1. Understanding crystal structures: How are more complex crystal structures built up from simpler ones.

2. Structure-composition-property relations in inorganic materials: Some examples of subscript engineering in luminescent, catalytic, and magnetic oxides

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You can't say the phrase, "structure-property relations", without saying the word, "structure".

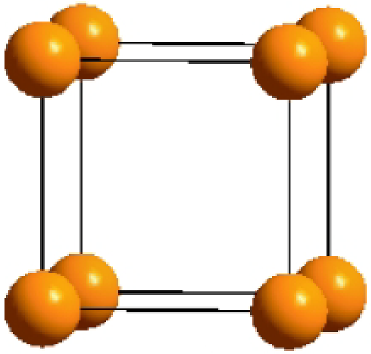
1. Understanding crystal structures: How are more complex crystal structures built up from simpler ones.

http://www.mrl.ucsb.edu/~seshadri/teach.html

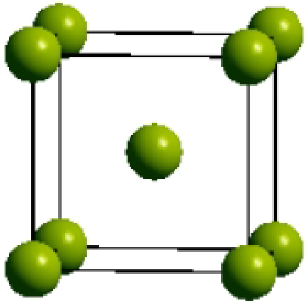
Materials 218: Introduction to Inorganic Materials
Materials 286G: Structural Families of Functional Materials

Courses for senior undergraduates, and graduate students from varied backgrounds

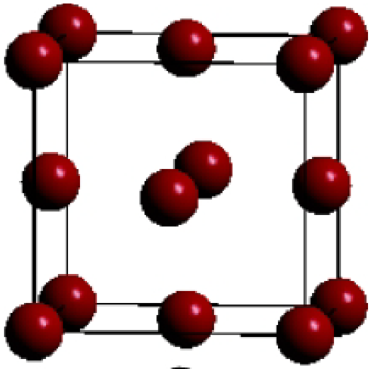
Simple crystal structures



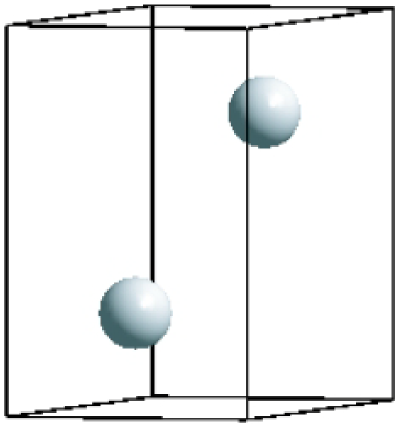
α−Po



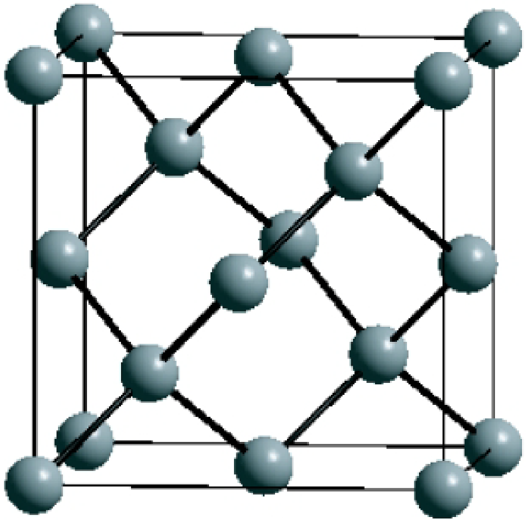
α−Fe



Cu

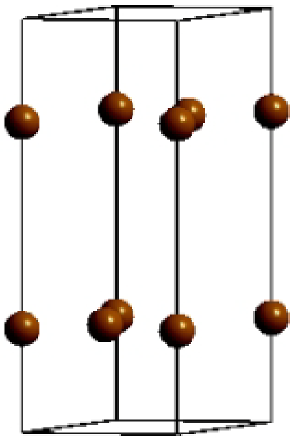


Mg

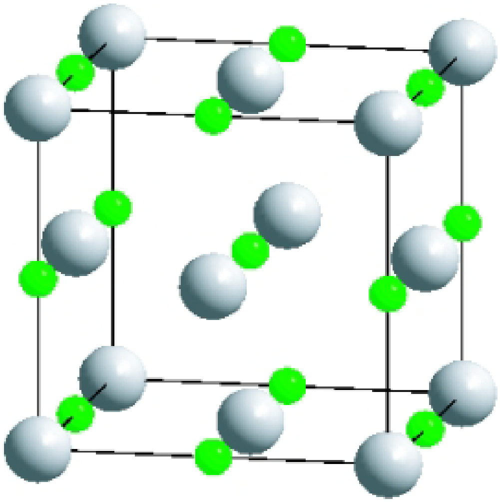


Si

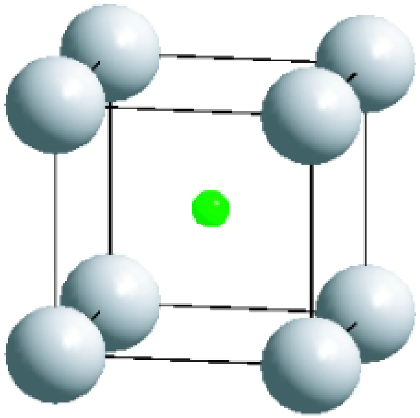
Simple crystal structures



C (graphite)



NaCl



CsCl

Simple crystal structures

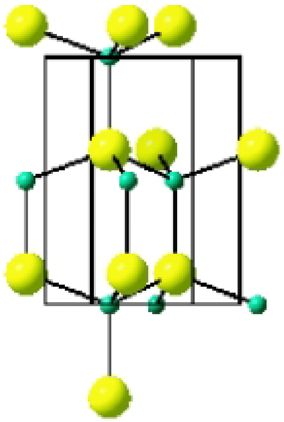
Use of the International Tables: The example of space group *Fd-3m* (No. 227) Origin Choice 1 (at -1/8, -1/8, -1/8)

Coordinates: (0,0,0)+ (0,1/2,1/2)+ (1/2,0,1/2)+ (1/2,1/2,0)+

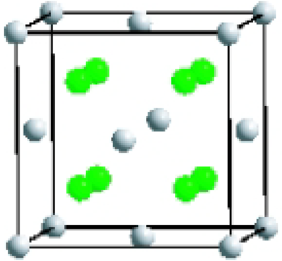
Si at: 8*a* -43m 0,0,0 3/4,1/4,3/4

Sketch the structure! Mention VESTA !

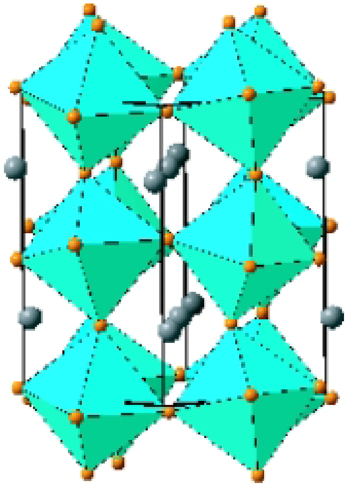
Simple crystal structures



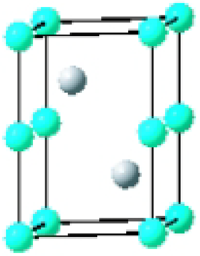
ZnS wurtzite



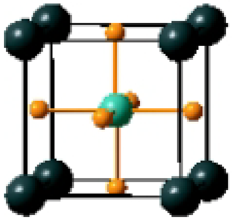
Fluorite



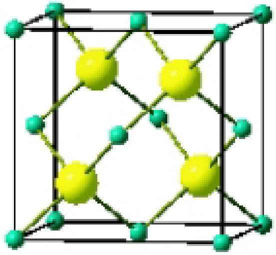
Perovskite
CaTiO3



NiAs



cubic perovskite (BaSnO3)



ZnS zinc blende

Simple crystal structures

The Coulombic potential (lattice energy) holding ionic solids together:

$$U = -AN_A q_1 q_2 e^2 / 4\pi\varepsilon_0 R$$

Sketch!

Madelung constants:

A = 1.76267 (CsCl)

A = 1.74756 (NaCl)

A = 1.64132 (wurtzite)

A = 1.63805 (blende)

Simple crystal structures

Paulings rules (approximately): *J. Am. Chem. Soc.* 51 (1929) 1010.

1. *Coordination Polyhedra:* … of anions formed around cations. Cation-anion distances are determined by the sum of the radii, and corrdination number by the radius ratio.
2. *Electrostatic valence rule:* In a stable ionic structure, the valence (ionic charge) of each anion with changed sign is exactly equal to the sum of the electrostatic bond strengths to it from adjacent cations. The electrostatic bond strength is defined as ratio of charge on cation to its coordination number.
3. *Linking of polyhedra:* The presence of shared edges and especially of shared faces decreases stability. The effect is large for cations with high charge and low coordination number.
4. *Sharing of anions:* Polyhedra around cations with high charge and low coordination number tend not to share features.
5. *Parsimony:* Structures tend to be simple

Simple crystal structures

Sketch radius rules!

Simple crystal structures

Sketch electrostatic valence rules!

Simple crystal structures

Paulings electrostatic valence rule disregards distance between atoms. Distance is particularly important when there is more than one cation in the structure.

Brown [The Chemical Bond in Inorganic Chemistry etc.] has (with others) suggested an extension of electrostatic valence by noting that the bond valence usually obeys a simple relation with distance:

$S_{\mathrm{ij}} = \exp[(R_{\mathrm{o}}-R_{\mathrm{ij}})/B]$ or $S_{\mathrm{ij}} = (R_{\mathrm{ij}}/R_{\mathrm{o}})^{-N}$

Where S_{ij} is the bond valence of the bond between i and j, and R_{ij} is the distance. B, R_{o} and N are chosen from crystallographic data so that the bond valence sum is equal to the formal valence.

The Bond Valence Sum is simply the sum of all bond valences to an atom: $V_{\mathrm{i}} = \Sigma_{\mathrm{j}}\, S_{\mathrm{ij}}$

Simple crystal structures

Some bond valence parameters $S_{ij} = \exp[(R_o - R_{ij})/B]$:

Al^{3+} and O^{2-} $R_o = 1.620$ $B = 0.37$
Mg^{2+} and O^{2-} $R_o = 1.693$ $B = 0.37$

Sketch bond network for $MgAl_2O_4$

The file bvsparm.cif: http://www.ccp14.ac.uk/

Simple crystal structures

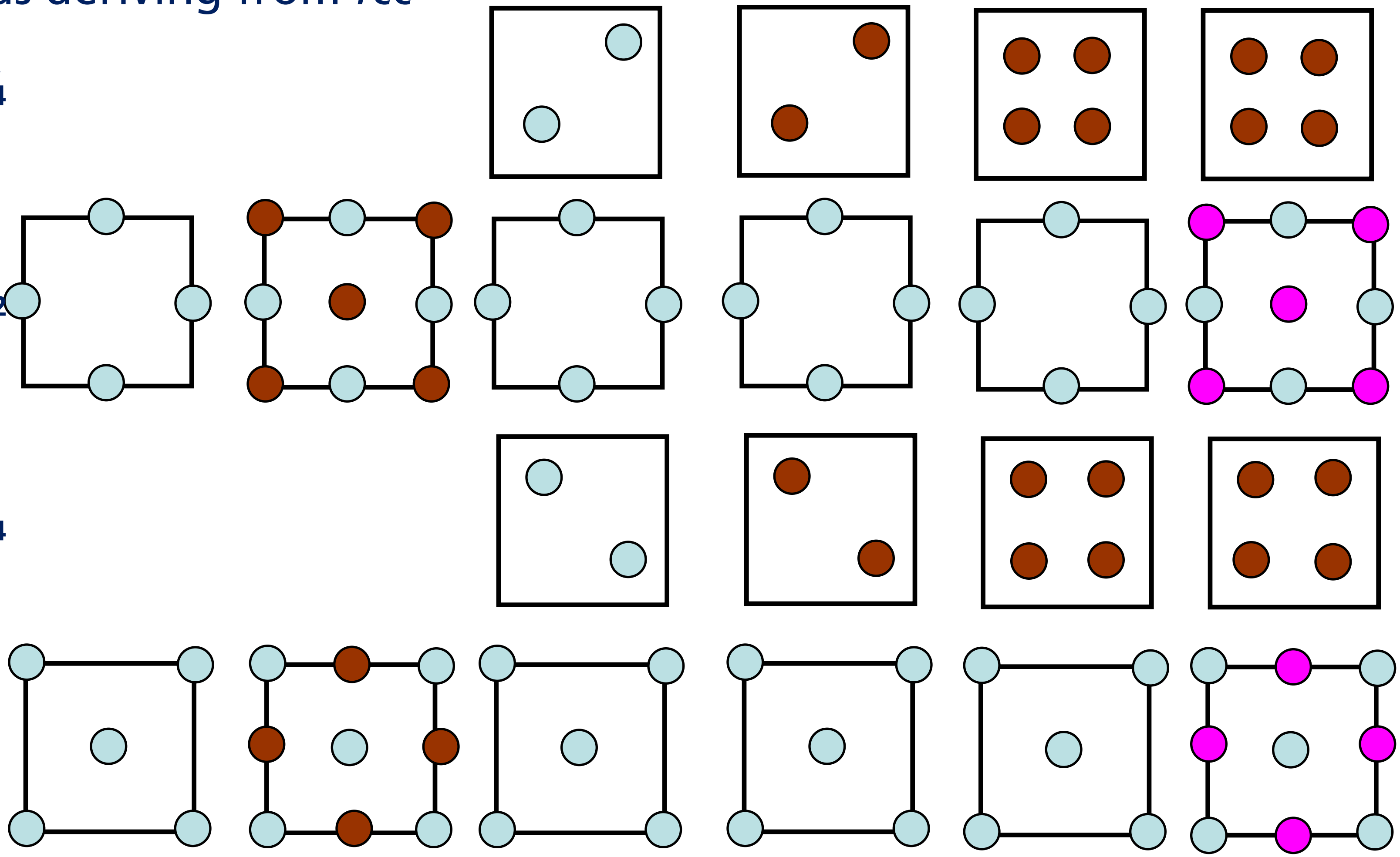
Look at:

The computer program SPuDs from Lufaso and Woodward.

We will also discuss a few publications on *ab-initio* structure prediction: Pannetier et al. *Nature* 346 (1990) 343; Schon and Jansen, *Angew. Chem. Int. Edn.* 35 (1996) 1304; Jansen, *Angew. Chem. Int. Edn.* 41 (2002) 3746.

Simple crystal structures

Solids deriving from *fcc*



z = ¾

z = ½

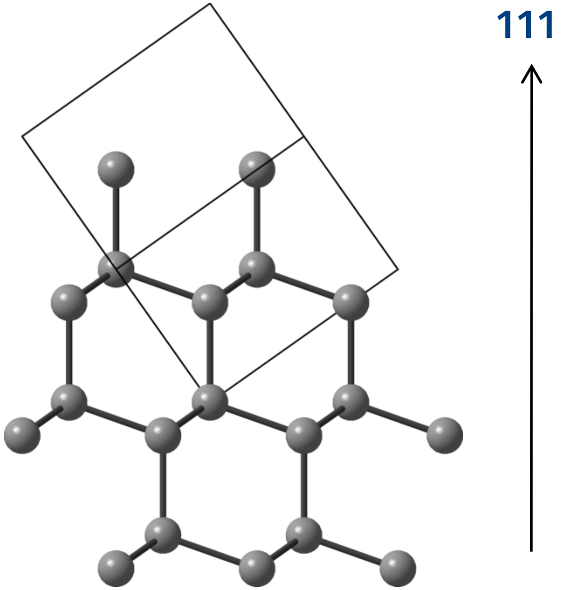
z = ¼

z = 0

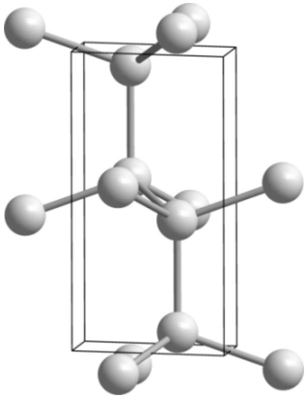
fcc	rock salt	diamond	zinc blende	fluorite	Heusler
Fm-3m	*Fm-3m*	*Fd-3m*	*F-43m*	*Fm-3m*	*Fm-3m*

Simple crystal structures

Stacking variants



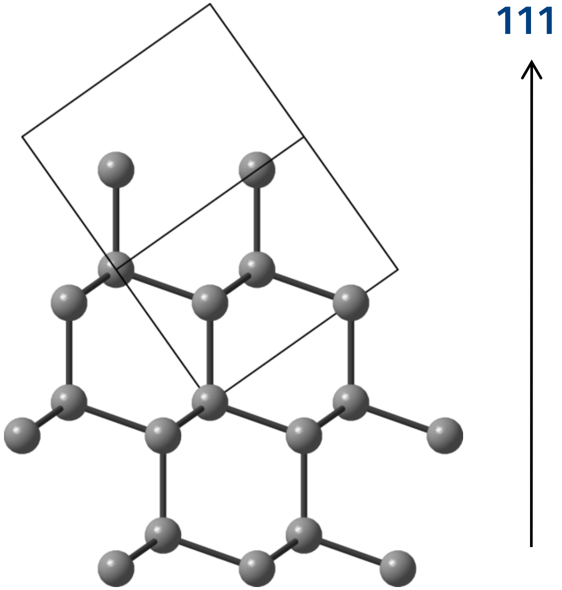
Diamond



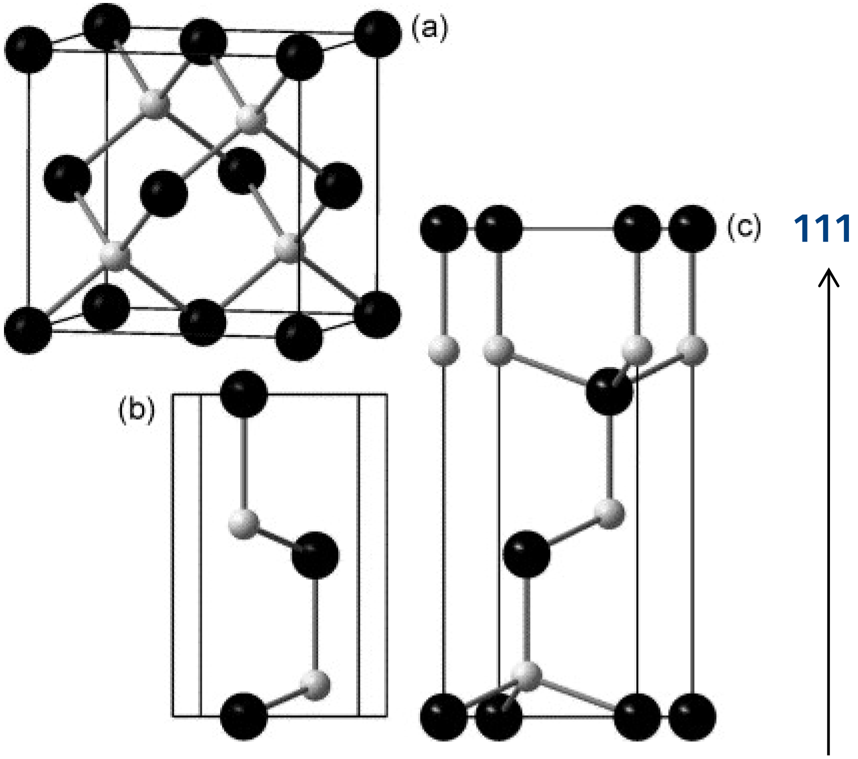
Lonsdaleite

Simple crystal structures

Stacking variants



Diamond



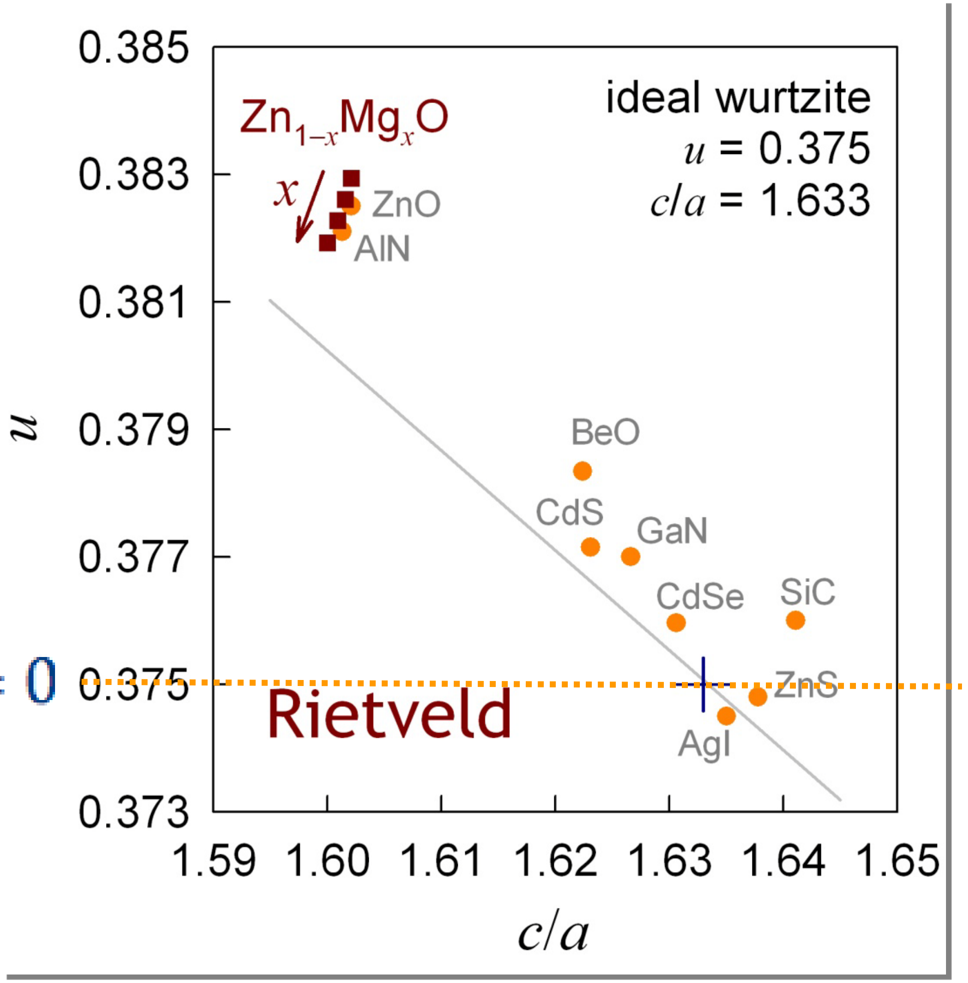
Wurtzite and zinc blende

P63mc and *R3m/F-43m*
2*H* and 3*R*

Simple crystal structures

Wurtzite structures and static polarization

[Dr. Young-Il Kim]



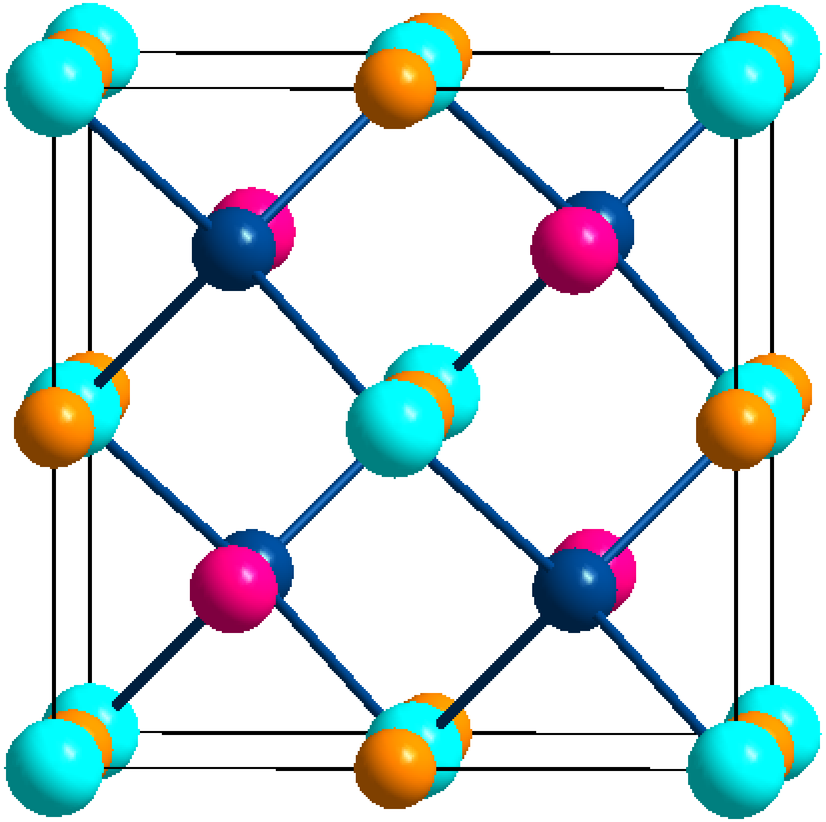
$$u = \frac{3}{8}; P_s = 0$$

Madelung constants:

A = 1.64132 (wurtzite)

A = 1.63805 (blende)

Semiconducting and half-metallic behavior in Heusler compounds



The Heusler crystal structure:
XY_2Z
F. Heusler (1903)
4 interpenetrating fcc lattices.

