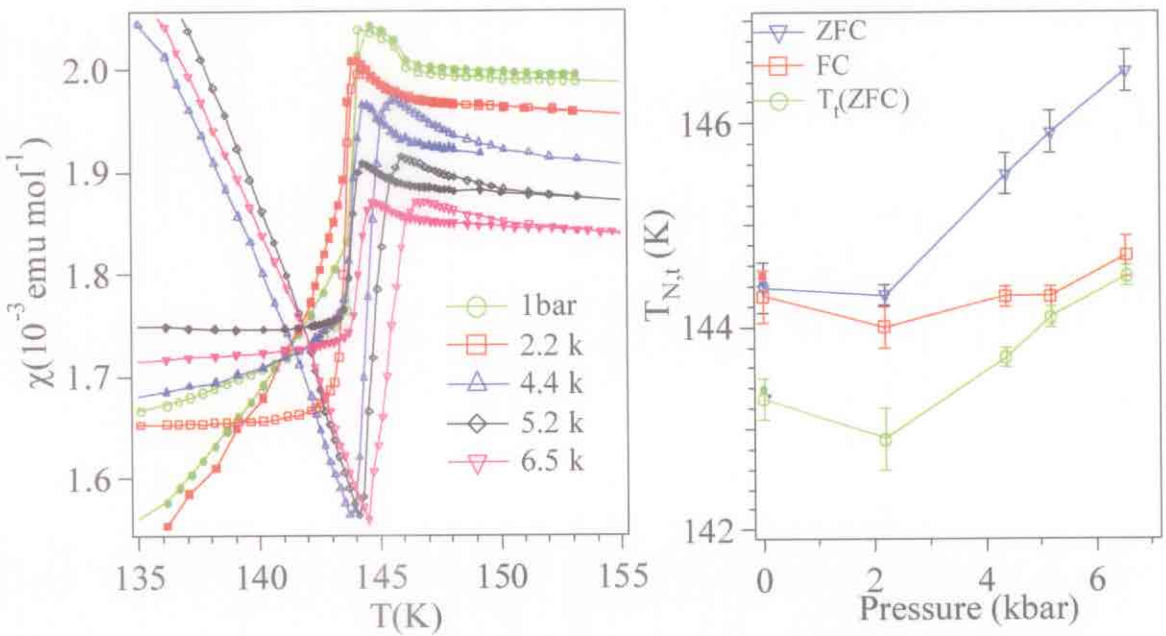


χ(ZFC)
χ(FC)
κ
ρ
χ(10^-3 emu mol^-1)
ρ(10^6 Ω cm)
κ(10^-3 W cm^-1 K^-1)
T(K)
2.0
1.8
1.6
1.4
50
40
30
3.0
2.5
2.0
1.5
136
140
144
148



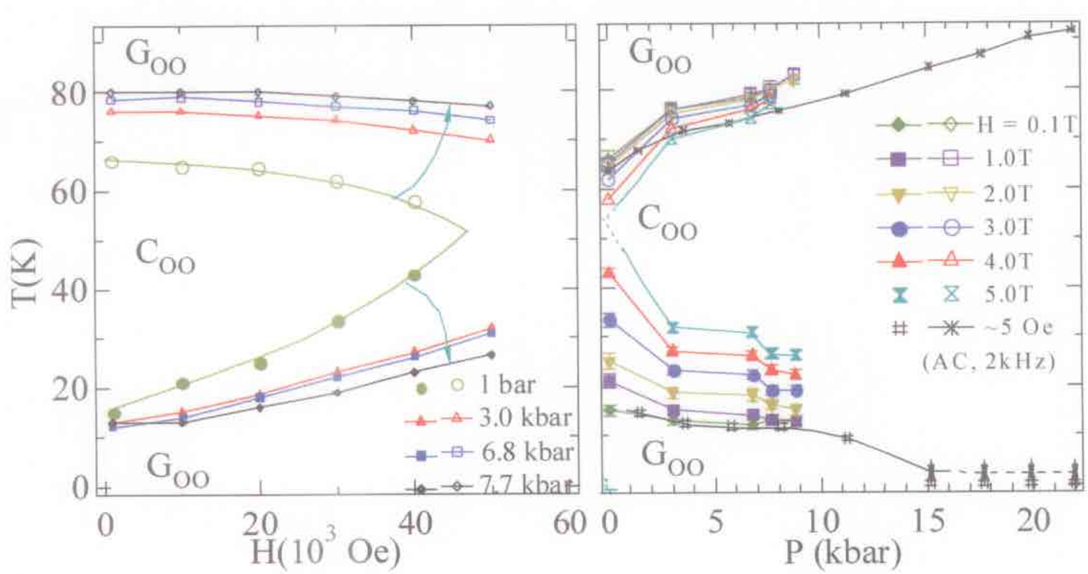
LaVO3
(a)
χ^-1(ZFC)
κ^-1(LaVO3)
κ^-1(LaGaO3)
χ^-1(emu^-1 mol)
κ^-1(W^-1 cm K)
S
dlnρ/d(1/T)
ρ
S(μV/K)
ρ(Ω cm)
T(K)