Cu_2MnAl

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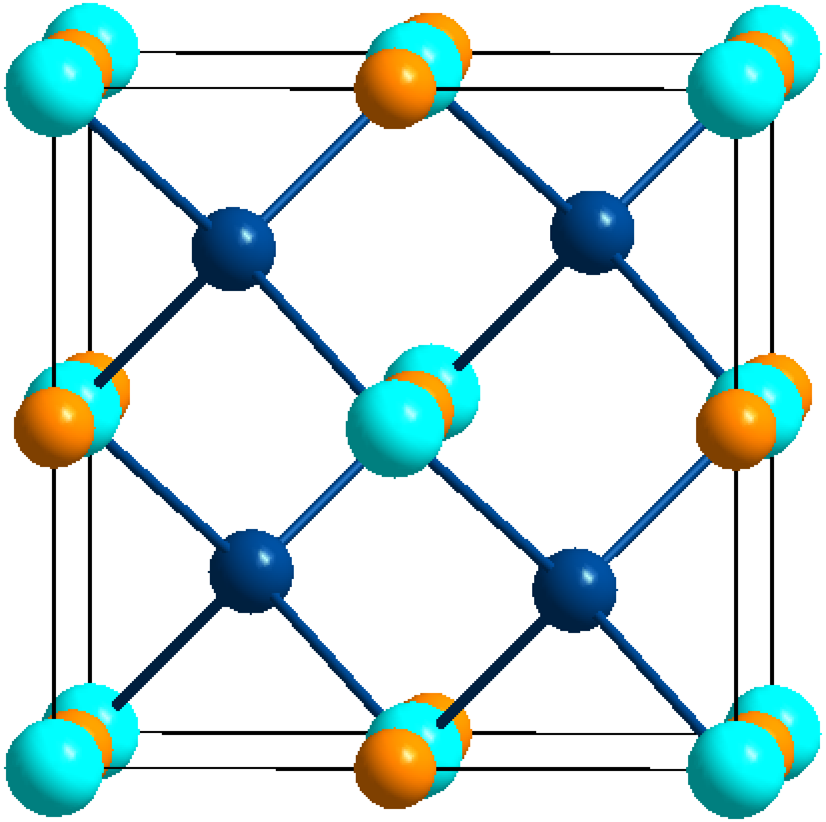
Semiconducting and half-metallic behavior in Heusler compounds

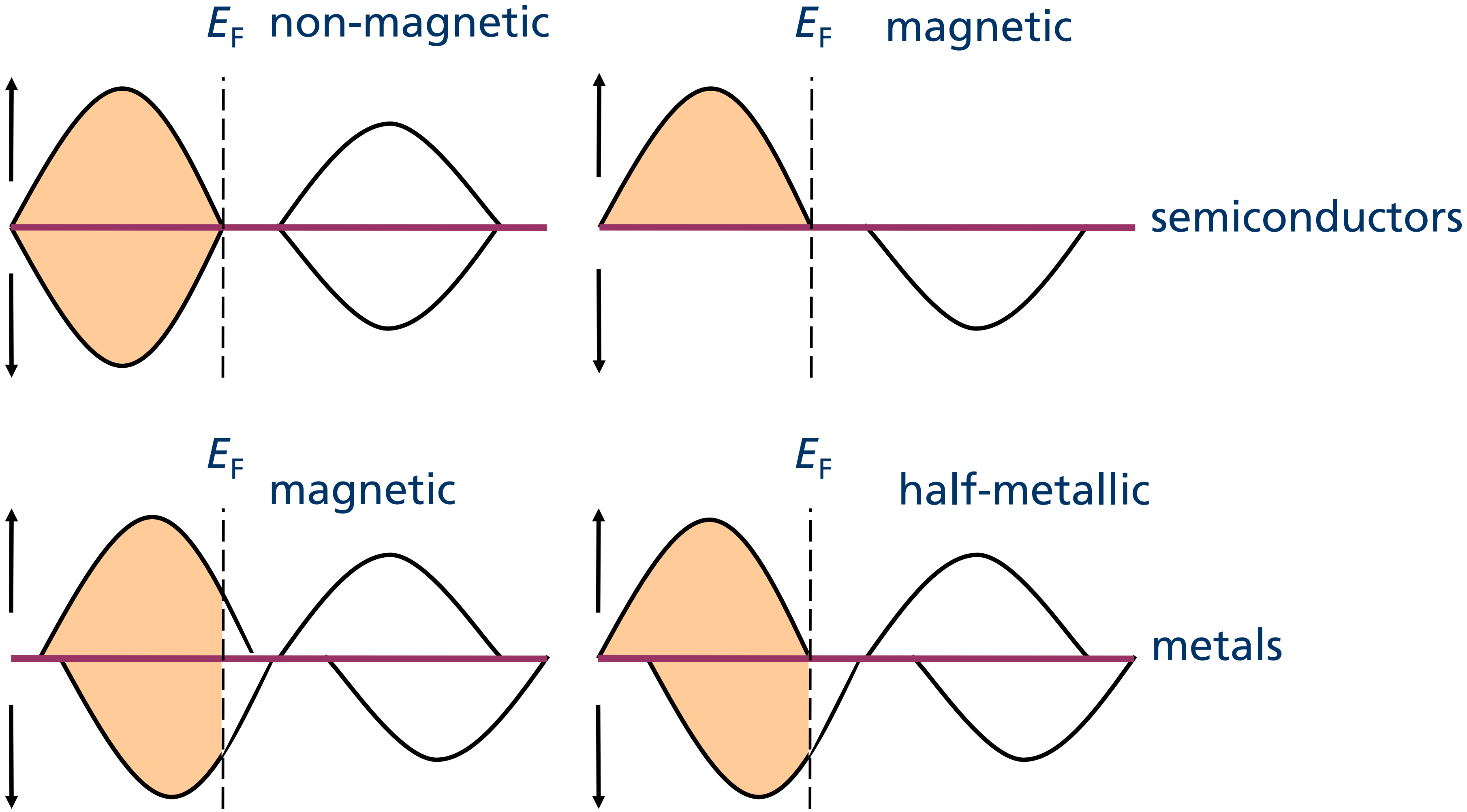


The half-Heusler crystal structure: XYZ. 3 interpenetrating fcc lattices.

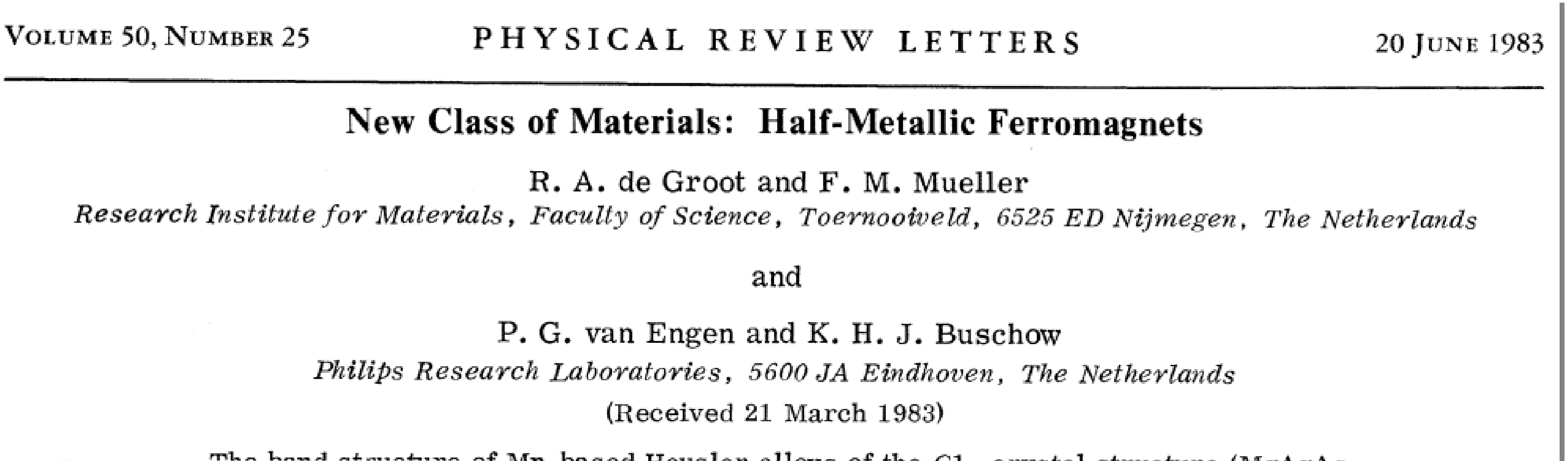
AXZ rock-salt with Y in one of the tetrahedral voids.

YZ zinc-blende with X in an octahedral void.

Semiconducting and half-metallic behavior in Heusler compounds



Semiconducting and half-metallic behavior in Heusler compounds



VOLUME 50, NUMBER 25 PHYSICAL REVIEW LETTERS 20 JUNE 1983

New Class of Materials: Half-Metallic Ferromagnets

R. A. de Groot and F. M. Mueller
Research Institute for Materials, Faculty of Science, Toernooiveld, 6525 ED Nijmegen, The Netherlands

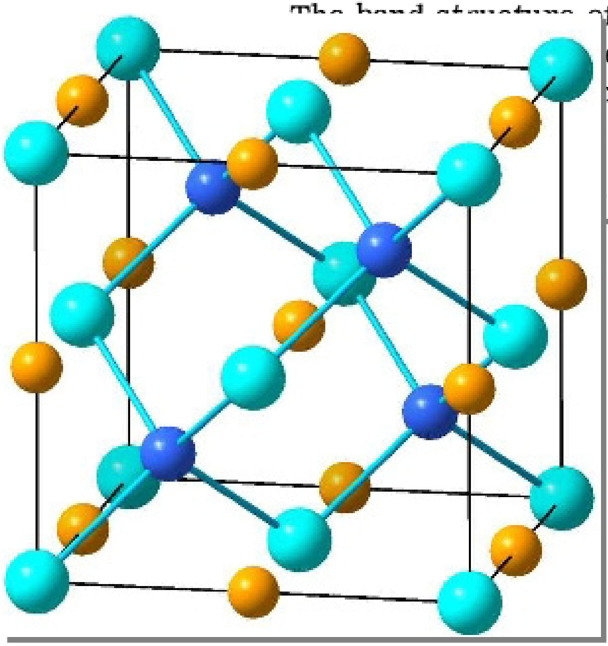
and

P. G. van Engen and K. H. J. Buschow
Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands

(Received 21 March 1983)

The band structure of Mn-based Heusler alloys of the $C1_b$ crystal structure (MgAgAs
ed with the augmented-spherical-wave method. Some of these
ow unusual electronic properties. The majority-spin electrons
the minority-spin electrons are semiconducting.

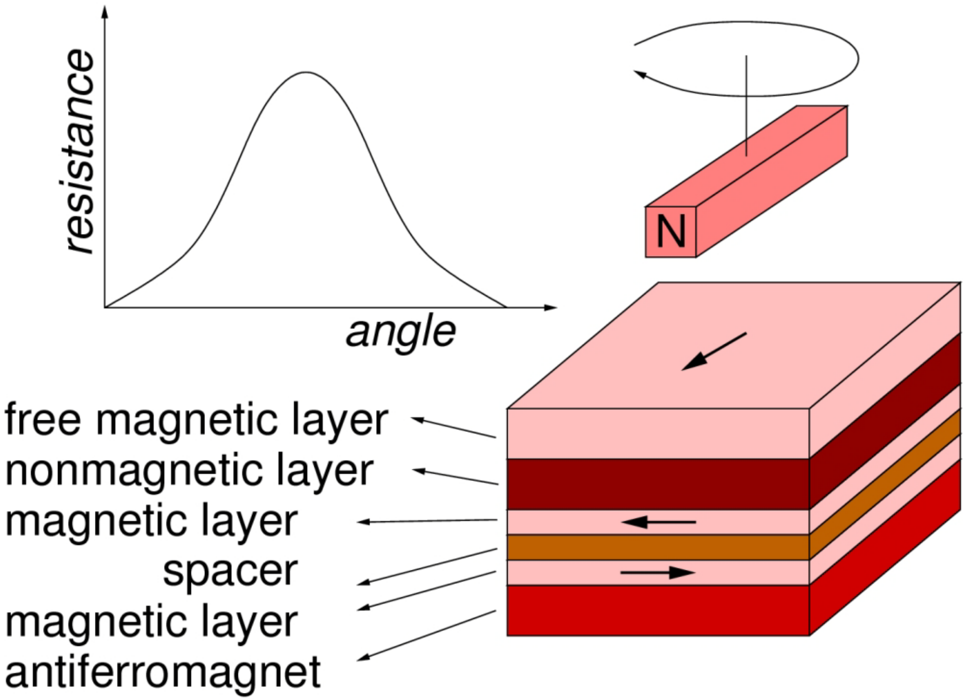
+x, 71.25.Pi, 75.20.En



Half Heusler MnNiSb

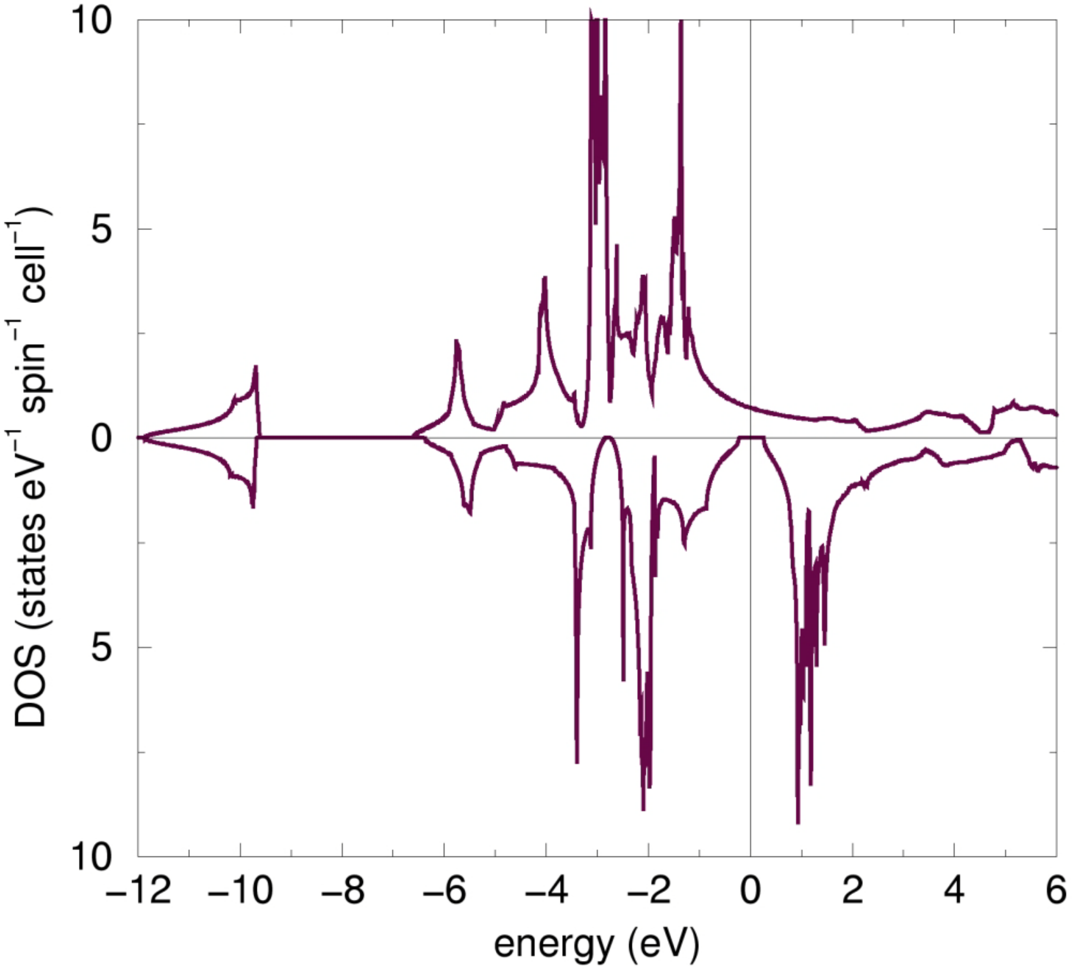
Semiconducting and half-metallic behavior in Heusler compounds

Magnetoresistive angle sensor:



Modified from Grünberg, *Phys. Today* 54 (2001) 34

Semiconducting and half-metallic behavior in Heusler compoundsh



MnNiSb (deGroot 1983) has states at the Fermi energy only in one spin direction, and is gapped in the other. The calculated magnetic moment is precisely 4 μ_B

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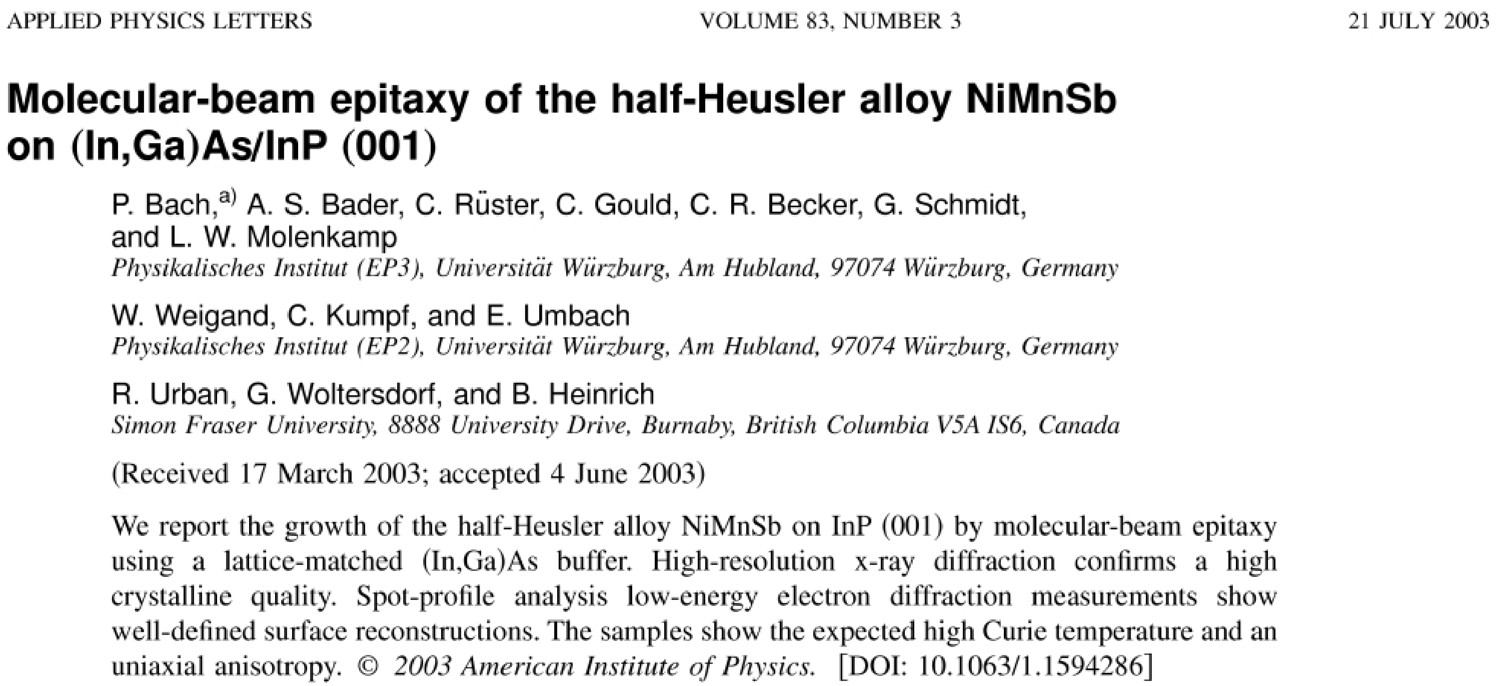
Semiconducting and half-metallic behavior in Heusler compounds



APPLIED PHYSICS LETTERS VOLUME 83, NUMBER 3 21 JULY 2003

Molecular-beam epitaxy of the half-Heusler alloy NiMnSb on (In,Ga)As/InP (001)

P. Bach,[a] A. S. Bader, C. Rüster, C. Gould, C. R. Becker, G. Schmidt, and L. W. Molenkamp
Physikalisches Institut (EP3), Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

W. Weigand, C. Kumpf, and E. Umbach
Physikalisches Institut (EP2), Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

R. Urban, G. Woltersdorf, and B. Heinrich
Simon Fraser University, 8888 University Drive, Burnaby, British Columbia V5A IS6, Canada

(Received 17 March 2003; accepted 4 June 2003)

We report the growth of the half-Heusler alloy NiMnSb on InP (001) by molecular-beam epitaxy using a lattice-matched (In,Ga)As buffer. High-resolution x-ray diffraction confirms a high crystalline quality. Spot-profile analysis low-energy electron diffraction measurements show well-defined surface reconstructions. The samples show the expected high Curie temperature and an uniaxial anisotropy. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1594286]

Half-Heuslers are nearly epitaxial with GaAs: The possibility of spin injection into semiconductors. This is important for any spin-based electronics.

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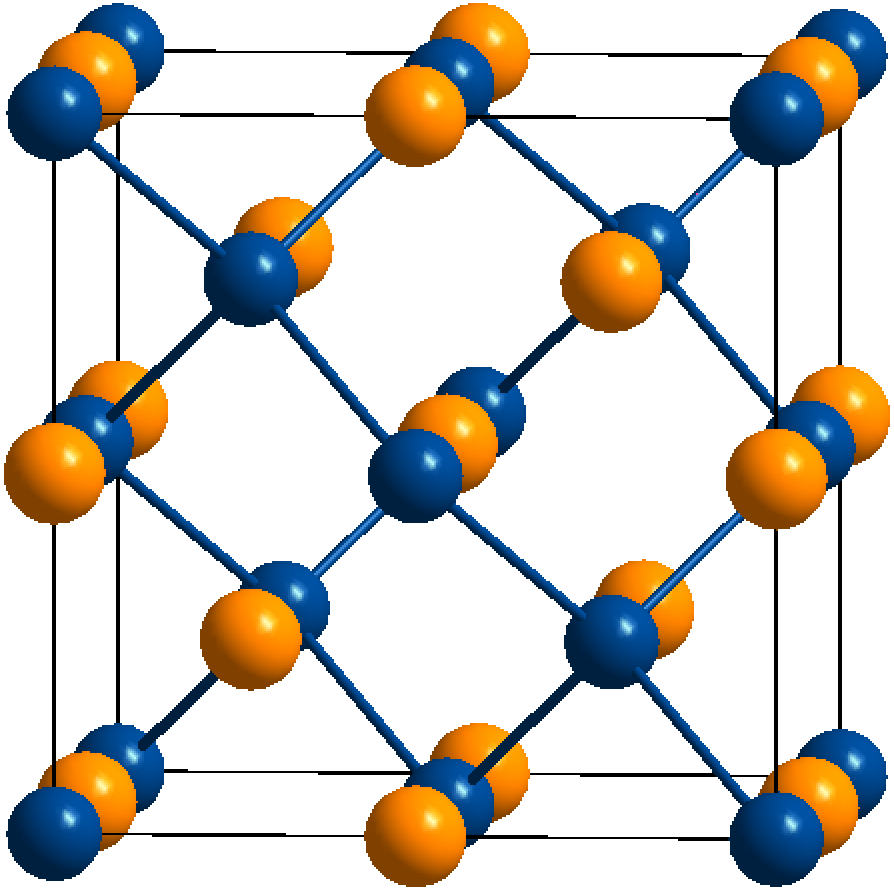
Semiconducting and half-metallic behavior in Heusler compounds



The Zintl-Klemm concept and valence compounds: The example of LiAl (Li^+Al^-). Al^- is isoelectronic with C and forms a diamond lattice. The Li^+ ions stuff the Al^- lattice. Note the 8 electron rule operates.

Semiconducting and half-metallic behavior in Heusler compounds

The contribution of Whangbo *et al.* (2000), also Öğüt and Rabe (1995), Galanakis *et al.* (2002):

Instead of 8 electrons, 18 valence electrons suggests a gap. For example, TiNiSn and TiCoSb are 18 electron semiconductors.

TiCoSb = Ti^{4+} + $(CoSb)^{4-}$; $(CoSb)^{4-}$ = GaSb forming a zinc-blende lattice. Ti is in the octahedral hole.

$18e^{-} = d^{0} + d^{10} + s^{2}p^{6}$

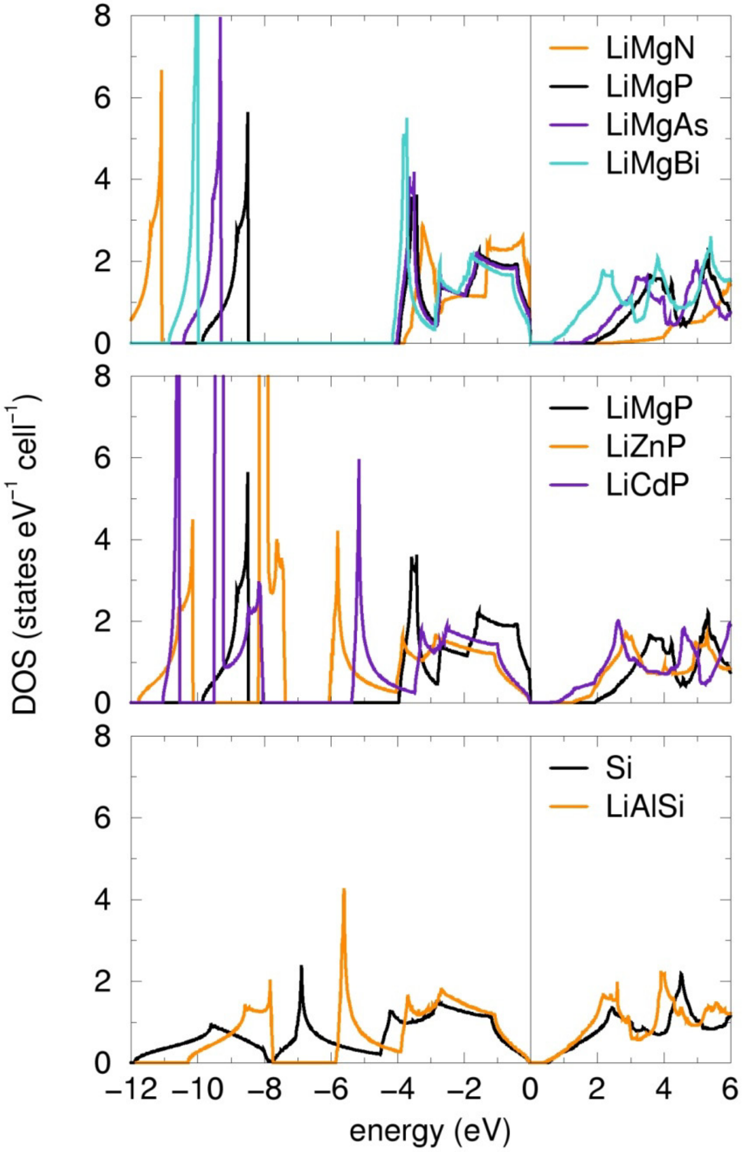
Semiconducting and half-metallic behavior in Heusler compounds

Magnetic compounds (Whangbo): If the number of electrons is 17 or 19, a paramagnet or a Stoner ferromagnet results depending on the DOS at the Fermi energy. If it is 22 (MnNiSb), a local-moment ferromagnet is formed.

What are the precise nature of the gaps ? How do different constituent elements affect the gaps ? How good is the covalent description of the zinc-blende lattice ?

Gaps in semiconductors as well as in the half-metals.

Semiconducting and half-metallic behavior in Heusler compounds



LMTO DOS of 8e half-Heuslers indicates a strong dependence of the band gap on composition of the zinc-blende lattice.

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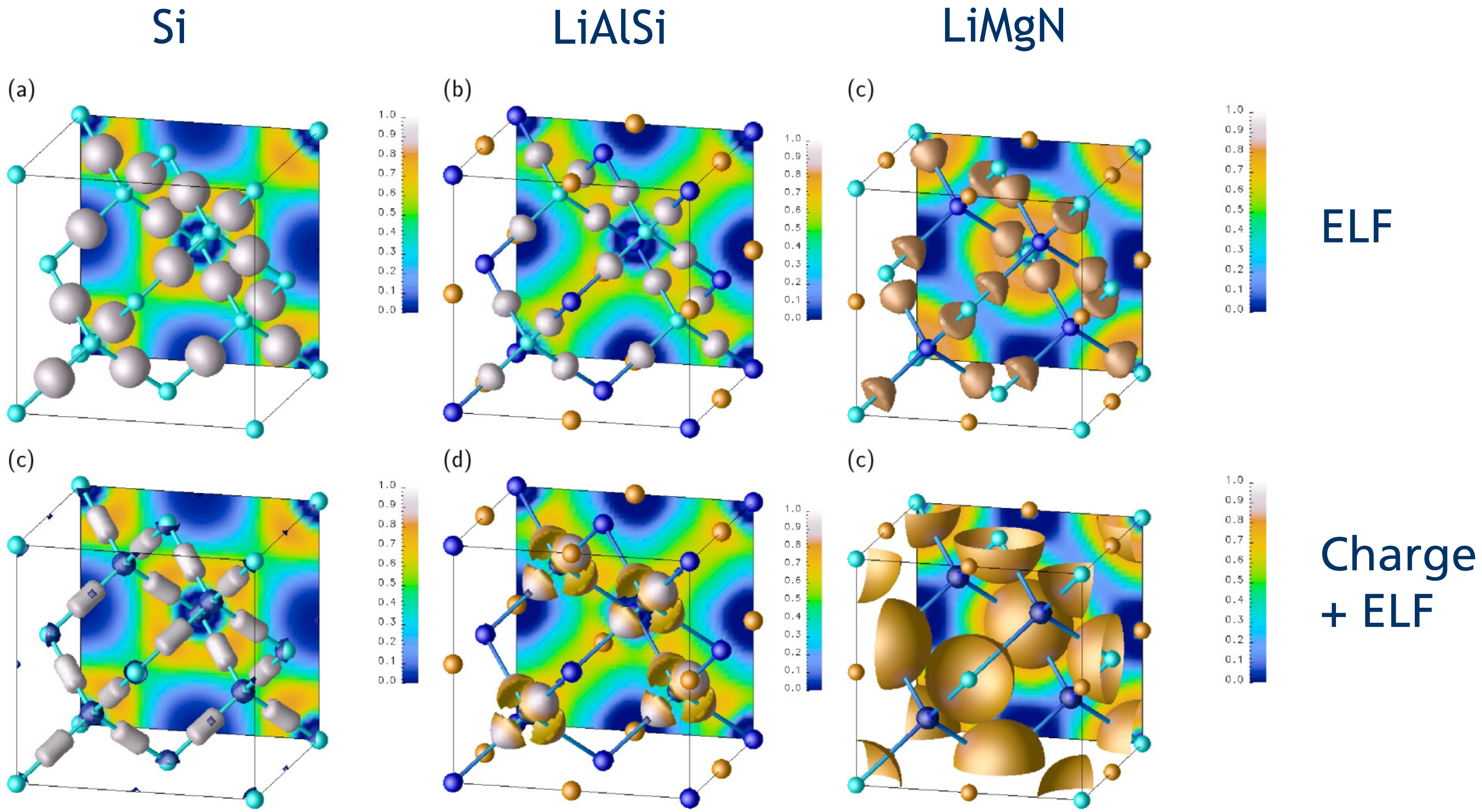
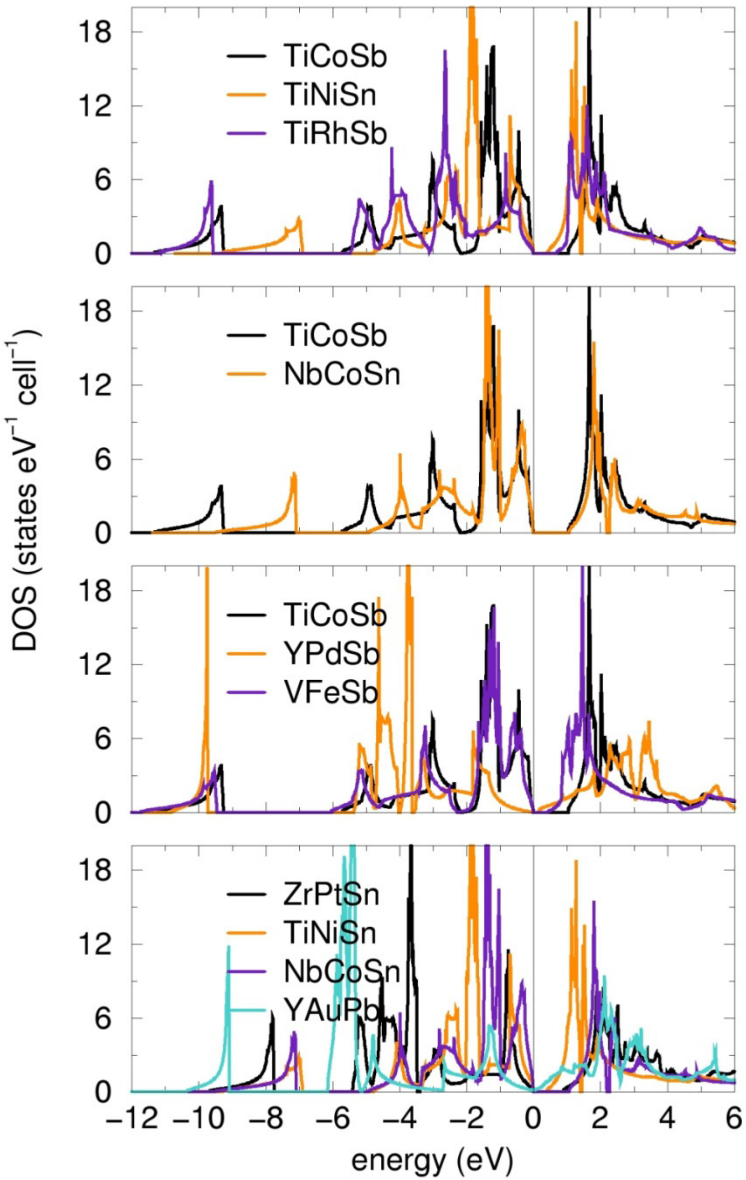
Semiconducting and half-metallic behavior in Heusler compounds



Electron localization functions of the 8e compounds show strongly localized bonding.

Semiconducting and half-metallic behavior in Heusler compounds



LMTO DOS of 18e half-Heuslers also show rather simple trends in their band gaps.

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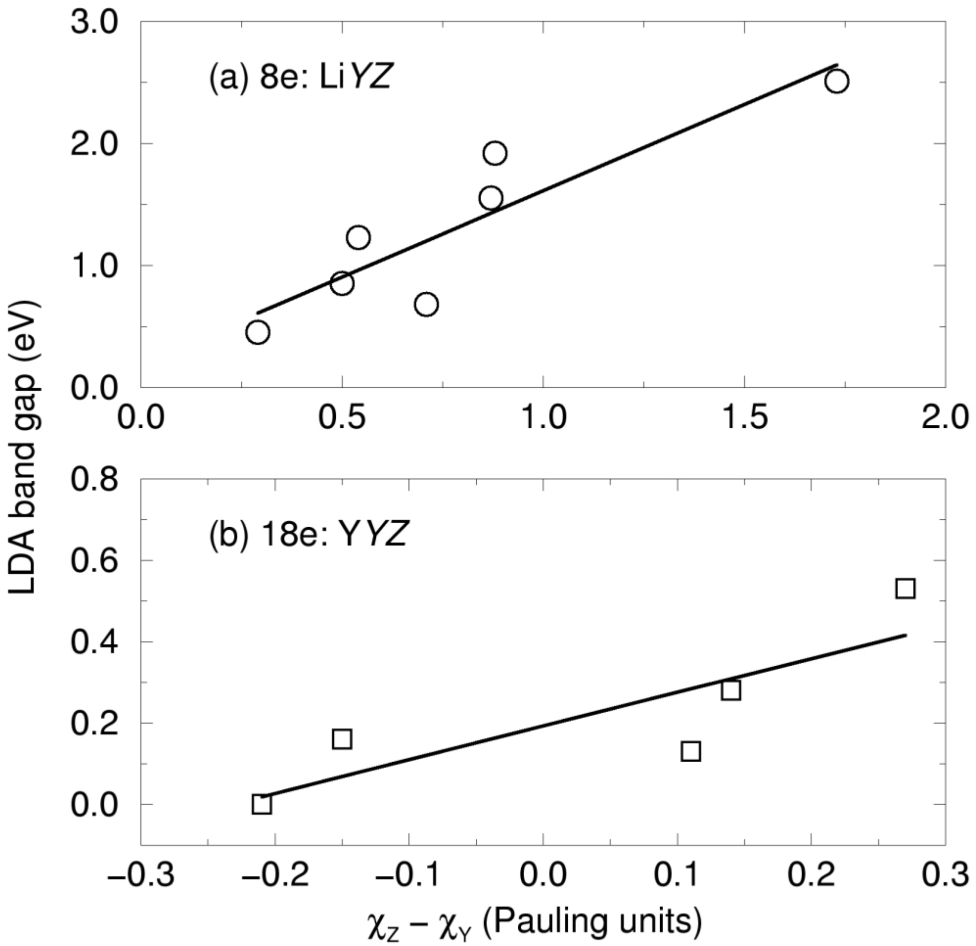
Semiconducting and half-metallic behavior in Heusler compounds



The band gaps of some 8e and 18e half-Heuslers depend on the electronegativity of the ions in the zinc-blende framework.

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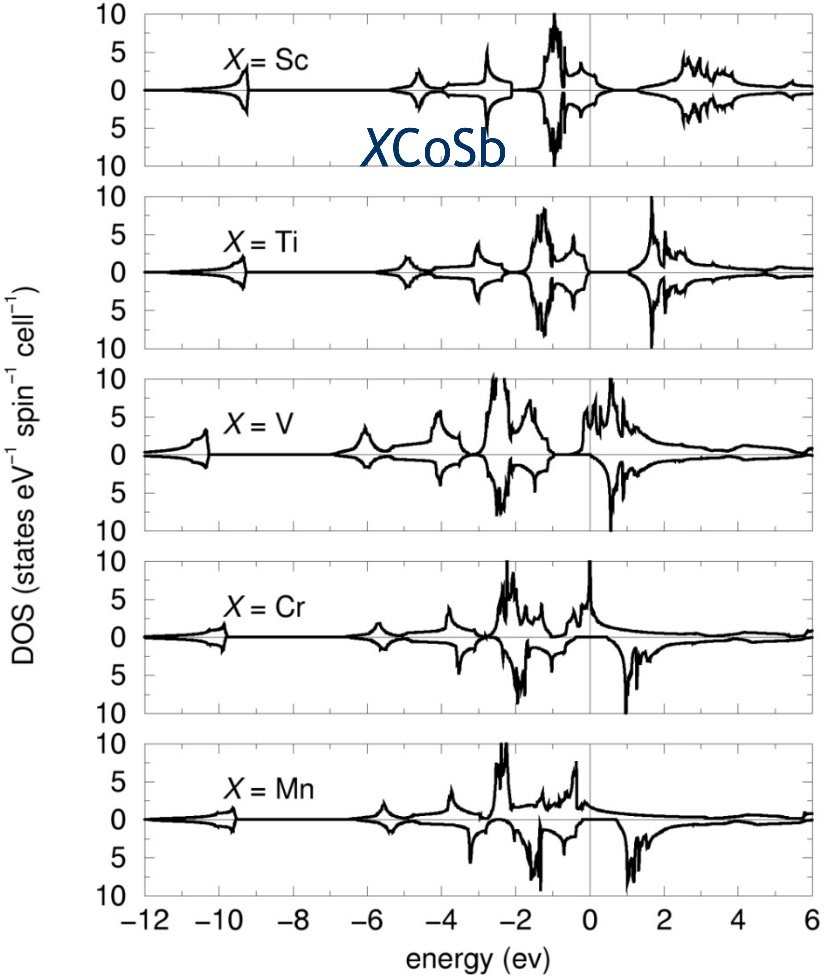
Semiconducting and half-metallic behavior in Heusler compounds



n=-1

n=0

n=1

n=2

n=3

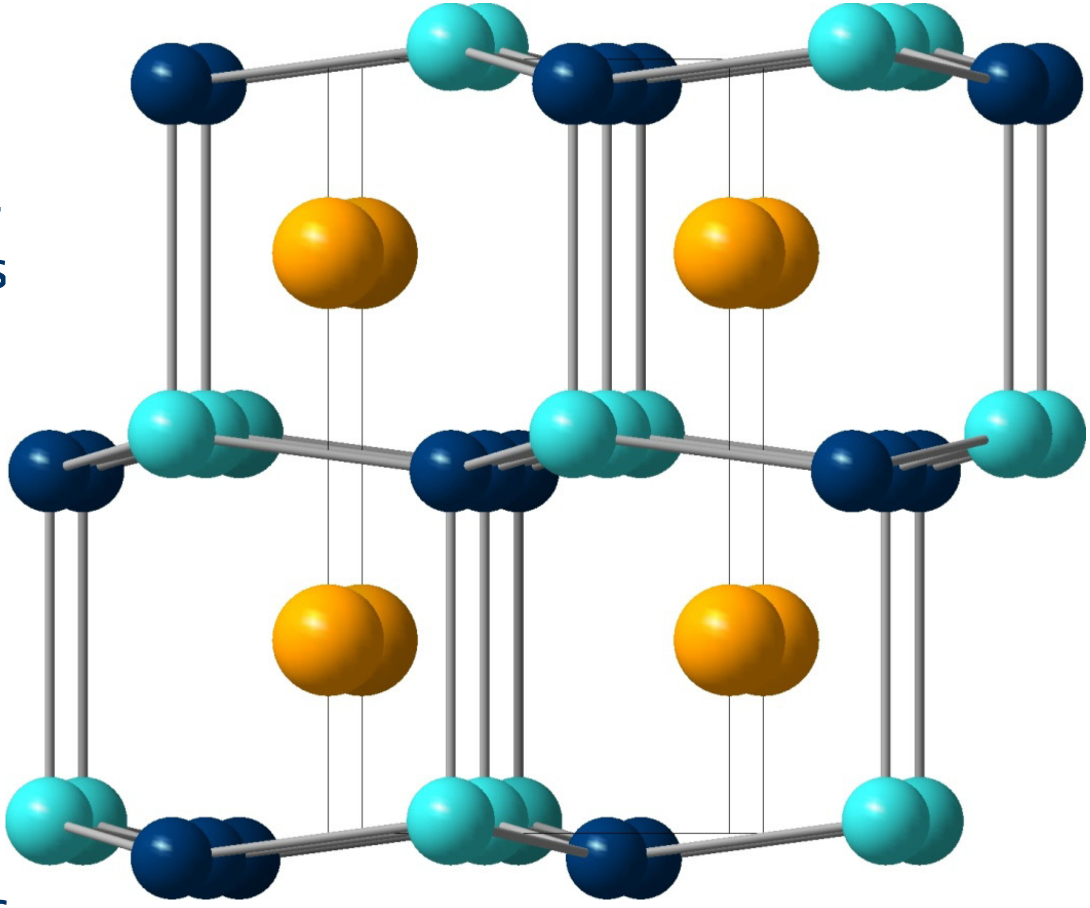
Magnetic half-Heusler compounds can also be thought of as stuffed zinc-blendes. The band/half-metallic gaps are a little more complex.

H. C. Kandpal, C. Felser, and R. Seshadri, *J. Phys. D.* **39** (2006) 776-785.

Semiconducting and half-metallic behavior in Heusler compounds

Can one equivalently look for stuffed wurtzites: *hexagonal* semiconducting and half-metallic analogues of the half-Heuslers ? The structure type is known: LiGaGe (SG. $P6_3mc$). Many possibly incorrect determinations in $CaIn_2$ structure.

The structure shown here is CePdSb. Best described as Ce^{3+} stuffing a $(PdSb)^{3-}$ wurtzite lattice, although the $(PdSb)^{3-}$ network is nearly flat/graphitic.



F. Casper, C. Felser, R. Seshadri, C. P. Sebastian, and R. Pöttgen, *J. Phys. D.* **41** (2008) 035002.

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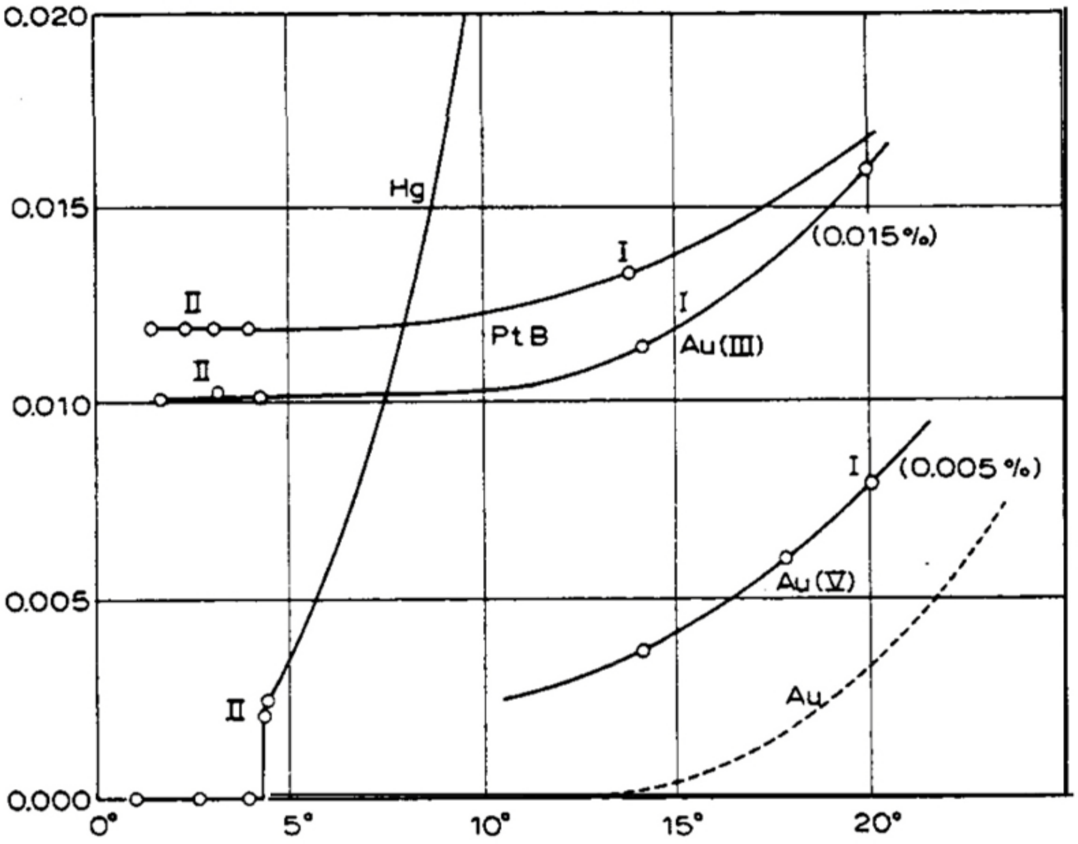
Superconductivity



Investigations into the Properties of Substances at Low Temperatures, which Have Led, amongst Other Things, to the Preparation of Liquid Helium [1913 Physics Nobel, Heike Kammerlingh Onnes]

Hg becomes superconducting, *ie.* loses all at electrical resistance at a little above 4 K

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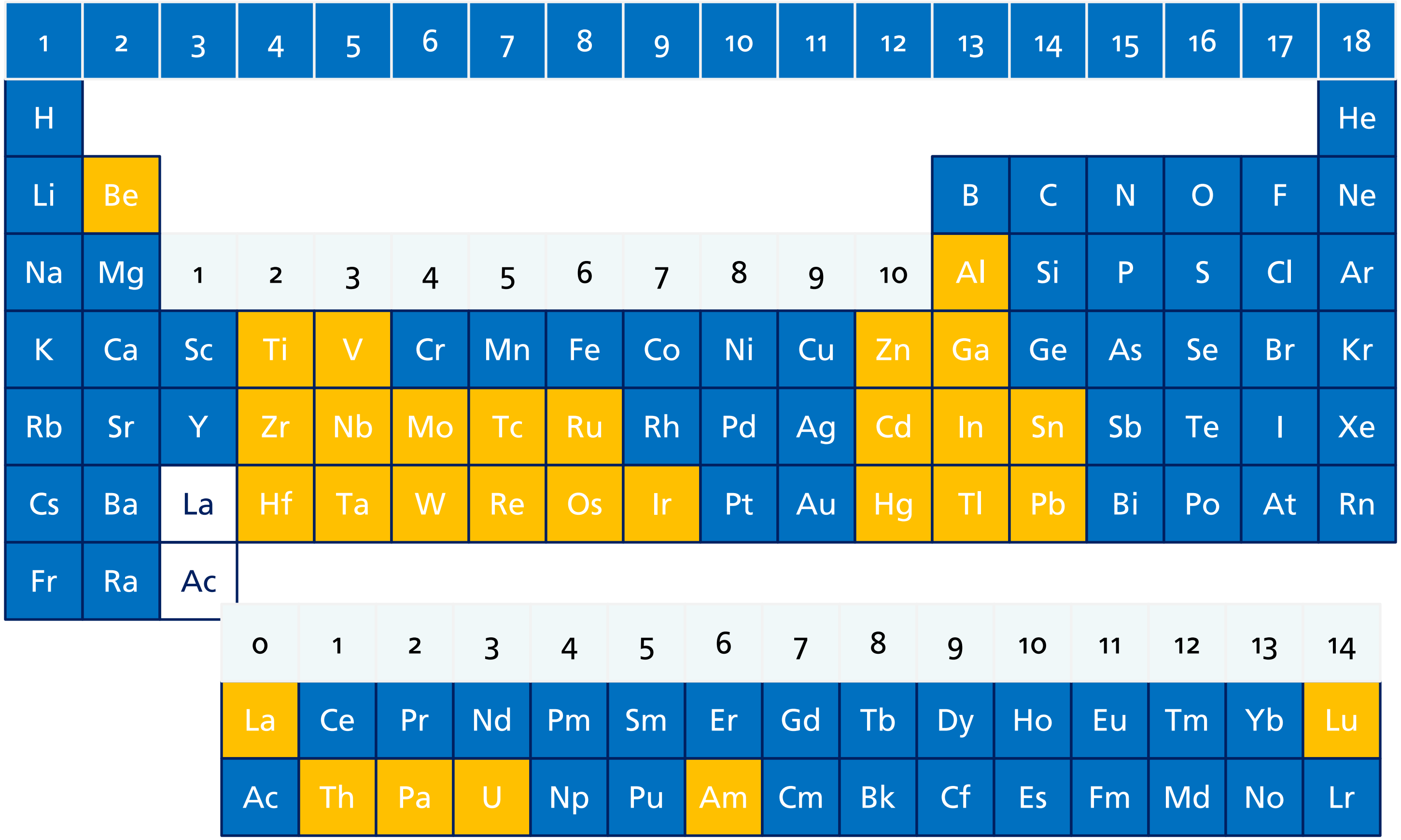
Superconductivity

The superconducting elements (bulk, ambient pressure)



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	1	2	3	4	5	6	7	8	9	10	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
La	Ce	Pr	Nd	Pm	Sm	Er	Gd	Tb	Dy	Ho	Eu	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

CRC Handbook of Physics and Chemistry [http://www.hbcpnetbase.com/]

Superconductivity

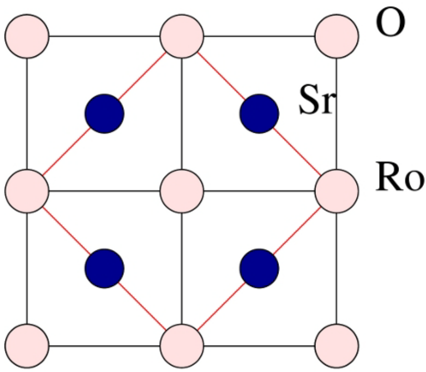
High T_C copper oxides References:

- R. J. Cava, Oxide Superconductors, *J. Am. Ceram. Soc.* **83** (2000) 5-28.
- J. Orenstein and A. J. Millis, Advances in the physics of high-temperature superconductivity, Science 288 (2000) 468-474.
- E. Pavarini *et al.* Band-structure trend in hole-doped cuprates and correlation with $T_{c\,\max}$, Phys. Rev. Lett. 87 (2001) 047003(1-4).