$LaVO_3$



χ(10^-3 emu mol^-1)
T(K)
1bar
2.2 k
4.4 k
5.2 k
6.5 k
T_N,t (K)
Pressure (kbar)
ZFC
FC
T_t(ZFC)

$DyVO_3$



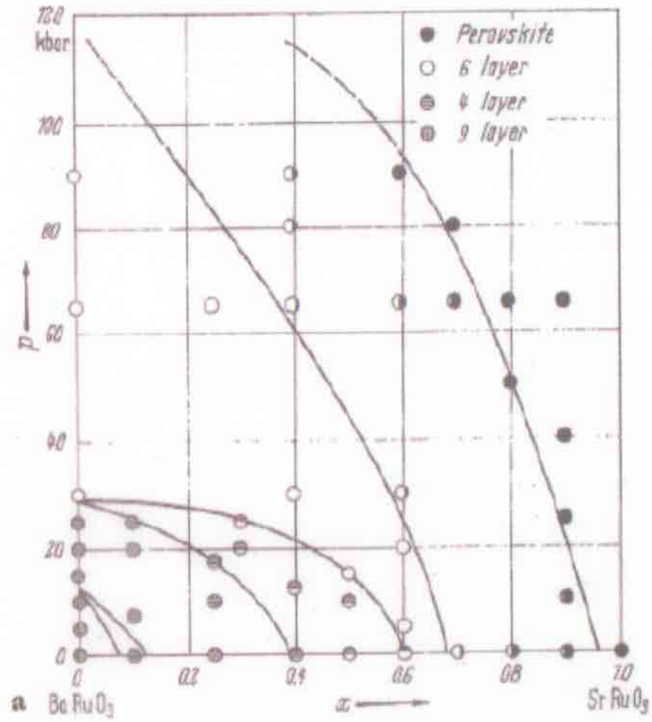
G_OO
C_OO
G_OO
T(K)
H(10^3 Oe)
1 bar
3.0 kbar
6.8 kbar
7.7 kbar
G_OO
C_OO
G_OO
P (kbar)
H = 0.1T
1.0T
2.0T
3.0T
4.0T
5.0T
~5 Oe
(AC, 2kHz)