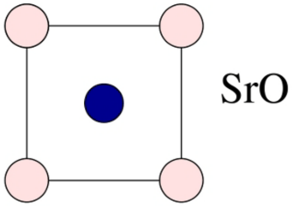
All high-T_c copper oxides can be described as possessing CuO_2 square planes and a charge reservoir that often comprises rock-salt like units.

We will start by examining the how perovskites can be thought to comprise rock-salt slabs interleaved with "perovskite" MO_2.

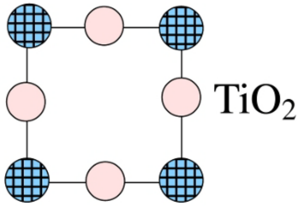
Superconductivity



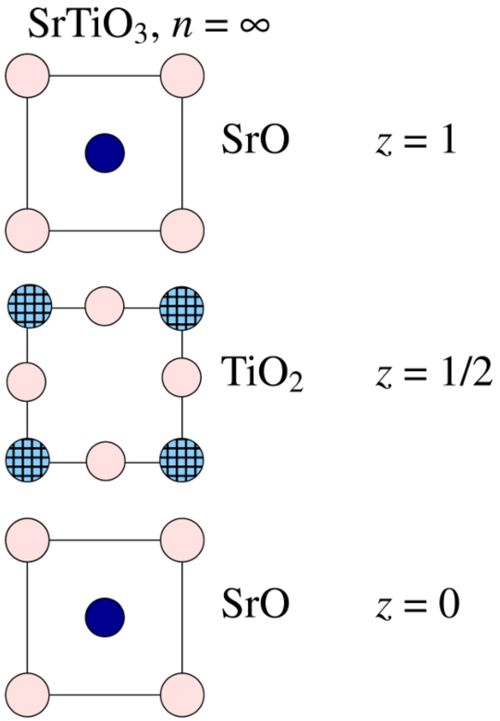
Rock salt lattice



Rock salt layer motif



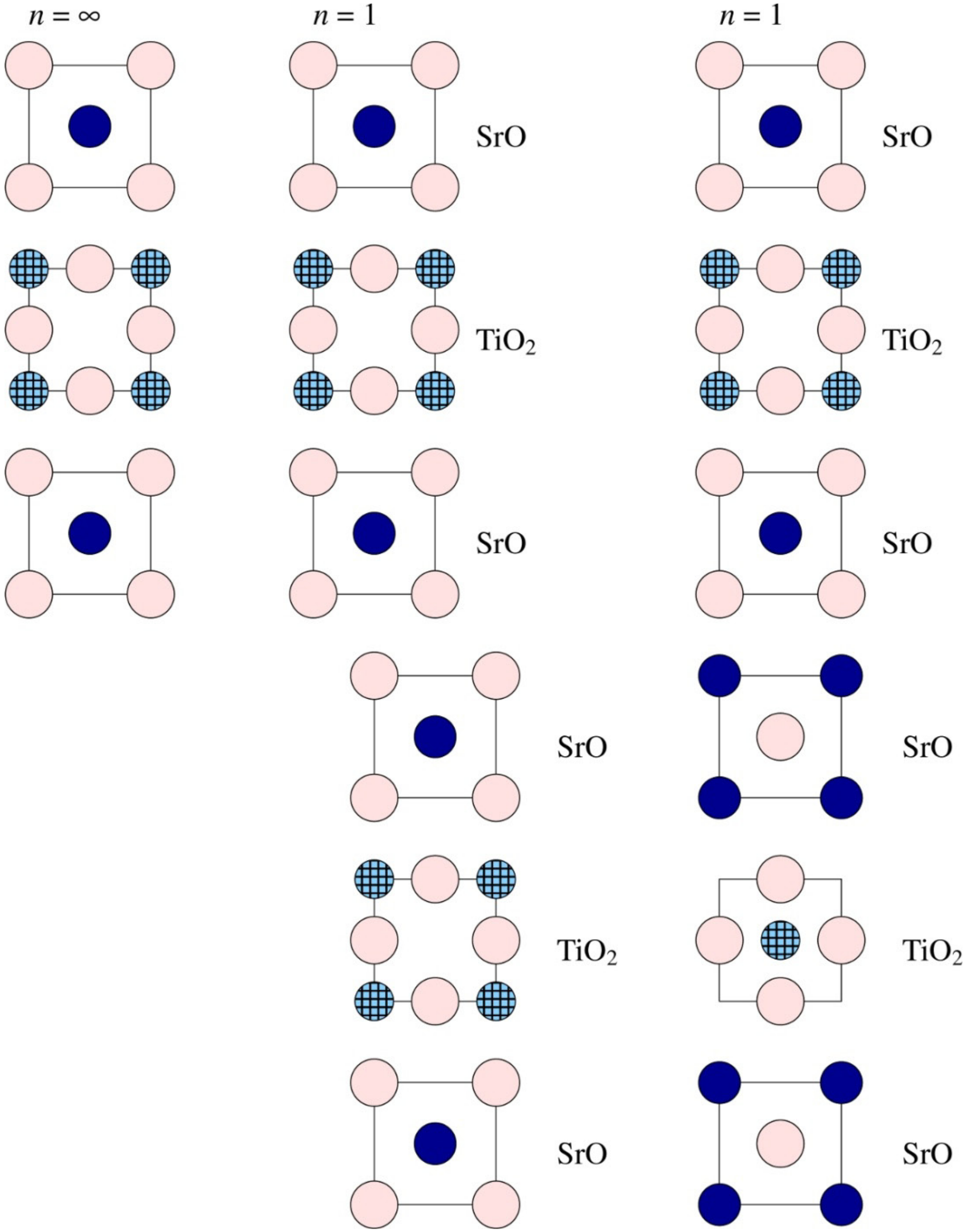
Perovskite layer motif



The perovskite structure ($SrTiO_3$ as an example) can be broken down into SrO and TiO_2 layers.

Talk about SPuDS

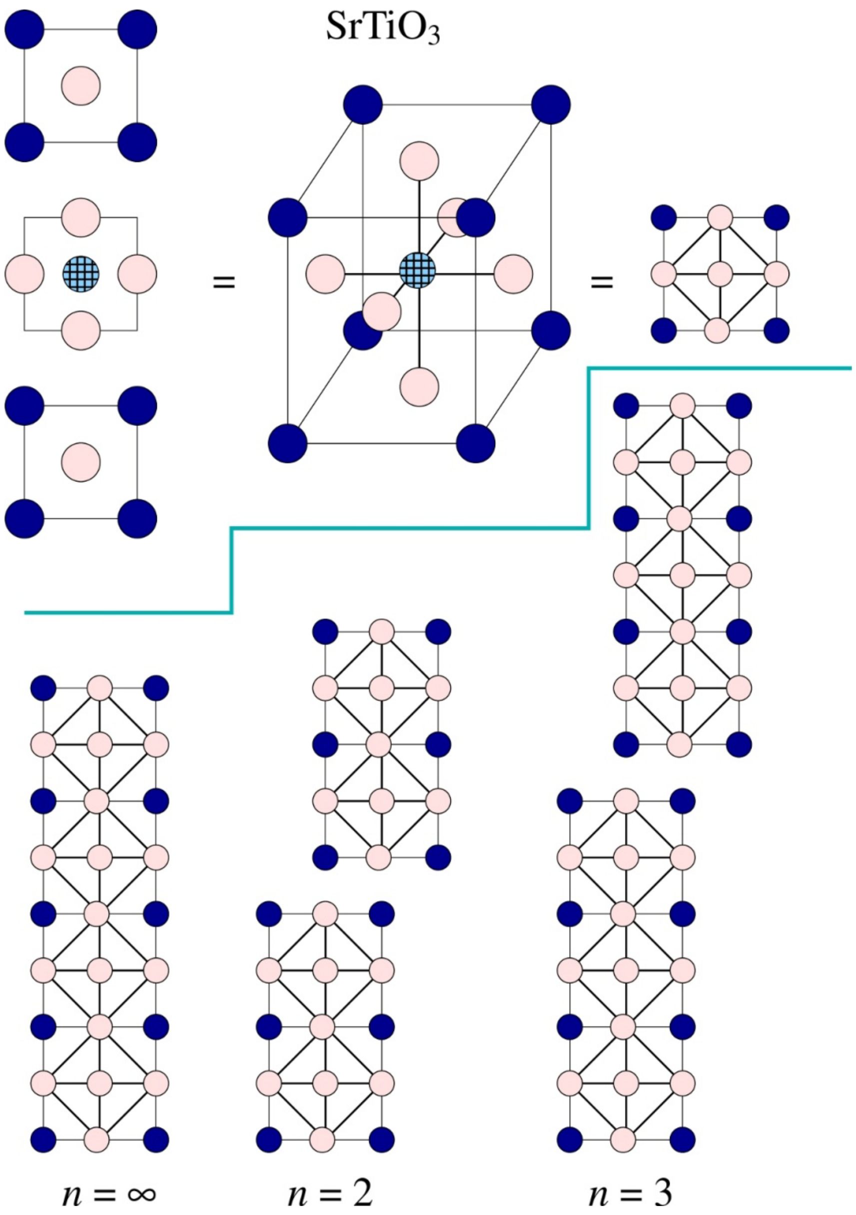
Superconductivity



The Ruddlesden-Popper compounds $(SrO)(SrTiO_3)_n$ can be built by breaking up the SrTiO3 ($n = \infty$) structure and inserting SrO slabs.

The n = 1 structure (also called the K_2NiF_4 structure is shown here.

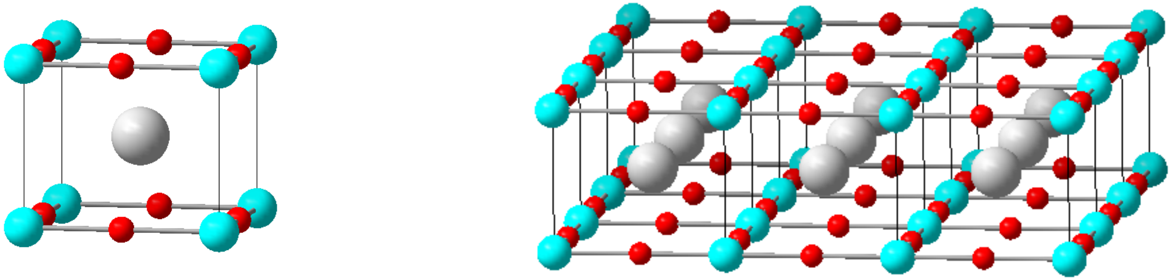
Superconductivity



The series of Ruddlesden-Popper compounds:

All the layered compounds are tetragonal, in the space group *I4/mmm*, provided the octahedra don't tilt or rotate.

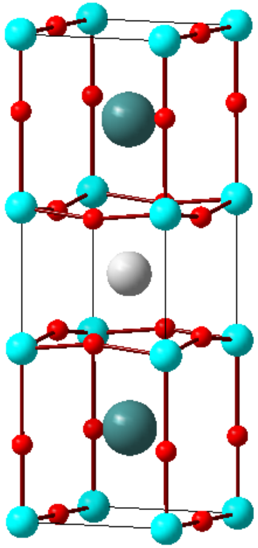
Superconductivity

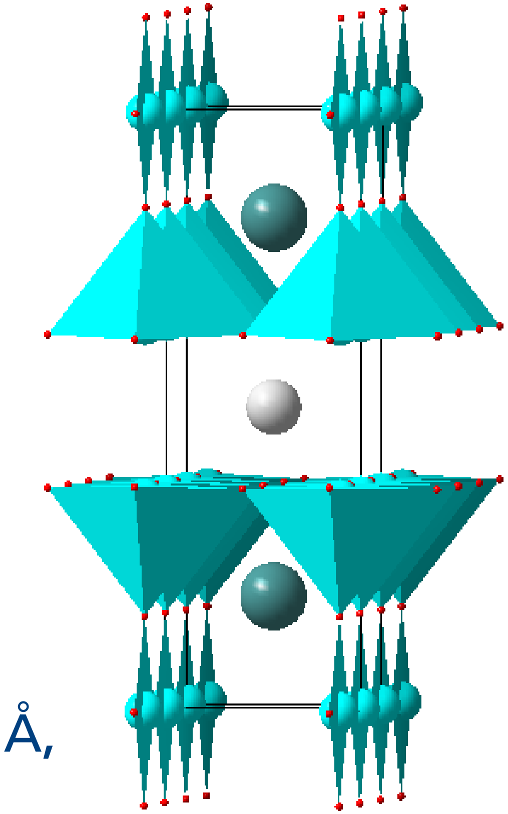


Views of the "parent" compound that only has CuO_2 sheets: $(Ca_{0.86}Sr_{0.14})CuO_2$

*P*4/*mmm*, *a* = 3.8611 Å, *c* = 3.1995 Å
Cu at 0 0 0
Ca/Sr at 0.5 0.5 0.5
O at 0 0.5 0

Superconductivity

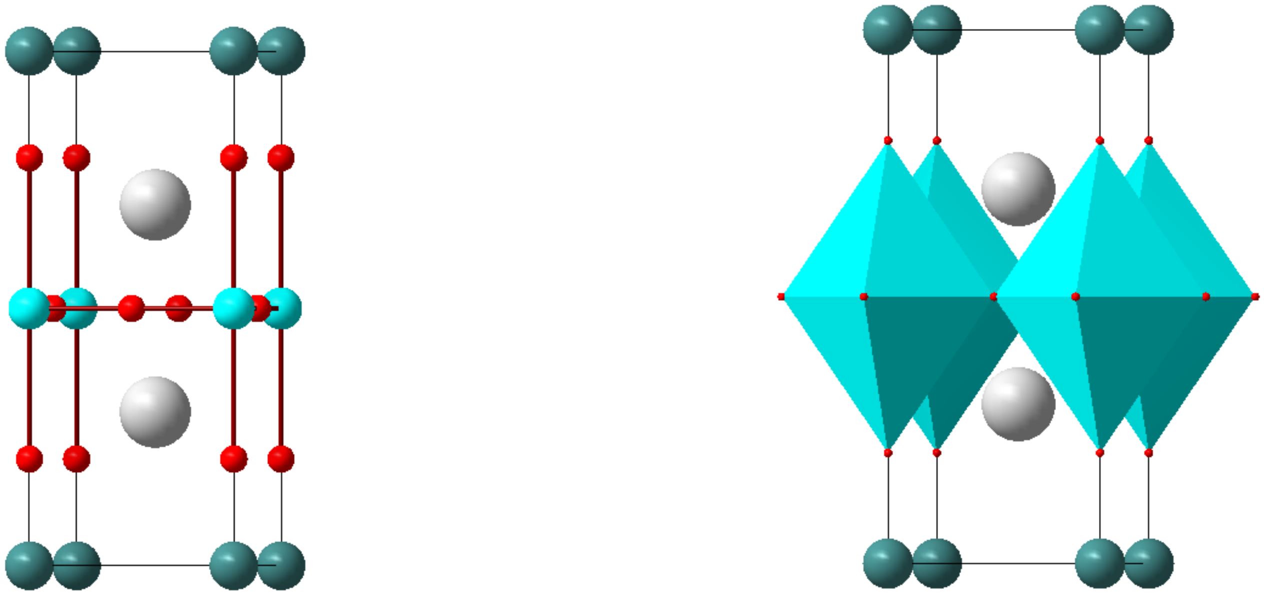




$YBa_2Cu_3O_7$: the "123" compound
Pmmm, *a* = 3.8203 Å, *b* = 3.8855 Å,
c = 11.6835 Å
Y at 0.5 0.5 0.5, Ba at 0.5 0.5 0.18393
Cu1 at 0 0 0, Cu2 at 0 0 0.3550
O1 at 0 0.5 0, O2 at 0.5 0 0.37819
O3 at 0 0.5 0.37693, O4 at 0 0 0.15840

Note the chains and sheets !

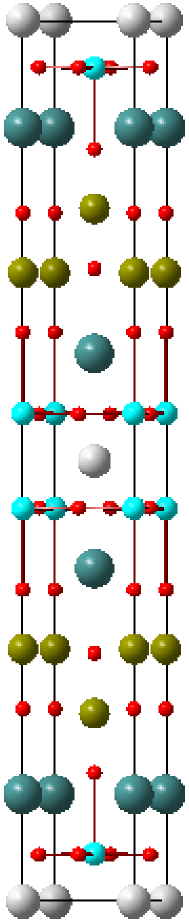
Superconductivity



Note J-T distorted CuO_6 octahedra, and HgO_2 rods (linear)

$HgBa_2CuO_4$: the class of compounds with the highest T_c's.
*P*4/*mmm*, *a* = 3.87630 Å, *c* = 9.50720 Å
Hg at 0 0 0, Ba at 0.5 0.5 0.2986, Cu at 0 0 0.5,
O1 at 0.5 0 0.5 and O2 at 0 0 0.2075

Superconductivity



Ca

CuO2

CuO2

BaO

TlO

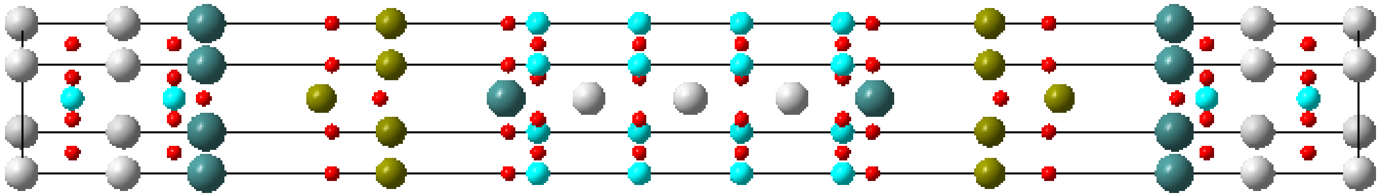
TlO

BaO

The O in the Tl layer is disordered. This is not shown in this depiction.

The two-layer Tl-based superconductor,
$Tl_2Ba_2CaCu_2O_8$
$I4/mmm$, a = 3.8550 Å, c = 29.318 Å

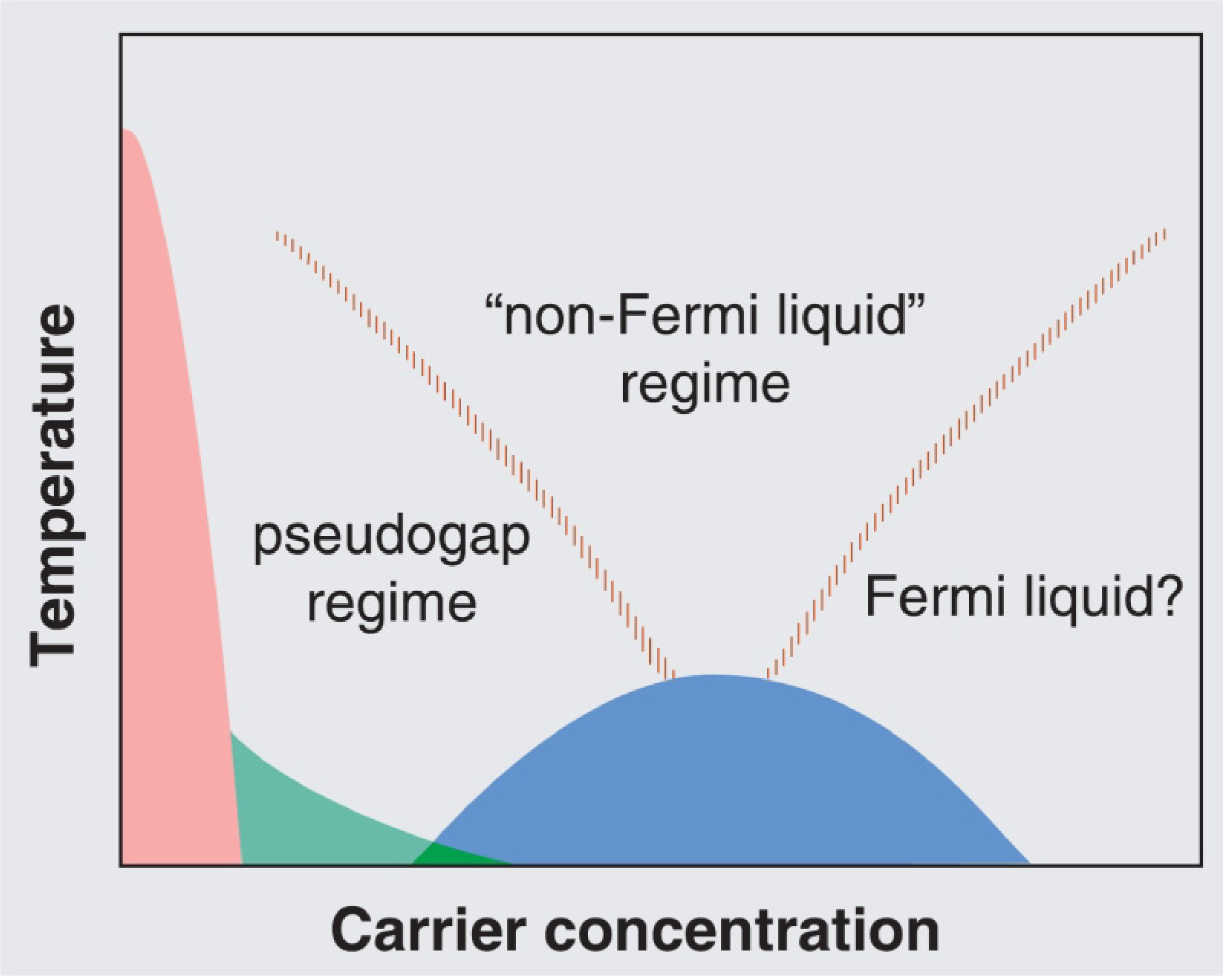
Superconductivity



The 4-copper layer compound
$Bi_2Sr_2Ca_3Cu_4O_{12}$

Many Bi superconductors display incommensurate modulation in the Bi-O layers. See for example, Petriček *et al. Phys. Rev. B* **42** (1990) 387.

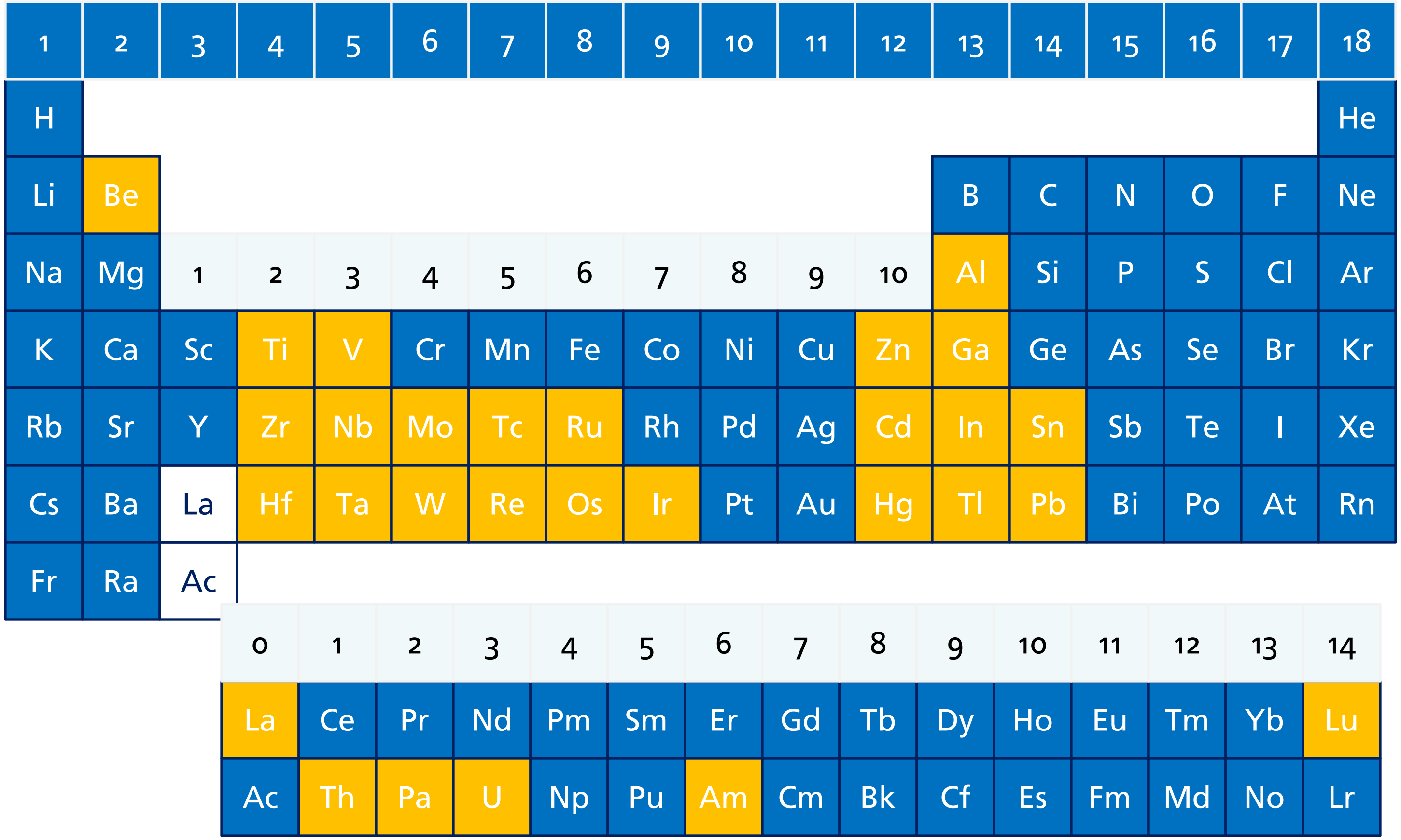
Superconductivity



Generic phase diagram of high-*T*c compounds (after Orenstein and Millis, Science, 2000.

Superconductivity

The superconducting elements (bulk, ambient pressure)



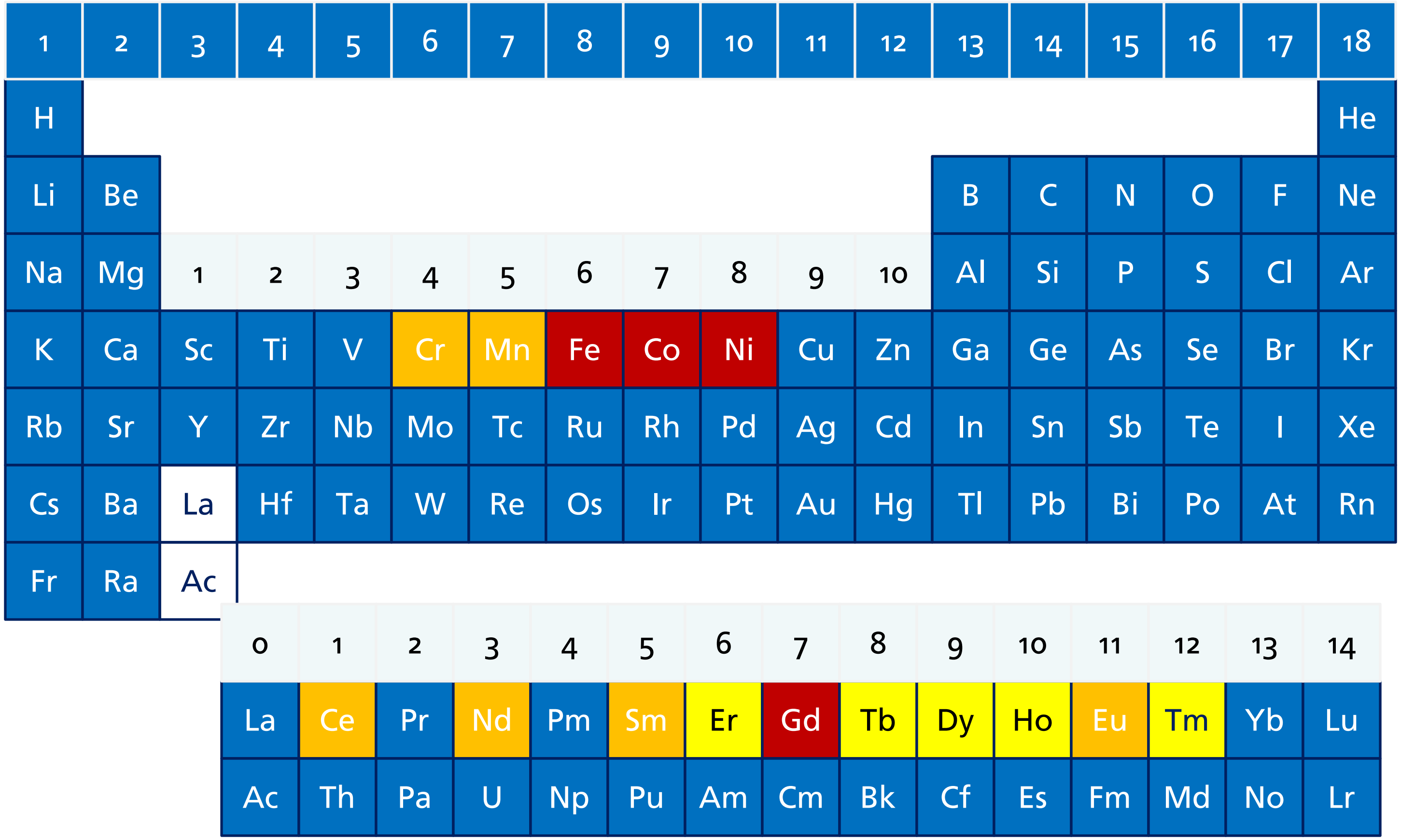
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	1	2	3	4	5	6	7	8	9	10	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
La	Ce	Pr	Nd	Pm	Sm	Er	Gd	Tb	Dy	Ho	Eu	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

CRC Handbook of Physics and Chemistry [http://www.hbcpnetbase.com/]

Superconductivity

The magnetic(ally ordered) elements [Ferromagnetic or antiferromagnetic]



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	1	2	3	4	5	6	7	8	9	10	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
La	Ce	Pr	Nd	Pm	Sm	Er	Gd	Tb	Dy	Ho	Eu	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fe ferromagnet

Mn antiferro

Tm mixed

Magnetism and superconductivity are largely incompatible

CRC Handbook of Physics and Chemistry [http://www.hbcpnetbase.com/]

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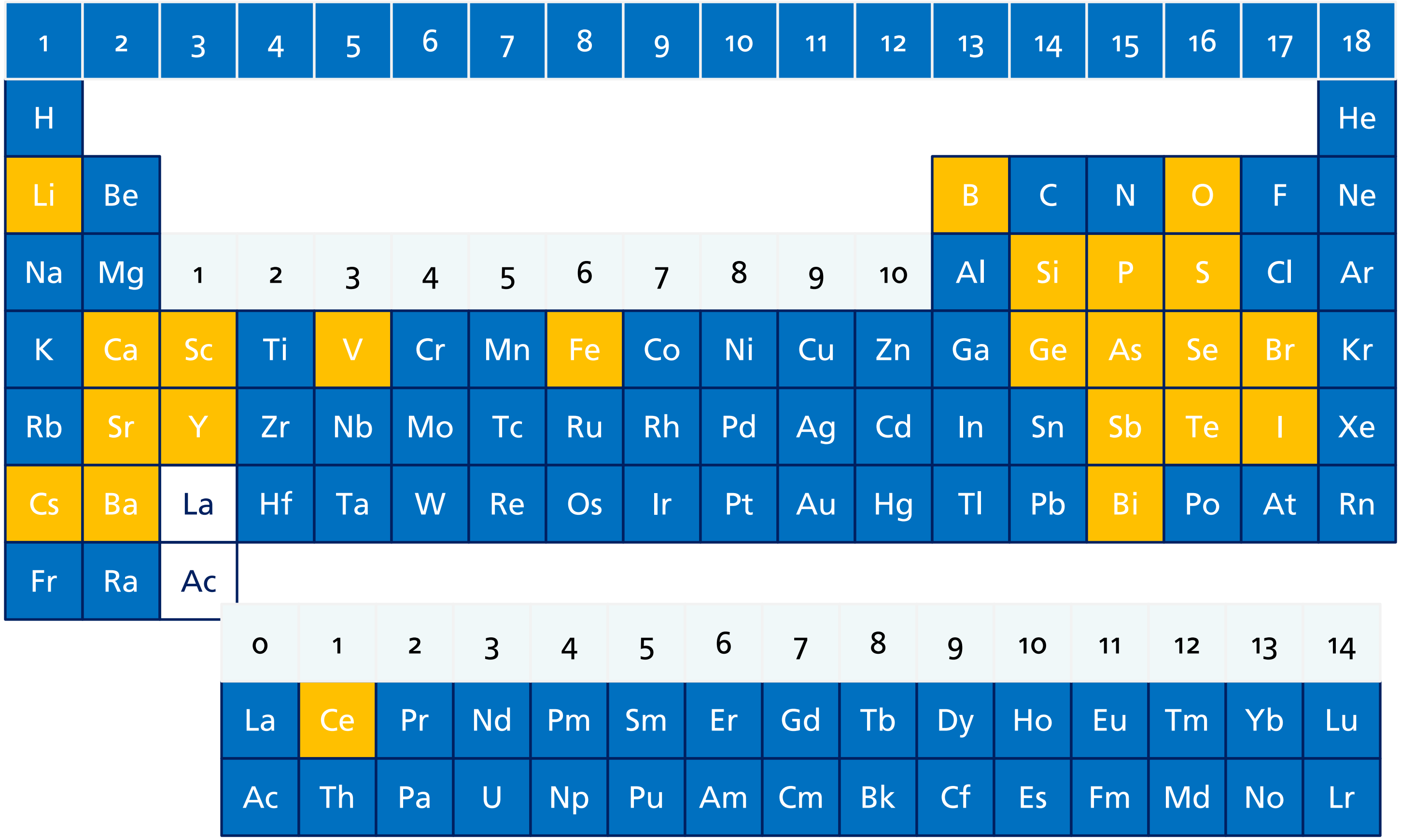
Superconductivity

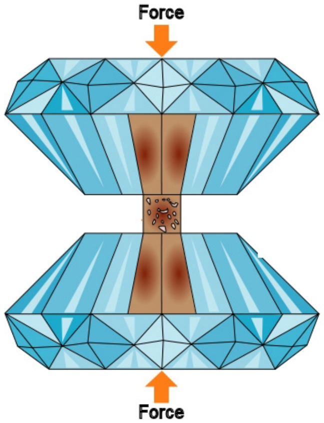
Some (new) superconducting elements (under pressure)



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	1	2	3	4	5	6	7	8	9	10	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
La	Ce	Pr	Nd	Pm	Sm	Er	Gd	Tb	Dy	Ho	Eu	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

High pressures (above ~10 GPa) generated with a diamond anvil cell.

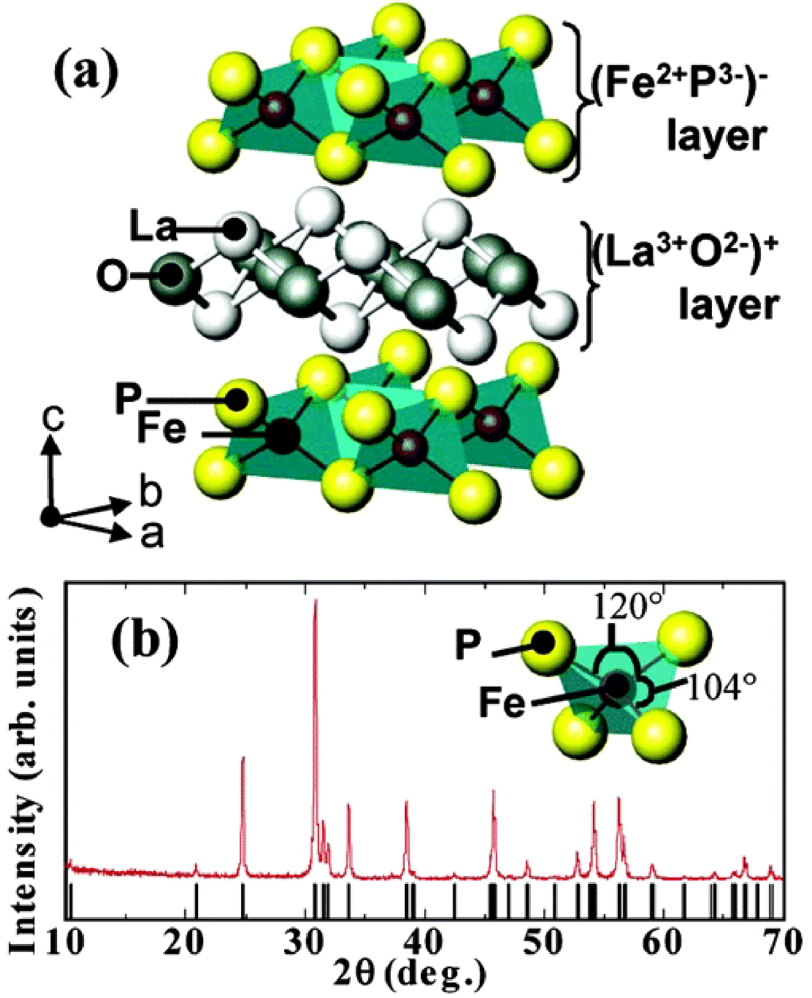


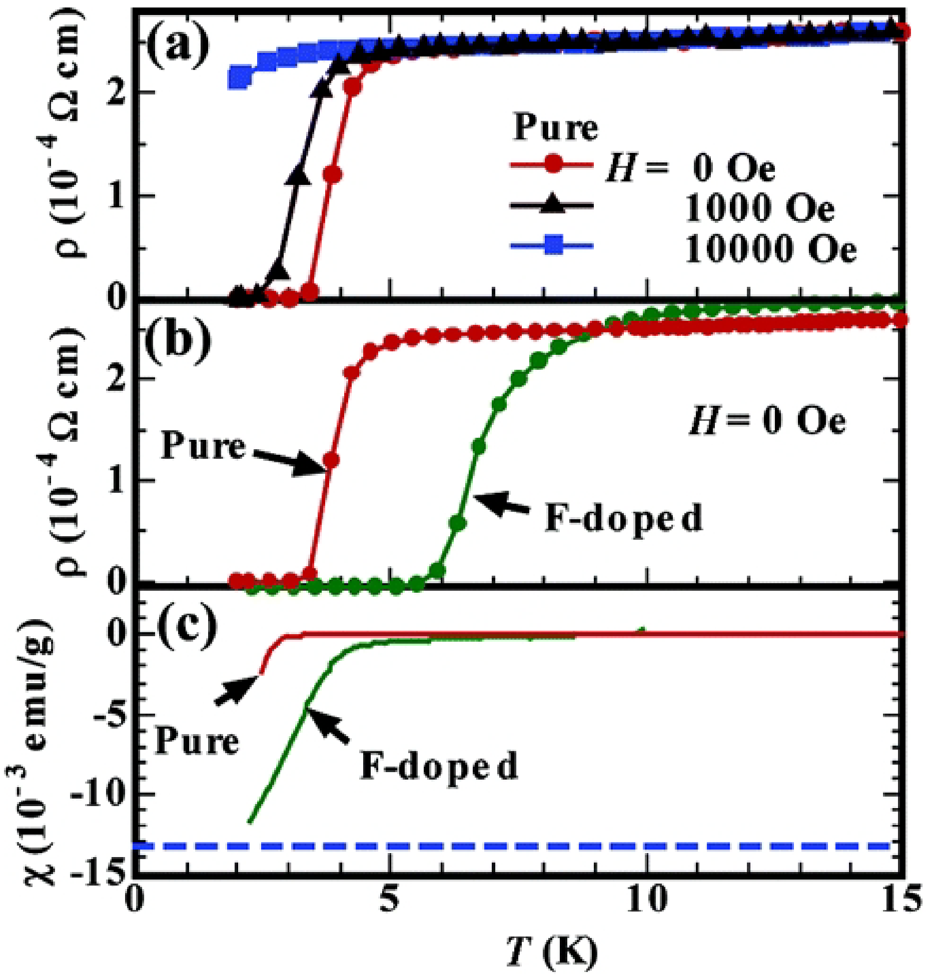
Pressure can drastically change electronic structure (for *eg.* Ba behaves like a transition metal)

Buzea, Robbie, *Supercond. Sci. Technol.* **18** (2005) R1-R8.

impetus mutat res

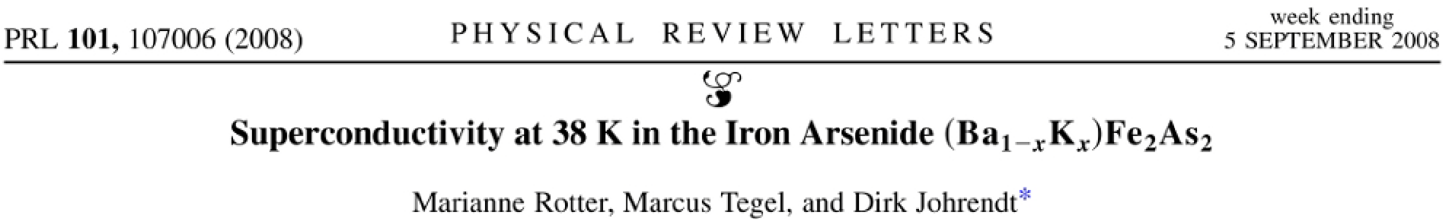
Superconductivity





Kamihara, Hiramatsu, Hirano, Kawamura, Yanagi, Kamiya, Hosono, *J. Am. Chem. Soc.* **128** (2006) 10012.

Superconductivity



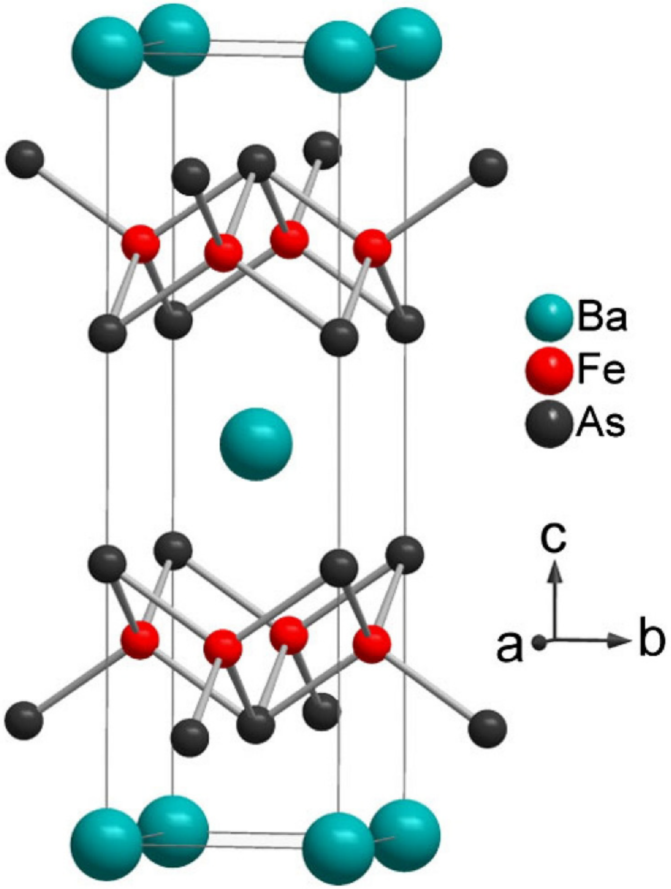
PRL **101,** 107006 (2008)

PHYSICAL REVIEW LETTERS

week ending
5 SEPTEMBER 2008

Superconductivity at 38 K in the Iron Arsenide $(Ba_{1-x}K_x)Fe_2As_2$

Marianne Rotter, Marcus Tegel, and Dirk Johrendt*



Superconductivity in arsenides with the $ThCr_2Si_2$ crystal structure.

Superconductivity

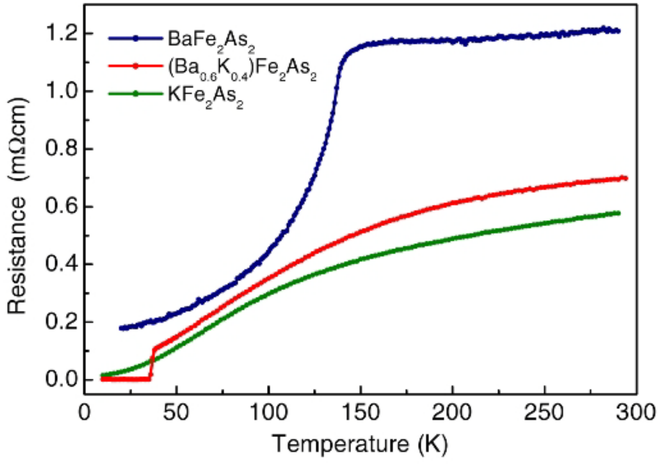


FIG. 3 (color online). Electrical resistance of BaFe$_2$As$_2$, KFe$_2$As$_2$, and (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$.

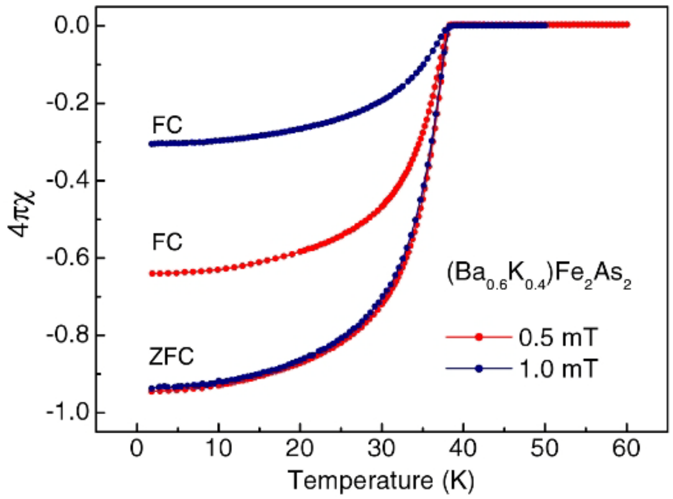


FIG. 5 (color online). Magnetic susceptibility of (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$ at 0.5 and 1 mT. FC is field cooled; ZFC is zero-field cooled.