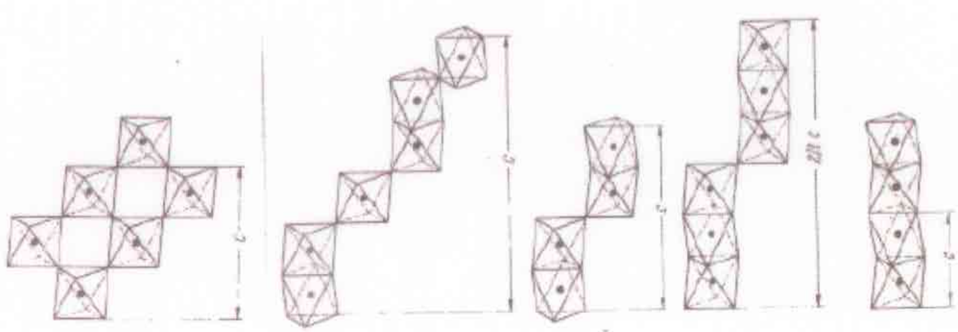
$Sr_{1-x}Ca_xRuO_3$

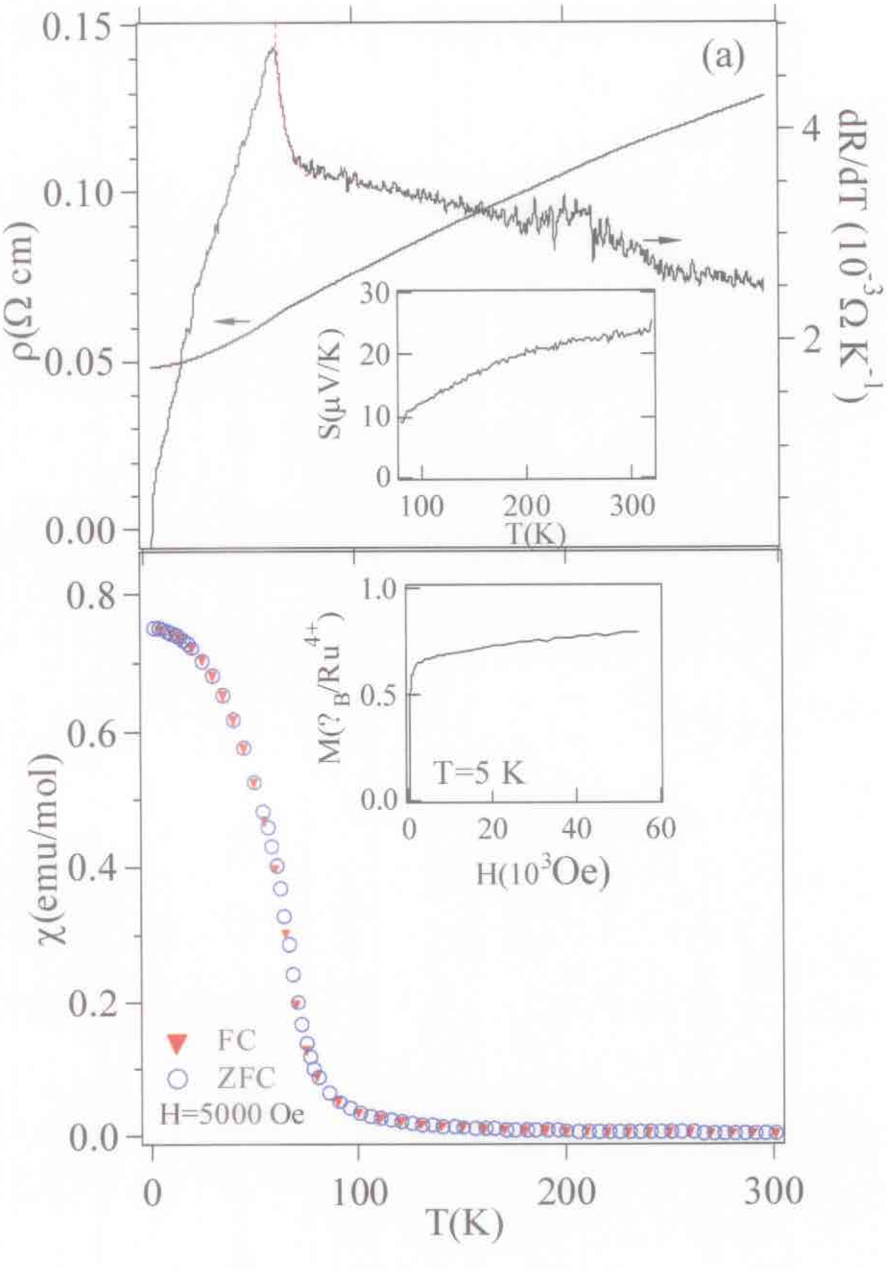
$SrRuO_3$: Itinerant-electron ferromagnet
Low-spin Ru^{4+}:$\pi^{*4}\sigma^{*0}$
$T_c = 164$ K, $\mu_{Ru} = 1.4\ \mu_B$ @ 5 K
$\mu_{eff} = 2.6\ \mu_B$/Ru
(S = 1 μ_{eff} (spin-only) = 2.8 μ_B/Ru)

$Sr_{1-x}Ca_xRuO_3$: Weiss $\theta > T_c$ for x = 0 decreases faster than T_c with increasing x. $T_c \rightarrow 0$ and θ changes sign at $x \approx 0.8$