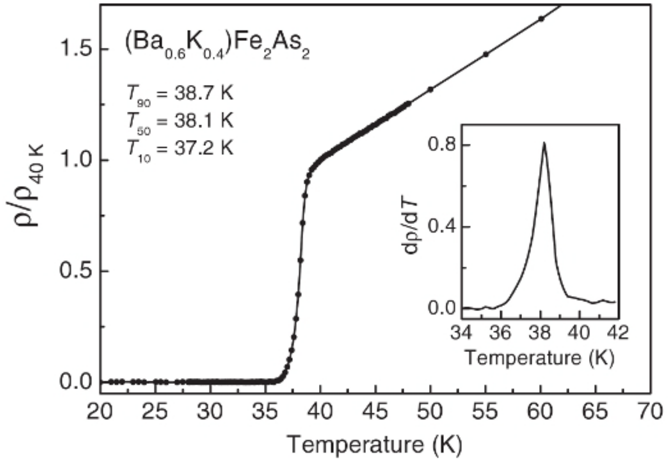
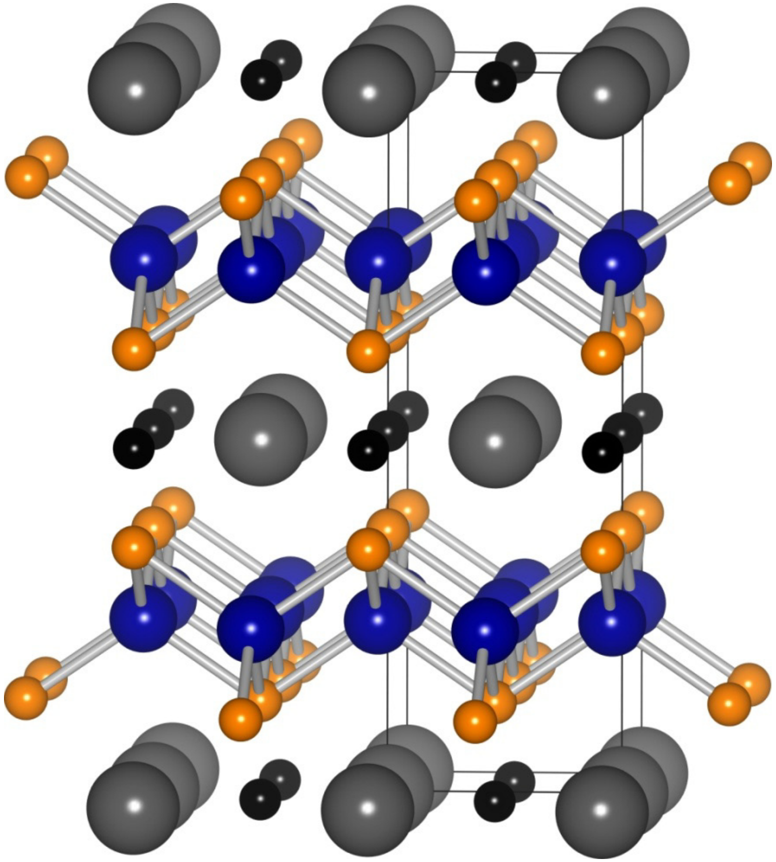


FIG. 4. Resistivity transition of (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$.

Characterization of the superconducting state.

Superconductivity

LuNi2B2C is a related superconductor with a stufed ThCr2Si2 crystal structure.



Nagarajan, Mazumdar, Hossain, Dhar, Gopalakrishnan, Gupta, Godart, Padalia, Vijayaraghavan, Bulk superconductivity at an elevated temperature (*Tc*≊12 K) in a nickel containing alloy system Y-Ni-B-C, *Phys. Rev. Lett.* **72** (1994) 274;

Cava, Takagi, Zandbergen, Krajewski, Peck, Siegrist, Batlogg, van Dover, Felder, Mizuhashi, Lee, Eisaki, Uchida, Superconductivity in the quaternary intermetallic compounds $LnNi_2B_2C$, *Nature* **367** (1994) 252

2. Structure-composition-property relations in inorganic materials: Some examples of subscript engineering in luminescent, catalytic, and magnetic oxides

The game of x*

Composition, along with pressure and temperature, are key variables in the study of the properties of crystalline solids, and in the development of functionality:

Examples:

$La_{2-x}Sr_xCuO_4$: Superconductivity

$La_{1-x}Ca_xMnO_3$: Colossal magnetoresistance, charge-ordering

$PbZr_{1-x}Ti_xO_3$: Piezoelectric tuning

$Ba_{1-x}Sr_xTiO_3$: Capacitors

$V_{2-x}Cr_xO_3$: Insulator-metal transitions

*Referred to, on occasion, as subscript chemistry/engineering.

Phosphors for solid state lighting

Dr. Won-Bin Im [SSLEC]

Steve DenBaars, Hisahi Masui, Natalie Fellows

A. K. Cheetham [Cambridge]

Phosphors for solid state lighting

Incandescent (no ballast)	10—18 lm/W
Halogen incandescent (no ballast)	15—20
Compact fluorescent (incl. ballast)	35—60
Linear fluorescent (incl. ballast)	50—100
Metal halide (incl. ballast)	50—90
Cool white LED 5000 K (incl. driver)	47—64
Warm white LED 3300 K (incl. driver)	25—44

Source: DOE (http://www.netl.doe.gov/ssl/)

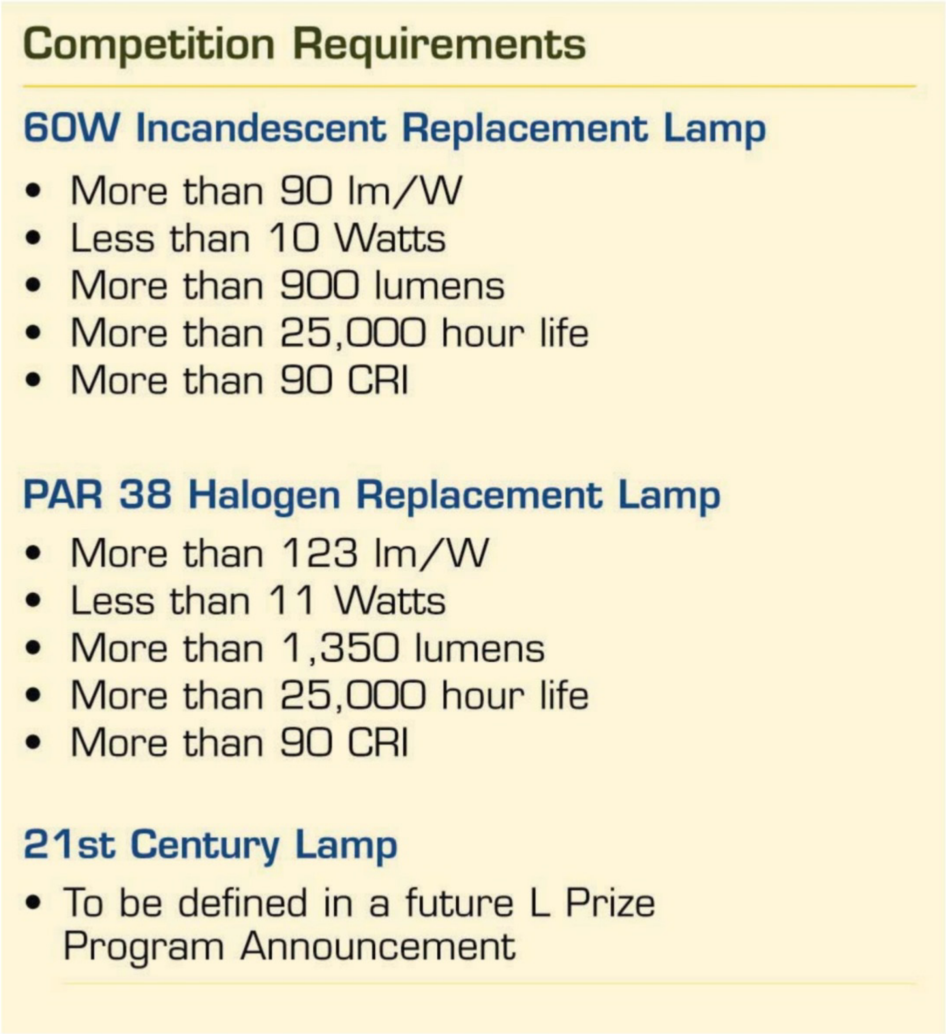
Phosphors for solid state lighting

The L Prize:

Supported by California utilities, the Department of Energy …

Assembly Bill (AB) 1109 — California Lighting Efficiency and Toxics Reduction Act

Goals: By 2018, reduce lighting energy consumption by 50% for residential indoor, and by 25% for commercial and outdoor



Competition Requirements

60W Incandescent Replacement Lamp

- More than 90 lm/W
- Less than 10 Watts
- More than 900 lumens
- More than 25,000 hour life
- More than 90 CRI

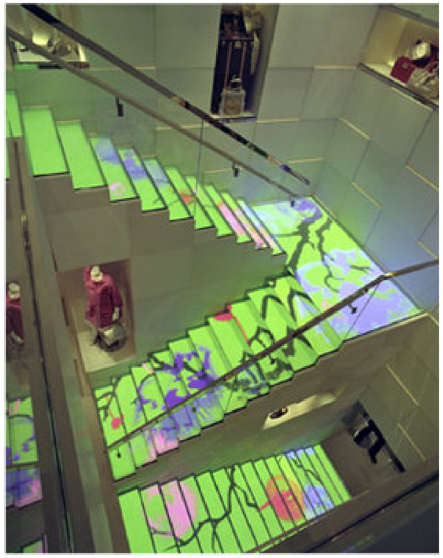
PAR 38 Halogen Replacement Lamp

- More than 123 lm/W
- Less than 11 Watts
- More than 1,350 lumens
- More than 25,000 hour life
- More than 90 CRI

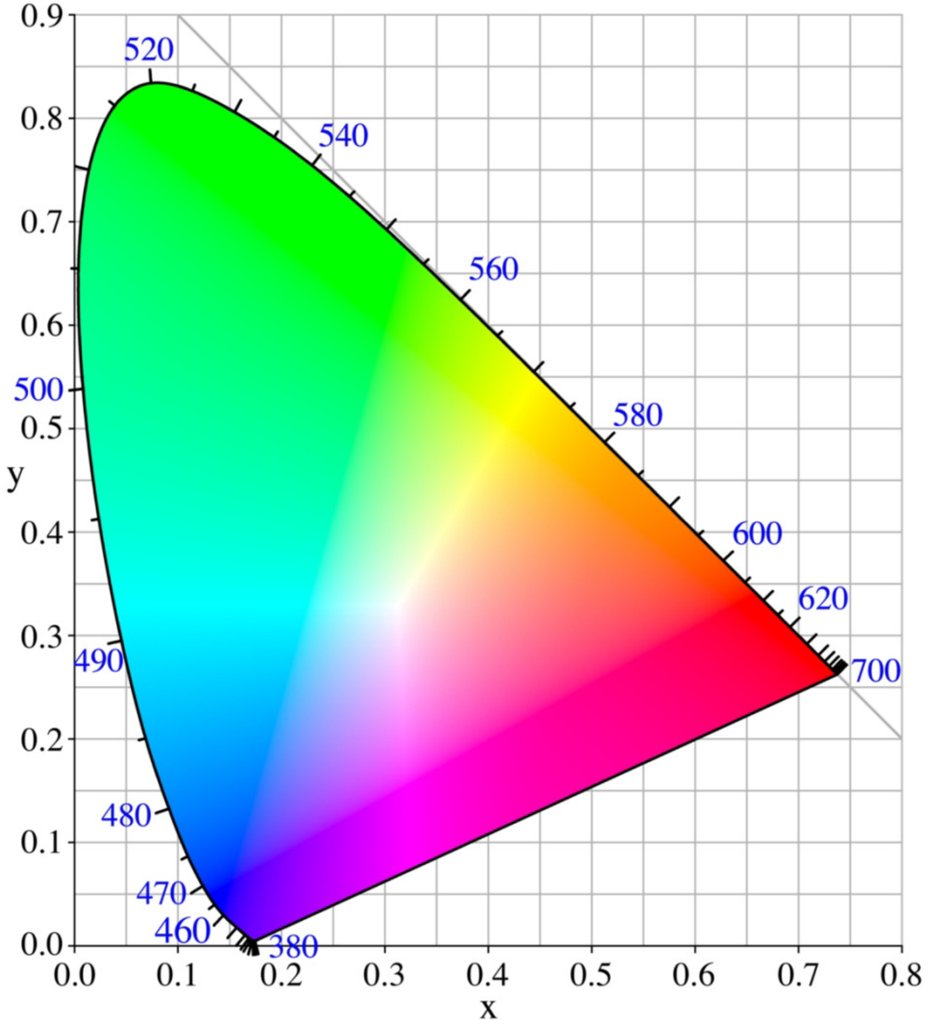
21st Century Lamp

- To be defined in a future L Prize Program Announcement

Phosphors for solid state lighting



Phosphors for solid state lighting



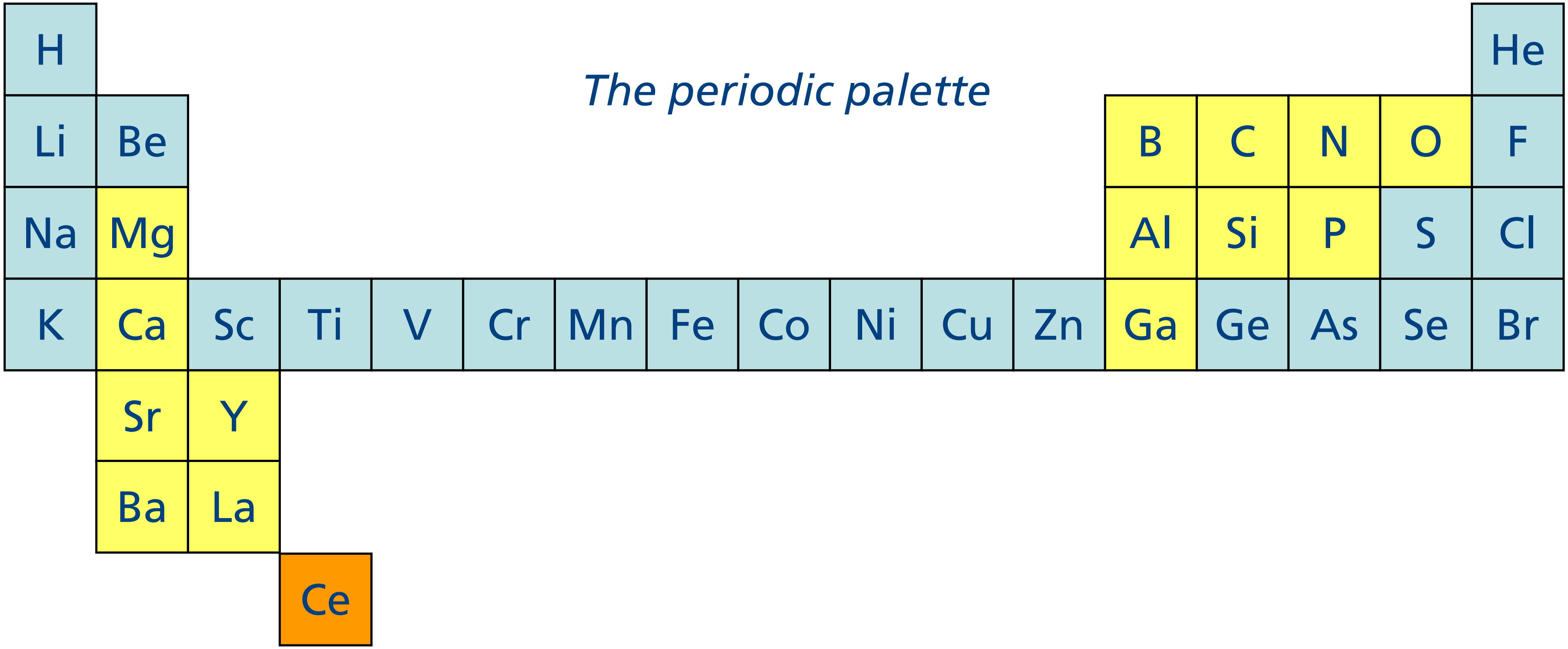
Combination of red, green and blue phosphors can give good quality white light

Combination of only two colors limits the possibilities [blue + yellow]

Color rendering depends not only on the coordinates in the CIE diagram but also on the nature of the emission spectrum

Phosphors for solid state lighting

Ce^{3+} yellow phosphors: Host elements

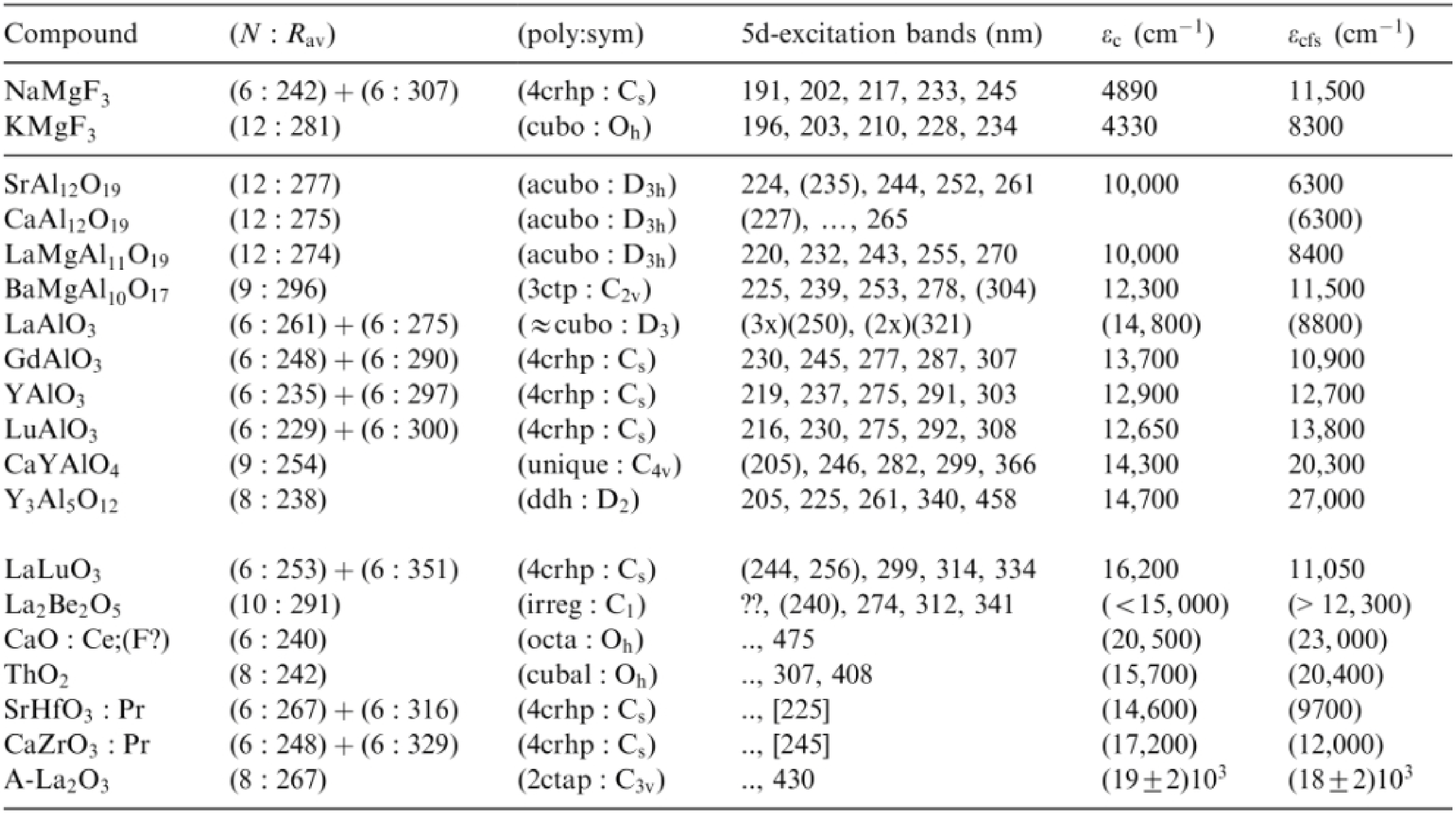


The periodic palette

H																He
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
	Sr	Y														
	Ba	La														
			Ce													

Phosphors for solid state lighting

Ce^{3+} phosphors:

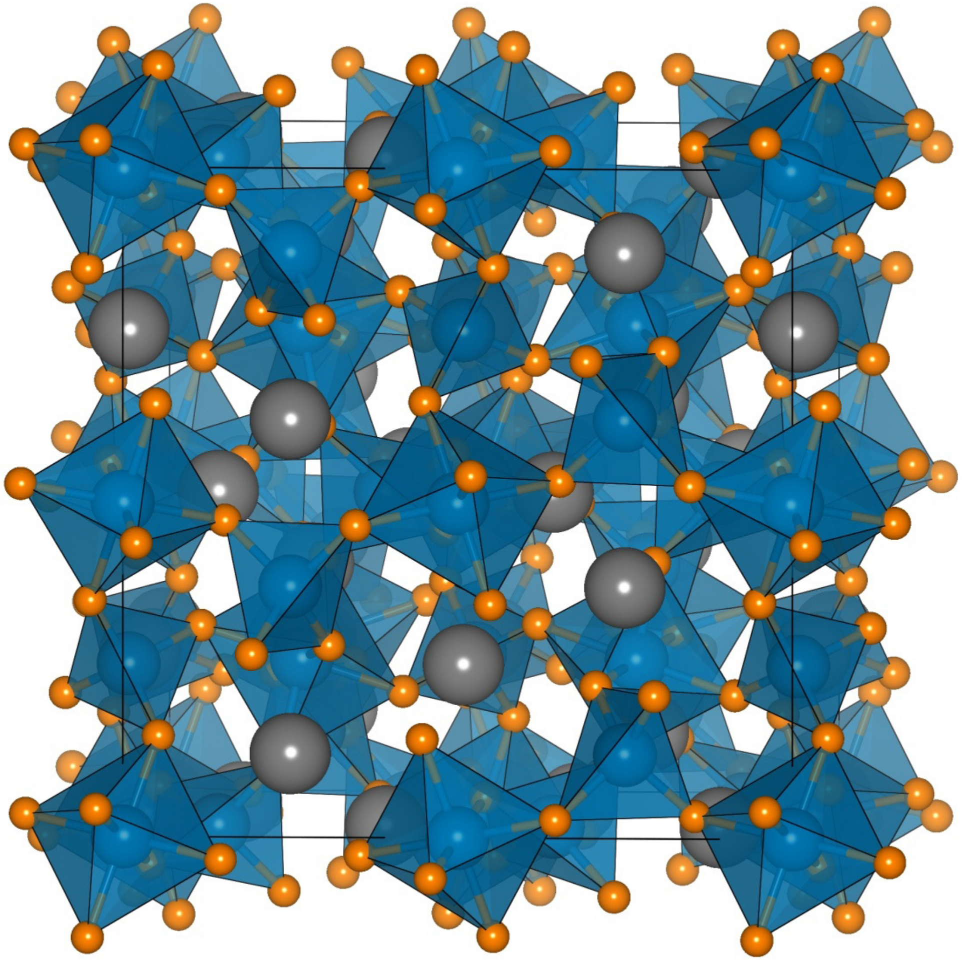


Compound	$(N:R_{av})$	(poly:sym)	5d-excitation bands (nm)	ε_c (cm^{-1})	ε_{cfs} (cm^{-1})
$NaMgF_3$	$(6:242)+(6:307)$	$(4crhp:C_s)$	191, 202, 217, 233, 245	4890	11,500
$KMgF_3$	$(12:281)$	$(cubo:O_h)$	196, 203, 210, 228, 234	4330	8300
$SrAl_{12}O_{19}$	$(12:277)$	$(acubo:D_{3h})$	224, (235), 244, 252, 261	10,000	6300
$CaAl_{12}O_{19}$	$(12:275)$	$(acubo:D_{3h})$	(227), …, 265		(6300)
$LaMgAl_{11}O_{19}$	$(12:274)$	$(acubo:D_{3h})$	220, 232, 243, 255, 270	10,000	8400
$BaMgAl_{10}O_{17}$	$(9:296)$	$(3ctp:C_{2v})$	225, 239, 253, 278, (304)	12,300	11,500
$LaAlO_3$	$(6:261)+(6:275)$	$(\approx cubo:D_3)$	(3x)(250), (2x)(321)	(14,800)	(8800)
$GdAlO_3$	$(6:248)+(6:290)$	$(4crhp:C_s)$	230, 245, 277, 287, 307	13,700	10,900
$YAlO_3$	$(6:235)+(6:297)$	$(4crhp:C_s)$	219, 237, 275, 291, 303	12,900	12,700
$LuAlO_3$	$(6:229)+(6:300)$	$(4crhp:C_s)$	216, 230, 275, 292, 308	12,650	13,800
$CaYAlO_4$	$(9:254)$	$(unique:C_{4v})$	(205), 246, 282, 299, 366	14,300	20,300
$Y_3Al_5O_{12}$	$(8:238)$	$(ddh:D_2)$	205, 225, 261, 340, 458	14,700	27,000
$LaLuO_3$	$(6:253)+(6:351)$	$(4crhp:C_s)$	(244, 256), 299, 314, 334	16,200	11,050
$La_2Be_2O_5$	$(10:291)$	$(irreg:C_1)$	??, (240), 274, 312, 341	$(<15,000)$	$(>12,300)$
$CaO:Ce;(F?)$	$(6:240)$	$(octa:O_h)$	…, 475	(20,500)	(23,000)
ThO_2	$(8:242)$	$(cubal:O_h)$	…, 307, 408	(15,700)	(20,400)
$SrHfO_3:Pr$	$(6:267)+(6:316)$	$(4crhp:C_s)$	…, [225]	(14,600)	(9700)
$CaZrO_3:Pr$	$(6:248)+(6:329)$	$(4crhp:C_s)$	…, [245]	(17,200)	(12,000)
$A\text{-}La_2O_3$	$(8:267)$	$(2ctap:C_{3v})$	…, 430	$(19\pm2)10^3$	$(18\pm2)10^3$

Very versatile active ion with spin allowed (and hence efficient), and highly tunable $4f^1 5d^0 \leftarrow 4f^0 5d^1$ transition.
Table from: P. Dorenbos, *J. Luminescence* **99** (2002) 283–299.

Phosphors for solid state lighting

Why is YAG:Ce^{3+} such a great phosphor?



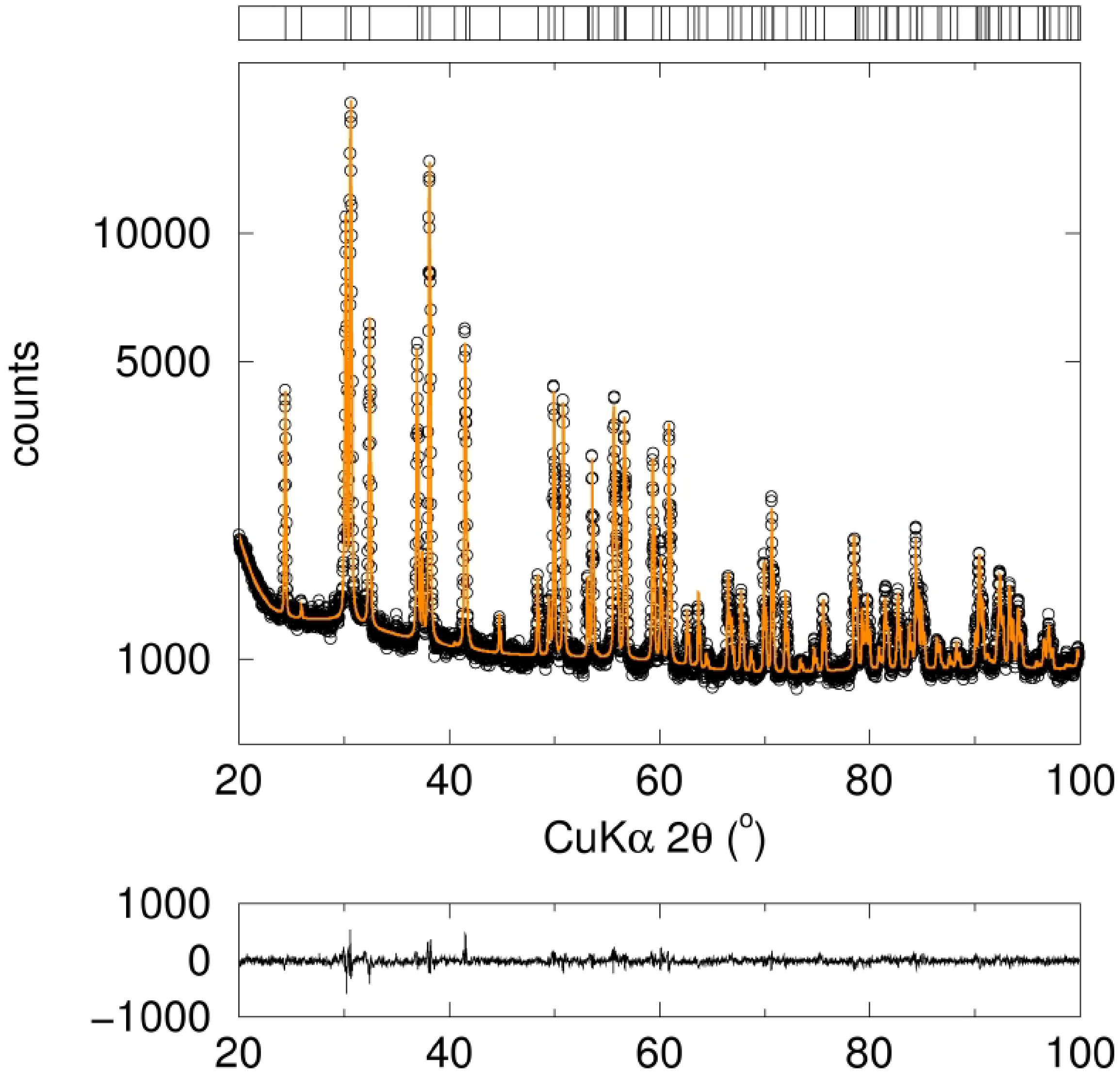
Rigid 3D connectivity—consequence of low charge on Al^{3+} [Paulings rules]. Also mixed Al coordination (4 and 6).

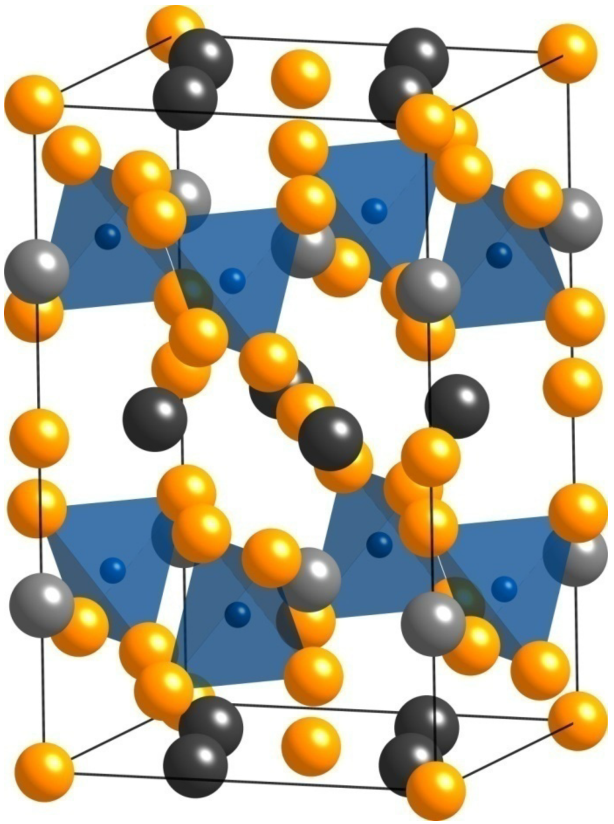
Stiff lattice because of light elements: Also low quenching (incl. thermal).

Single site for Ce^{3+}: Low disorder, and hence fewer non-radiative pathways.

Ce^{3+} substitutes smaller Y^{3+}: larger 5*d* crystal-field splitting on Ce^{3+}.

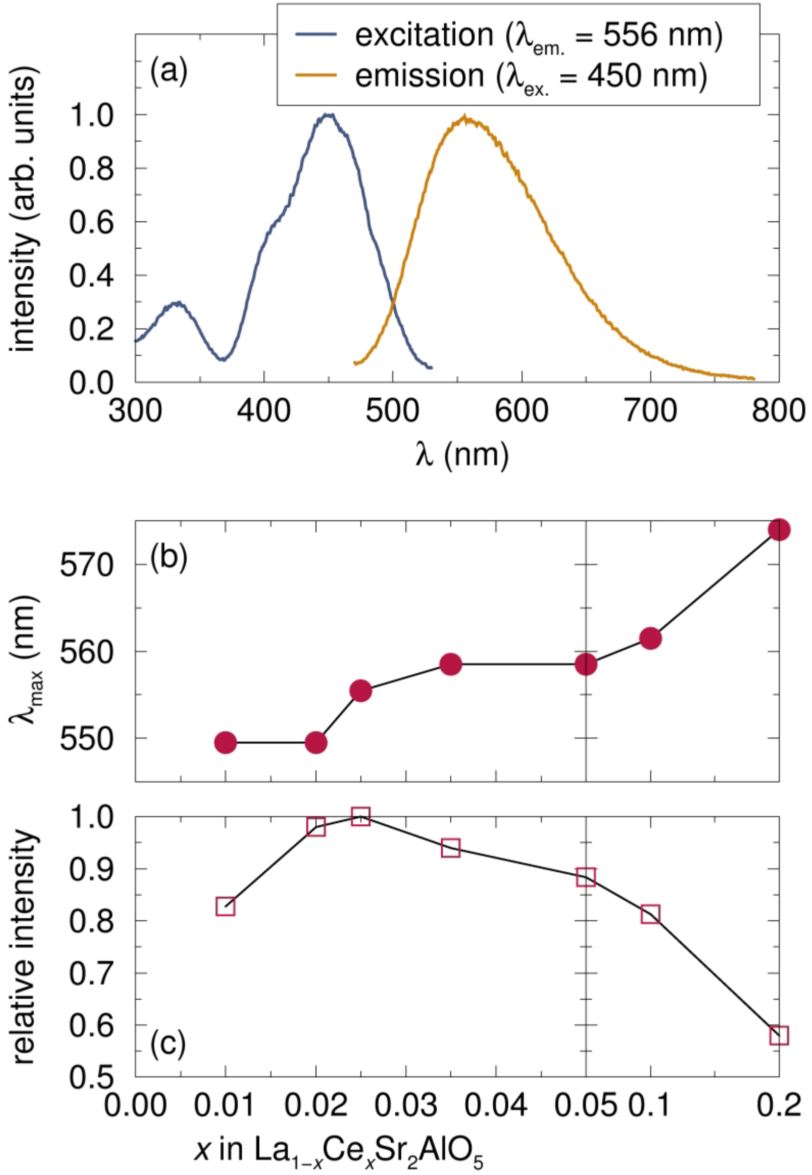
Phosphors for solid state lighting





LaSr2AlO5: A new host, isostructiral with tetragonal $EuSr_2AlO_5$/Cs_3CoCl_5.

Phosphors for solid state lighting



Appropriate absorption and emission positions for blue + yellow = white. Maximum emission intensity for 2.5 atom-% Ce^{3+} substitution.

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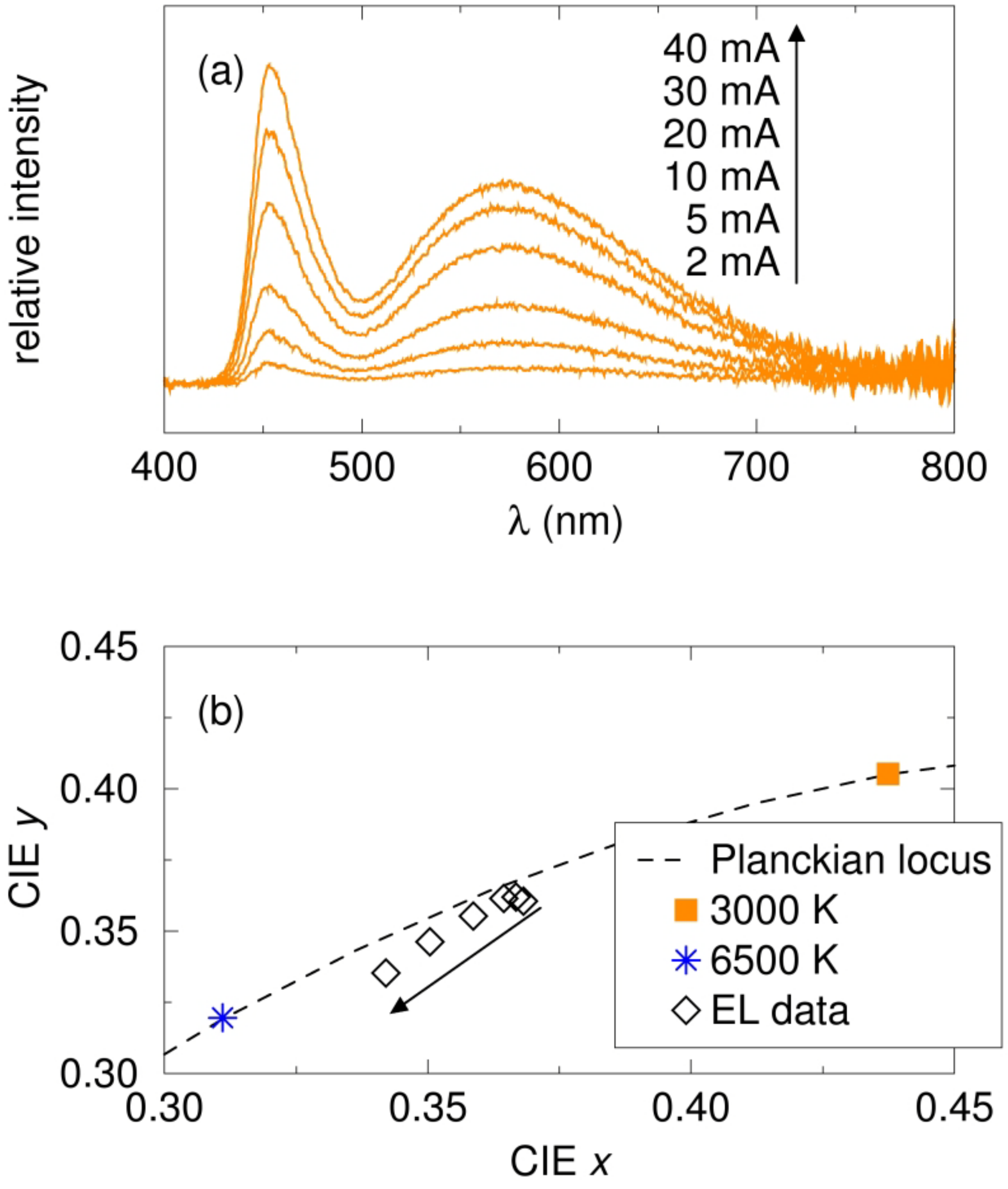
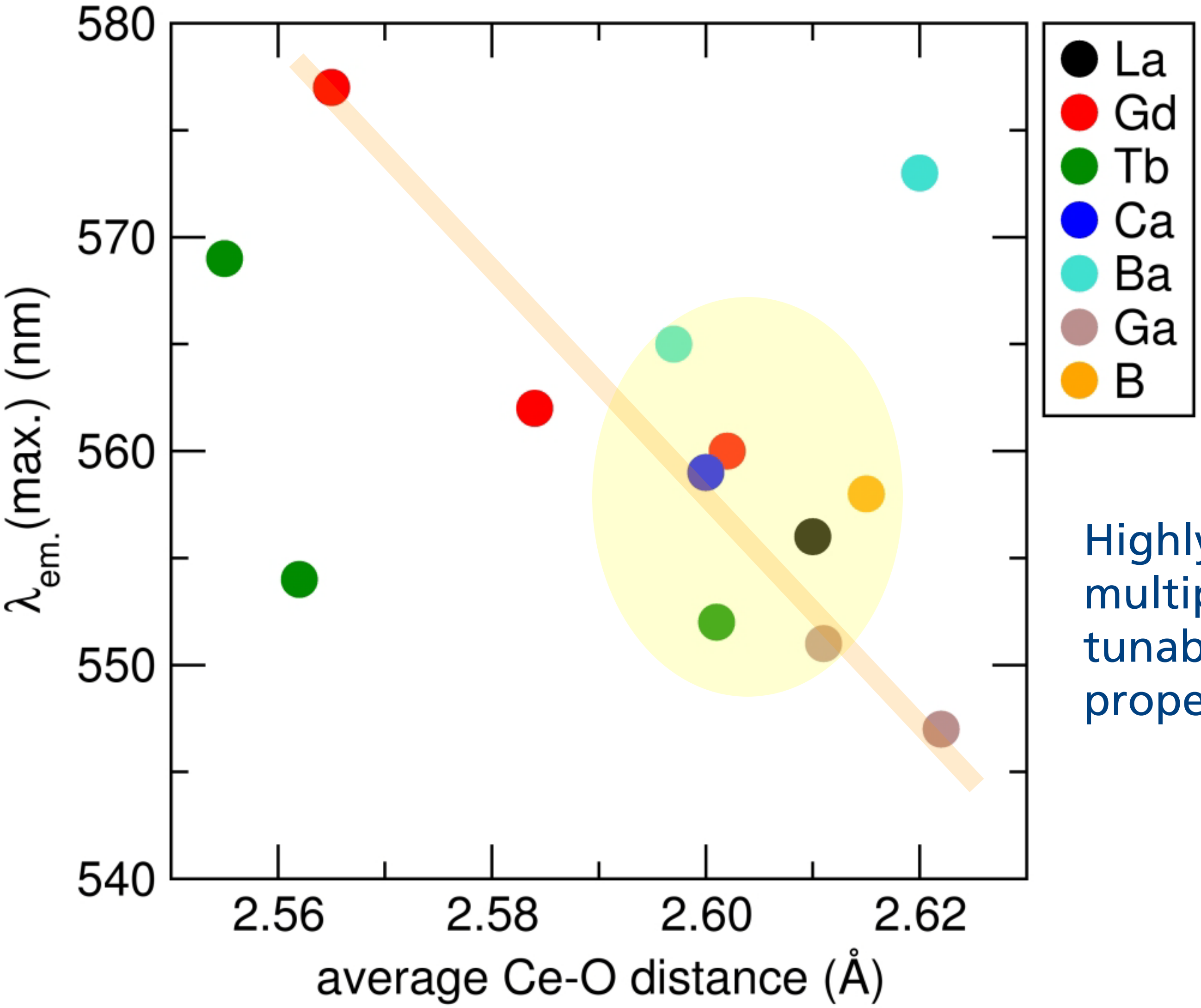
Phosphors for solid state lighting



Phosphor mounted on an InGaN chip (Natalie Fellows). Good color rendering, but efficiency poor compared to YAG:Ce^{3+}.

W. B. Im, Y.-I. Kim, N. N. Fellows, H. Masui, G. A. Hirata, S. P. DenBaars, and R. Seshadri, *Appl. Phys. Lett.* **93** (2008) 091905

Phosphors for solid state lighting



Highly versatile lattice with multiple substitutional sites: tunable phosphor properties.

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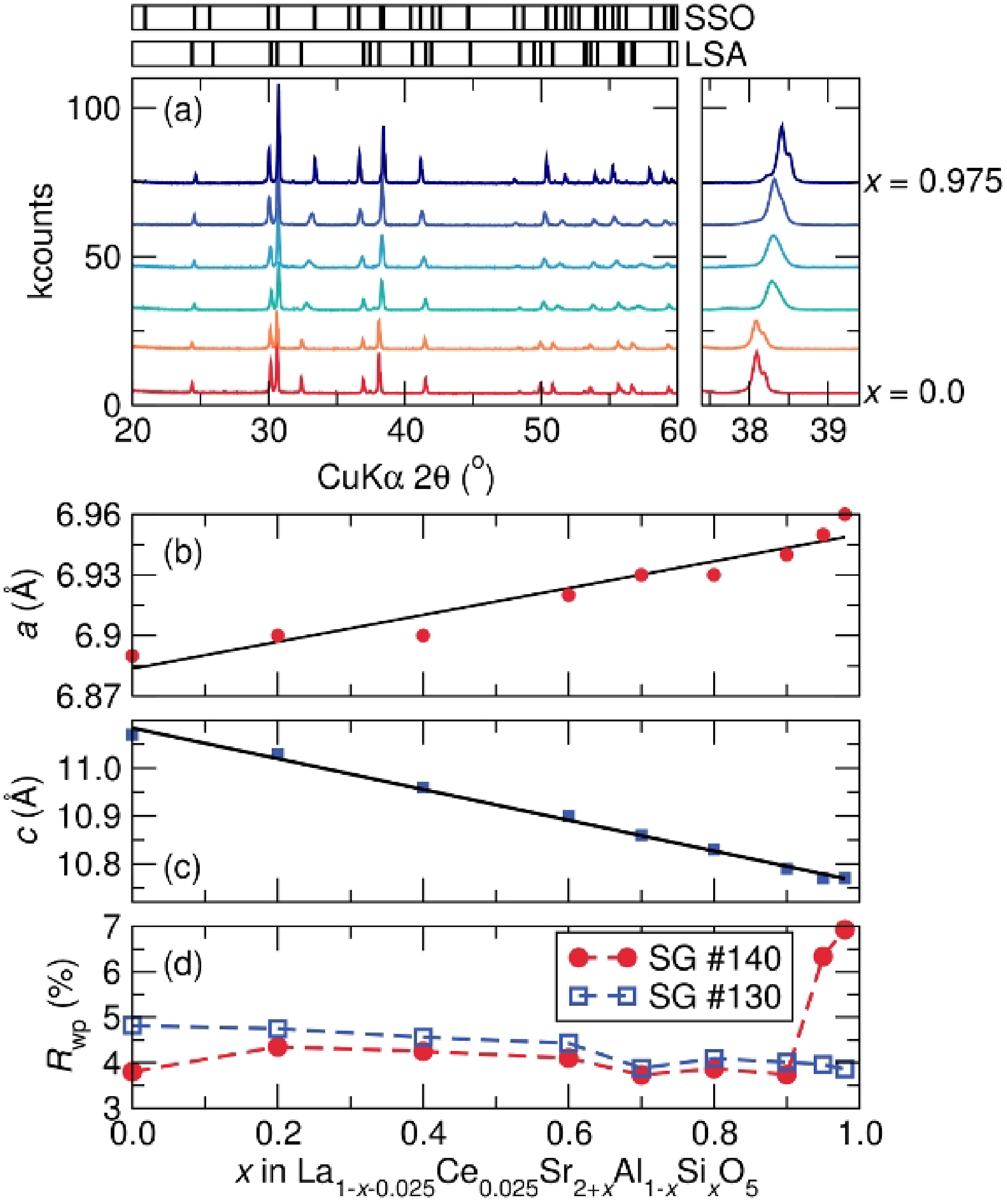
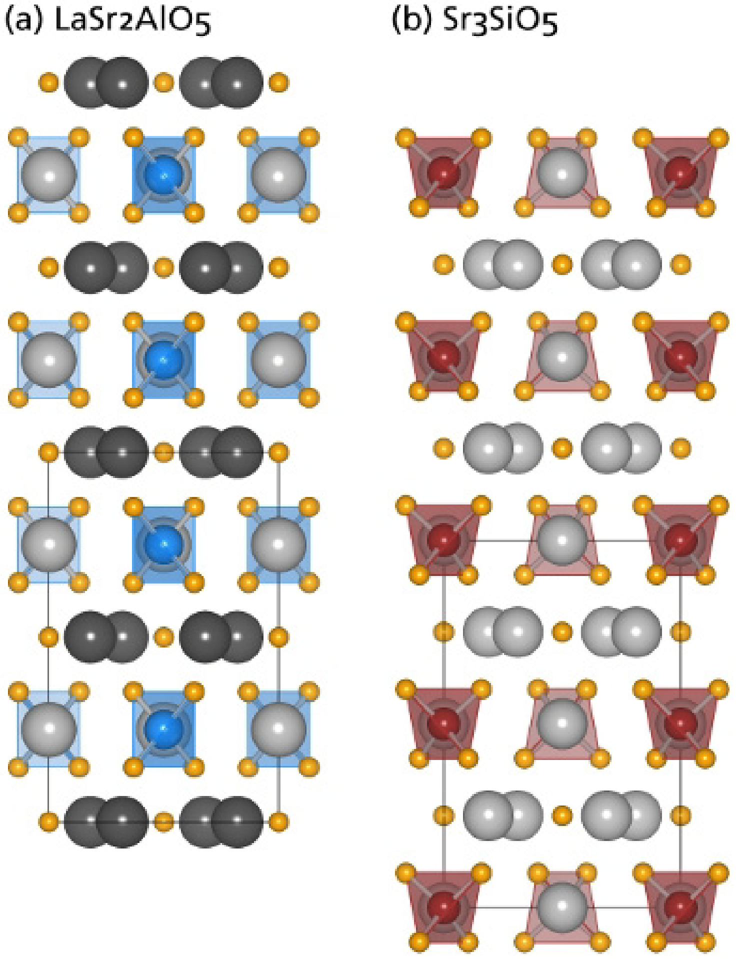


Solid solutions between two end-members with distinct crystal structures.