$CaRuO_3$: No long-range magnetic order.
Ti^{4+} substitution shows $CaRuO_3$ on verge of ferromagnetic order
[Cava & He, *Phys. Rev. B* **63**, 172403 (2001)]


120
kbar
100
80
60
40
20
0
p
0
0.2
0.4
0.6
0.8
1.0
a
Ba Ru O3
x
Sr Ru O3
Perovskite
6 layer
4 layer
9 layer

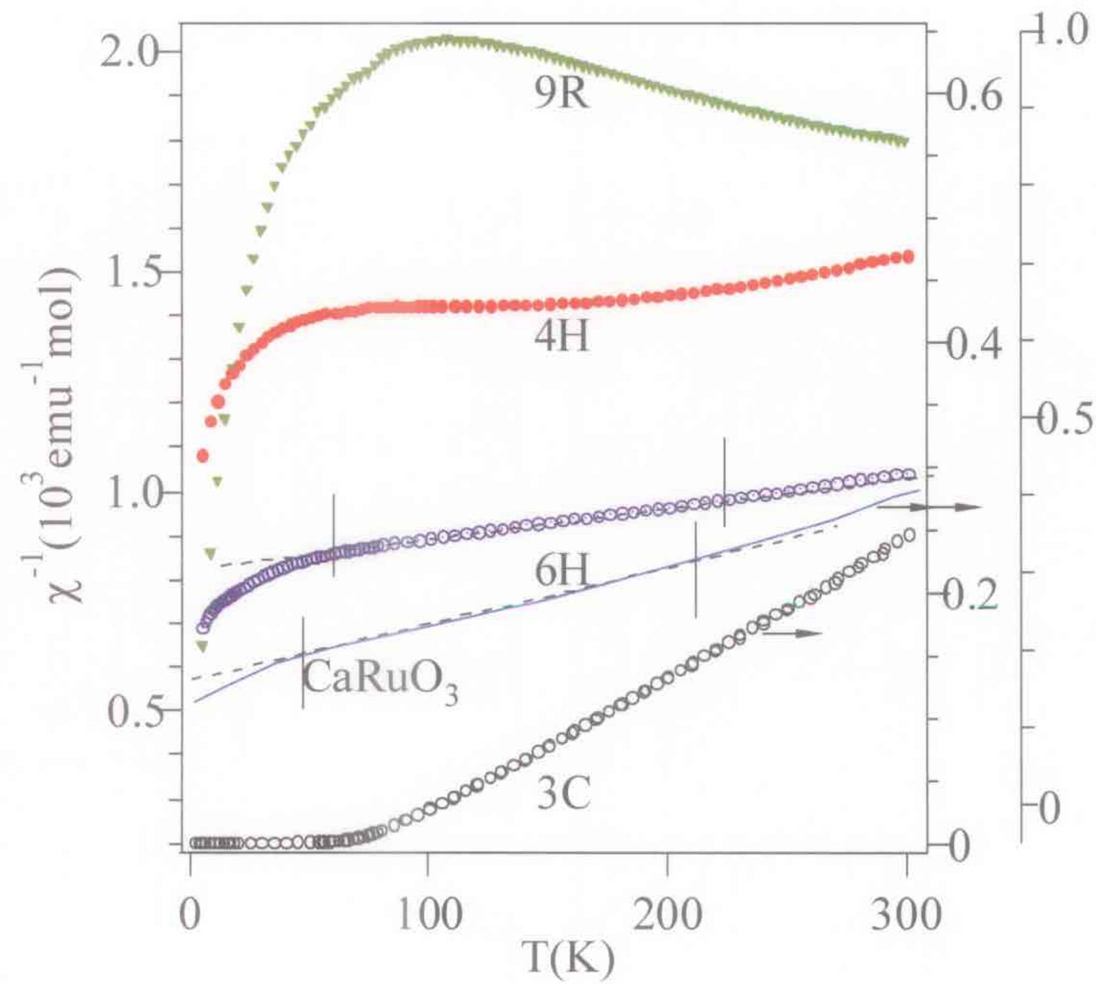


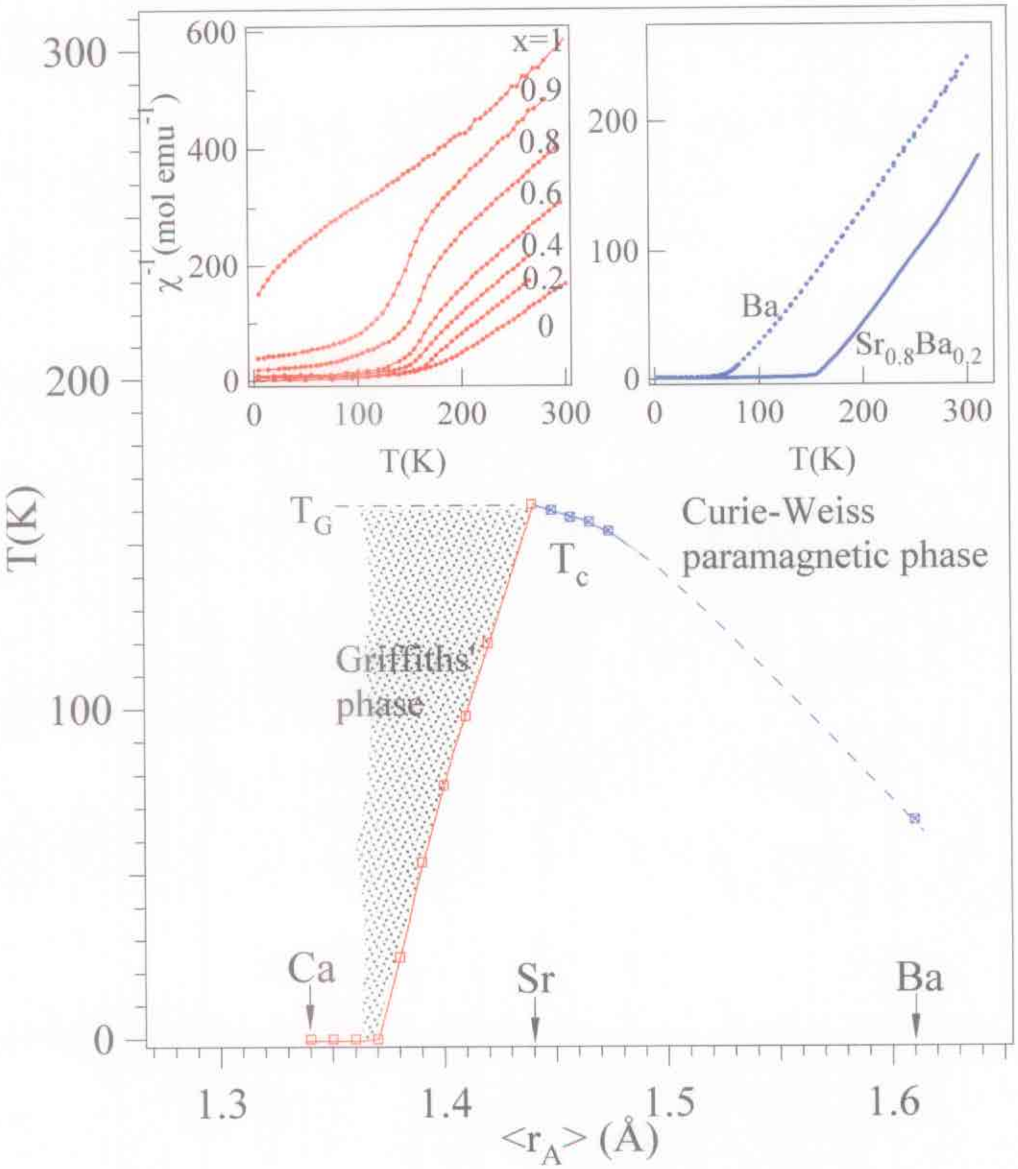


Cubic $BaRuO_3$: 1100°C @ 18 GPa KAWAI mutianvil press C.-Q. Jin *et al* (unpublished)

9R: Drillon *et al*, J. Chem. Soc. Faraday Transactions **75**, 1193 (1979)

$CaRuO_3$: Yashimura *et al*, Phys. Rev. Lett. **83**, 4397 (1999)





C.-Q. Jin *et al* (unpublished)

Conclusions:

- Acidity of A-O bond: Ca > Sr > Ba
- Intraatomic $\lambda\, L \cdot S$ on a Ru^{4+} ion supresses the interatomic spin-spin interaction in neighborhood of Ca.