(a) $LaSr_2AlO_5$ (b) Sr_3SiO_5

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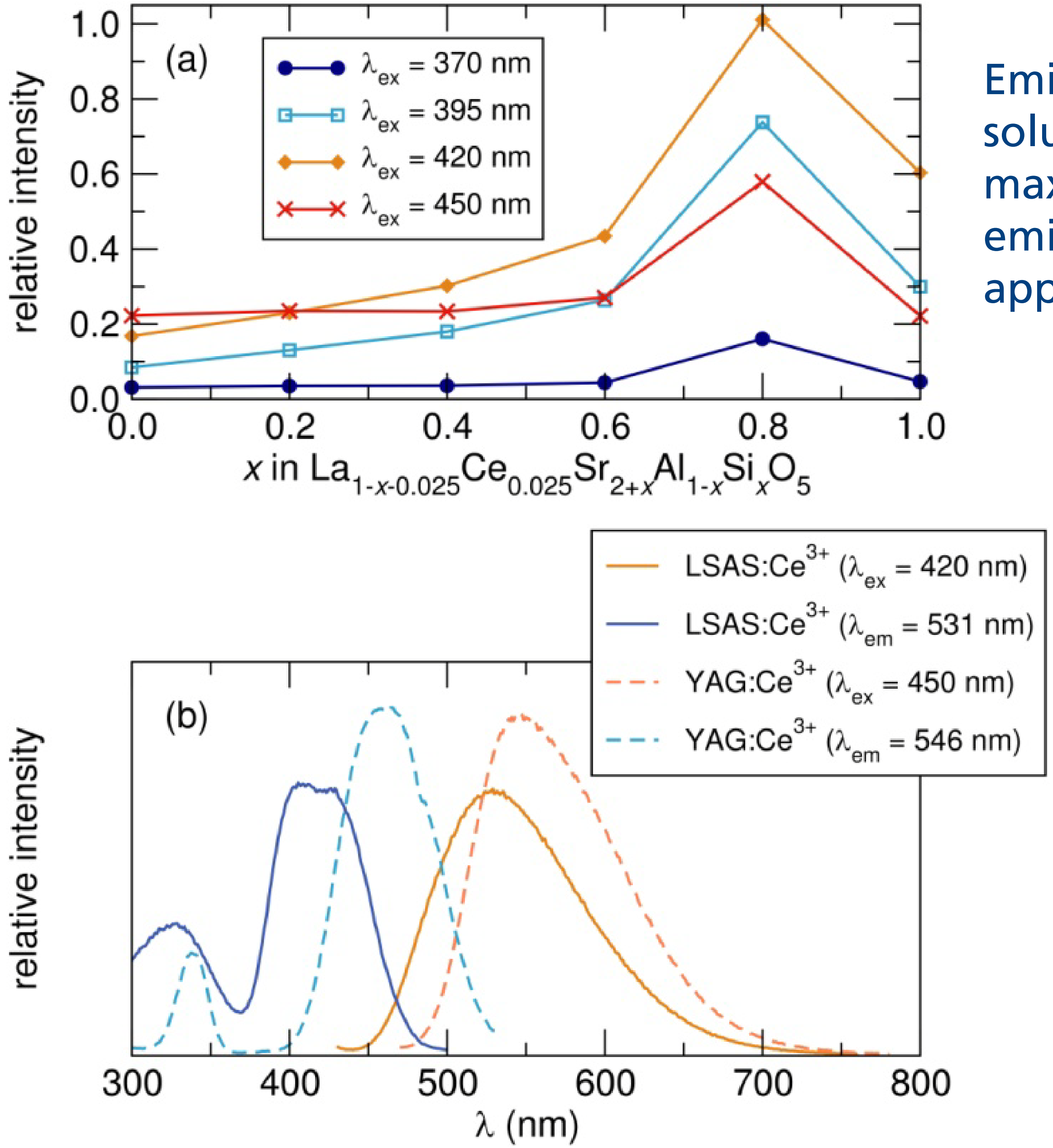
Phosphors for solid state lighting



Emission intensity in the solid solution goes through a maximum. Absorption and emission features remain appropriate for white lighting.

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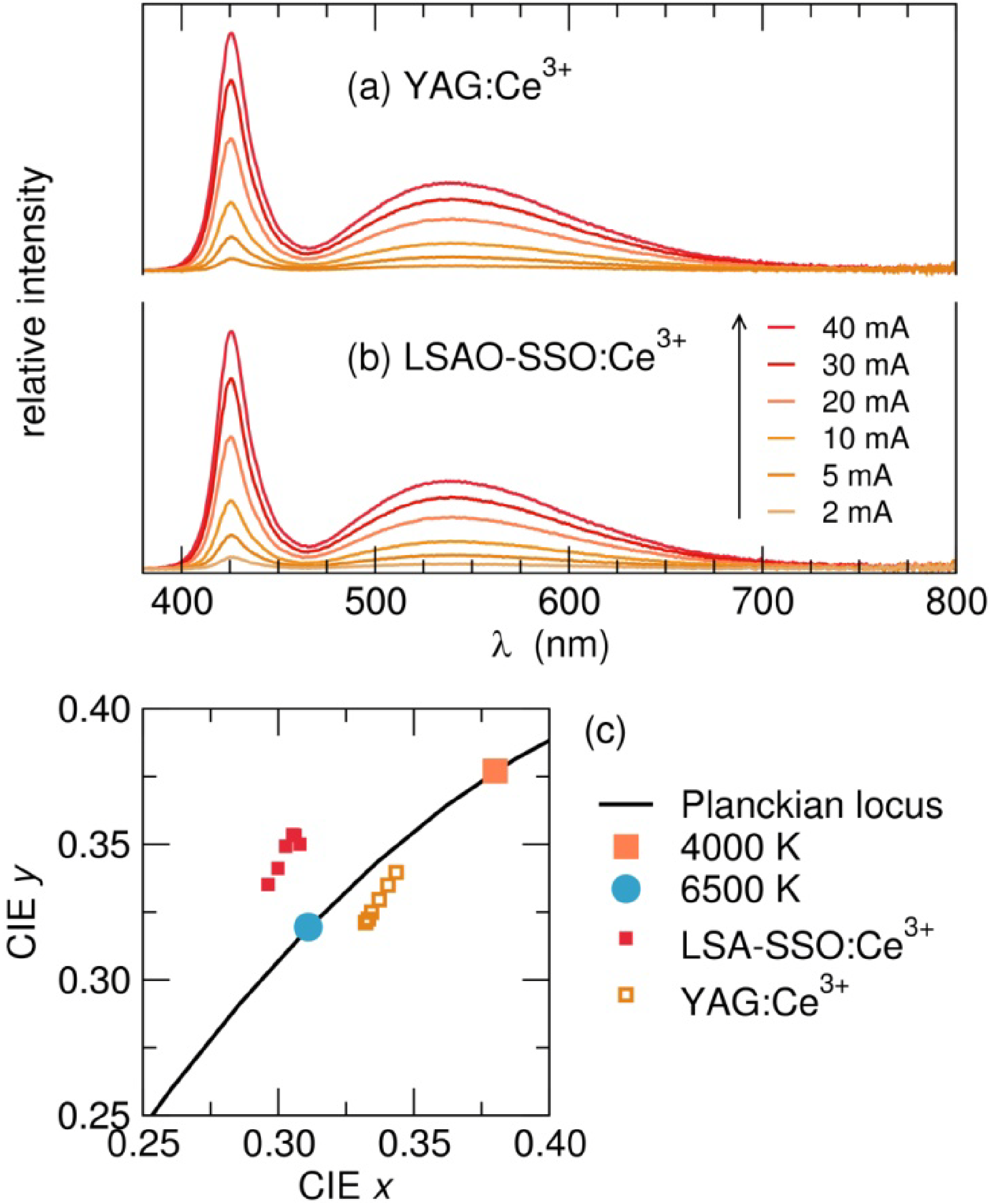
Phosphors for solid state lighting



Efficiencies of the solid solution comparable with YAG:Ce^{3+} with good color rendering.

Im, Fellows, DenBaars, Seshadri, *J. Mater. Chem.* (2009) in press.

Pd^{2+}— substituted oxide catalysts

Dr. Jun Li, Thomas Schladt, Katharine Page, Holly Szumila, Joshua Kurzman

Susannah Scott

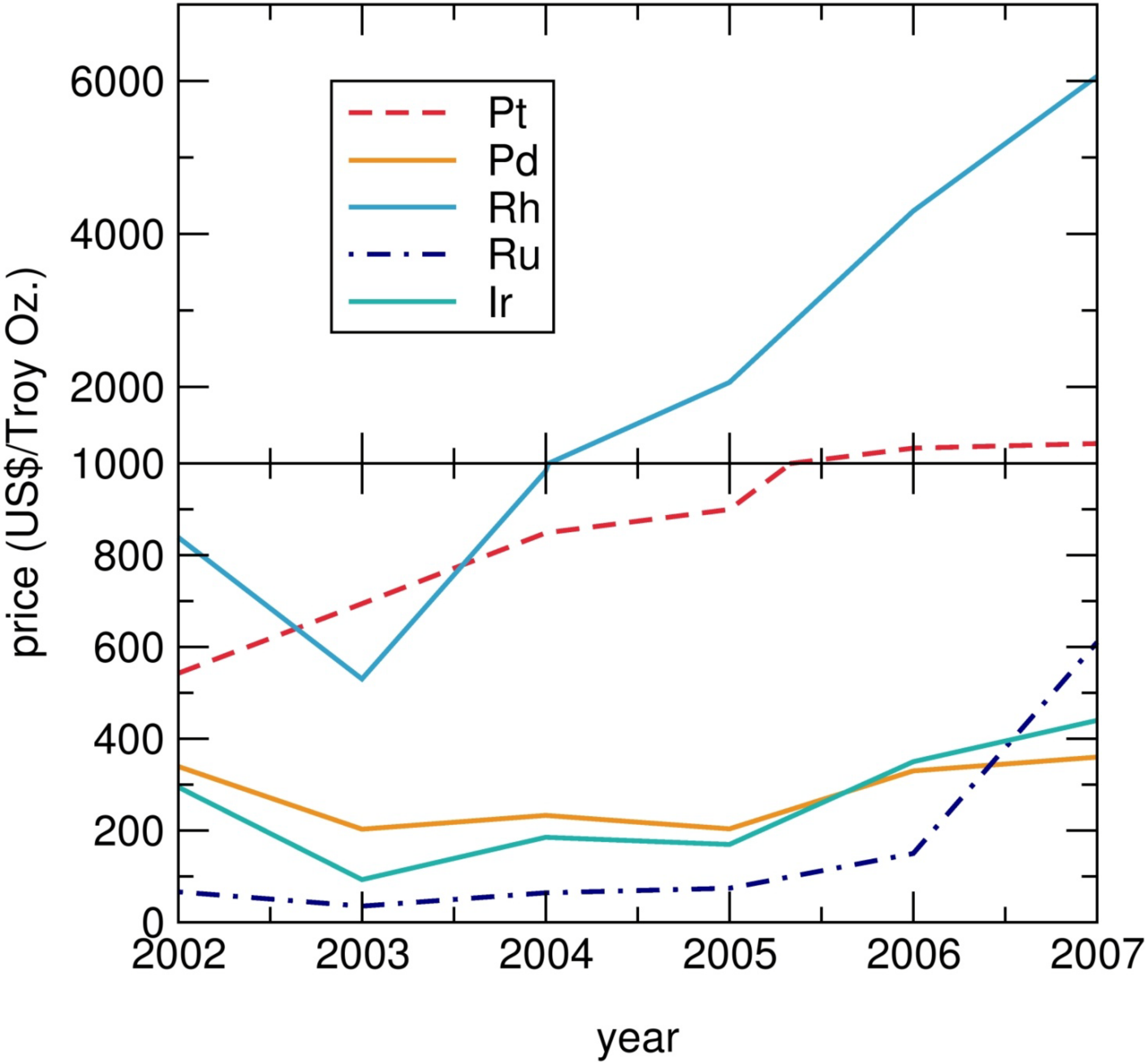
Dr. Udayshankar Singh, Xiaoying Ouyang [Scott Group]

Andrew Rappe, Joseph W. Bennett [Penn]

Dr. Thomas Proffen [LANSCE], Dr. Judith Stalick [NIST]

Pd^{2+}— substituted oxide catalysts

Motivation: Reducing PGM use in catalysts



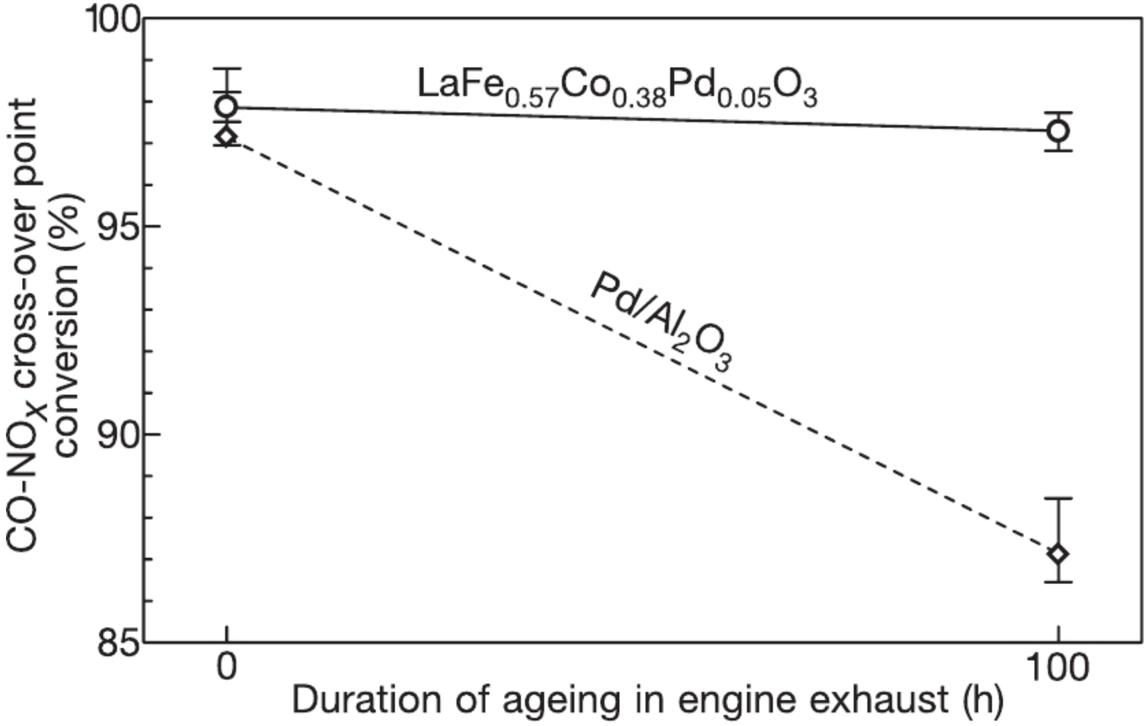
+ environmental problems with PGM release

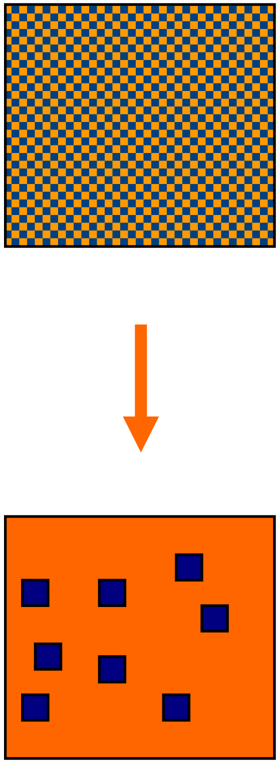
Data from usgs.gov

More that 50% of Pt use is in automotive catalysis: 3-way converters

Pd^{2+}— substituted oxide catalysts

Motivation: Reducing PGM use in catalysts





Oxidized state
(Pd^{2+} in lattice)

Reduced state
(supported Pd^{0}
nanoparticles)

Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, and N. Hamada, Self-regeneration of a Pd-perovskite catalyst for automotive emissions control, *Nature* **418** (2002) 164.

Pd^{2+}— substituted oxide catalysts

Questions:

- Does Pd really go into the host as ions and come out as Pd^{o} ?
- Are there other (perhaps better) hosts ?

Pd^{2+}— substituted oxide catalysts

Perovskite $BaCeO_3$ as a host:

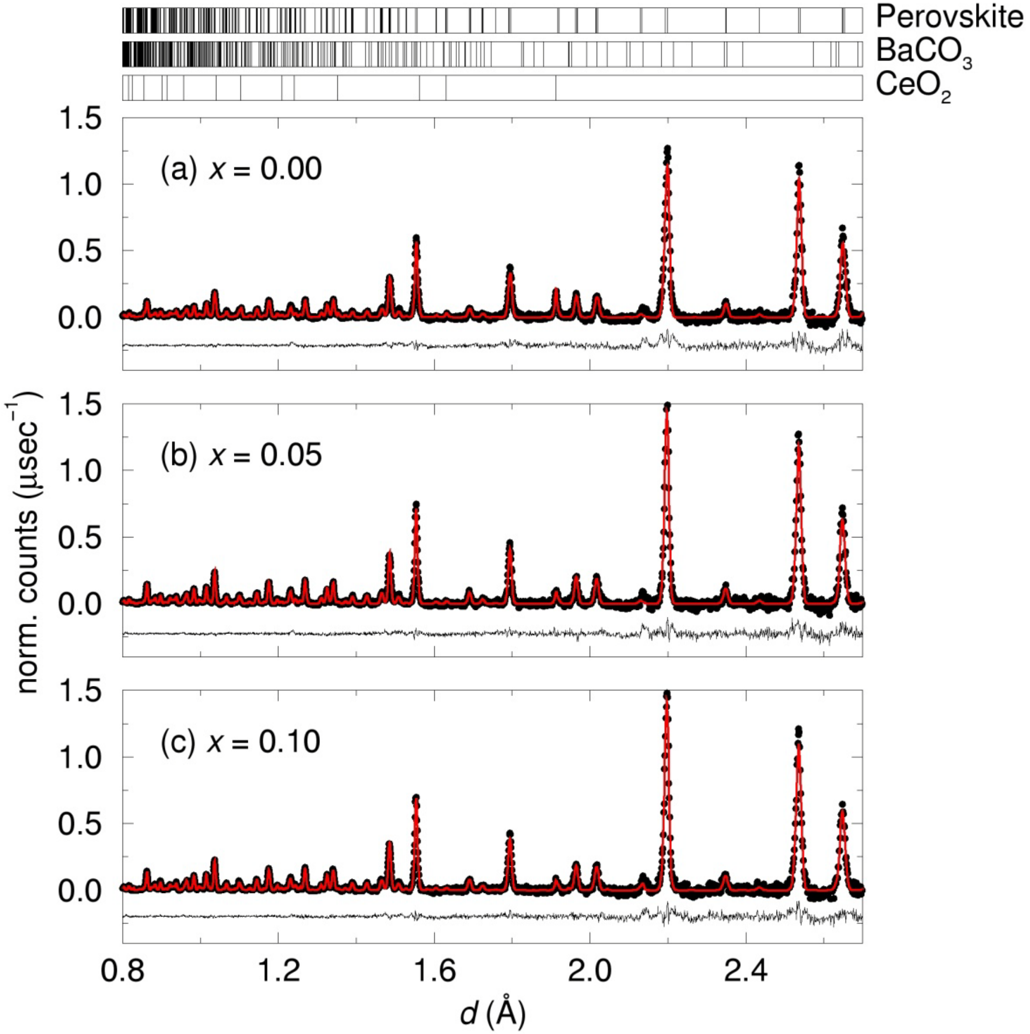
Ba^{2+} creates an oxide lattice that is highly oxidizing

Ce^{4+}/Ce^{3+} are large and somewhat forgiving in terms of coordination.

$BaCe_{1-x}Pd_xO_{3-\delta}$
with x = 0, 0.05, and 0.10

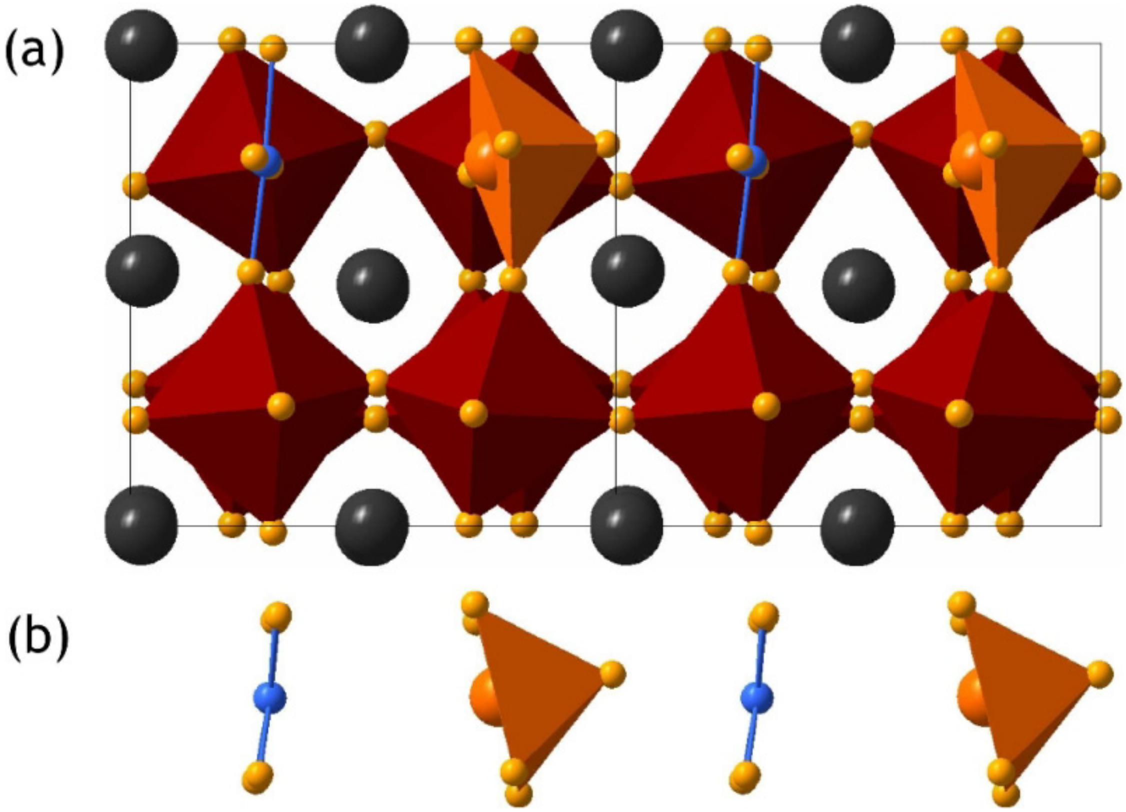
Samples prepared by solid state routes in O_2.

Neutron refinements
[NPDF, Los Alamos] $\Rightarrow \delta \sim x$
so Pd in lattice is Pd^{2+}



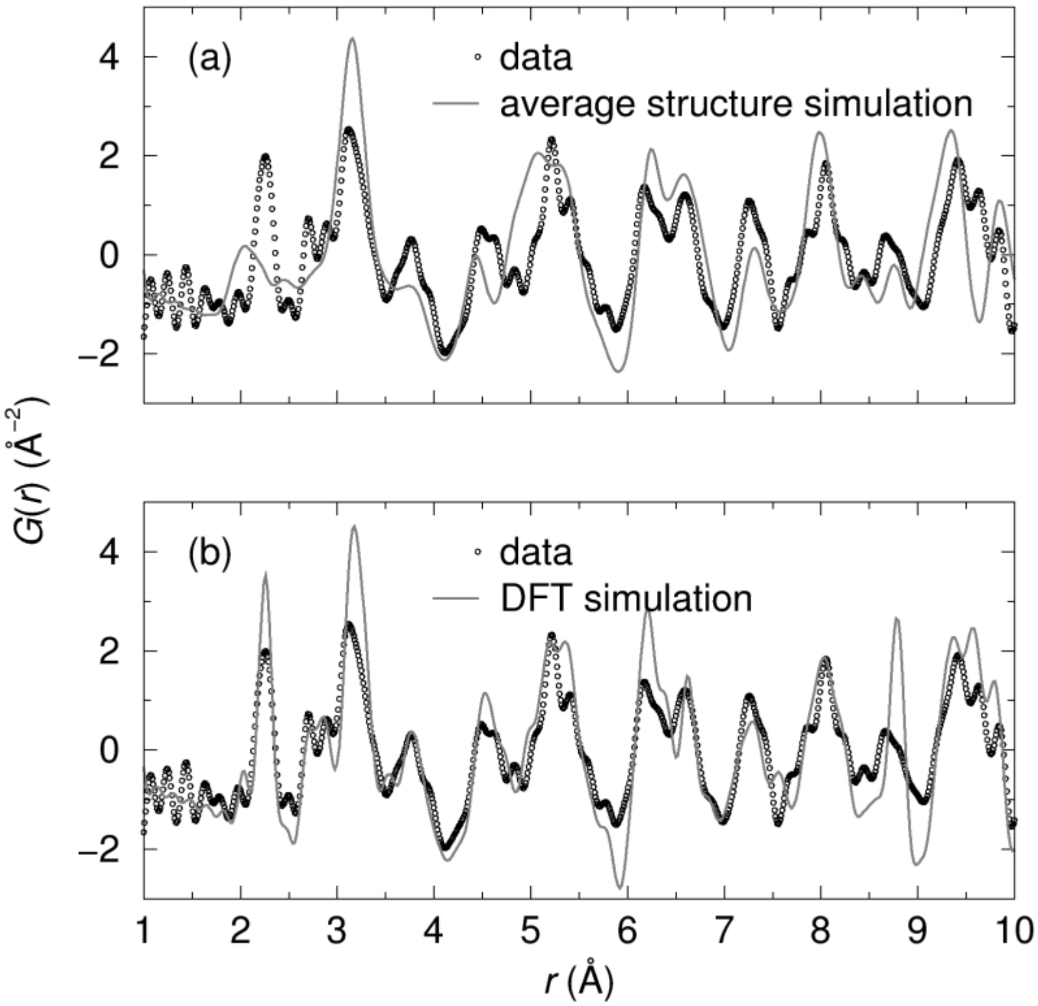
Pd^{2+}— substituted oxide catalysts

DFT optimized structure of 2x2x2 perovskite cell with one Pd^{2+} substituting Ce^{4+} and one oxygen vacancy: x = 12.5 [Bennett and Rappe, Penn]



The oxygen vacancy prefers to be proximal to Pd^{2+} and leaves it nearly square planar.

Pd^{2+}— substituted oxide catalysts



The neutron pair distribution function (PDF) for the $x = 0.10$ sample is well-modeled by the DFT structure, but not by the average structure. [K. Page]

Magnetic measurements suggest a diamagnetic system.

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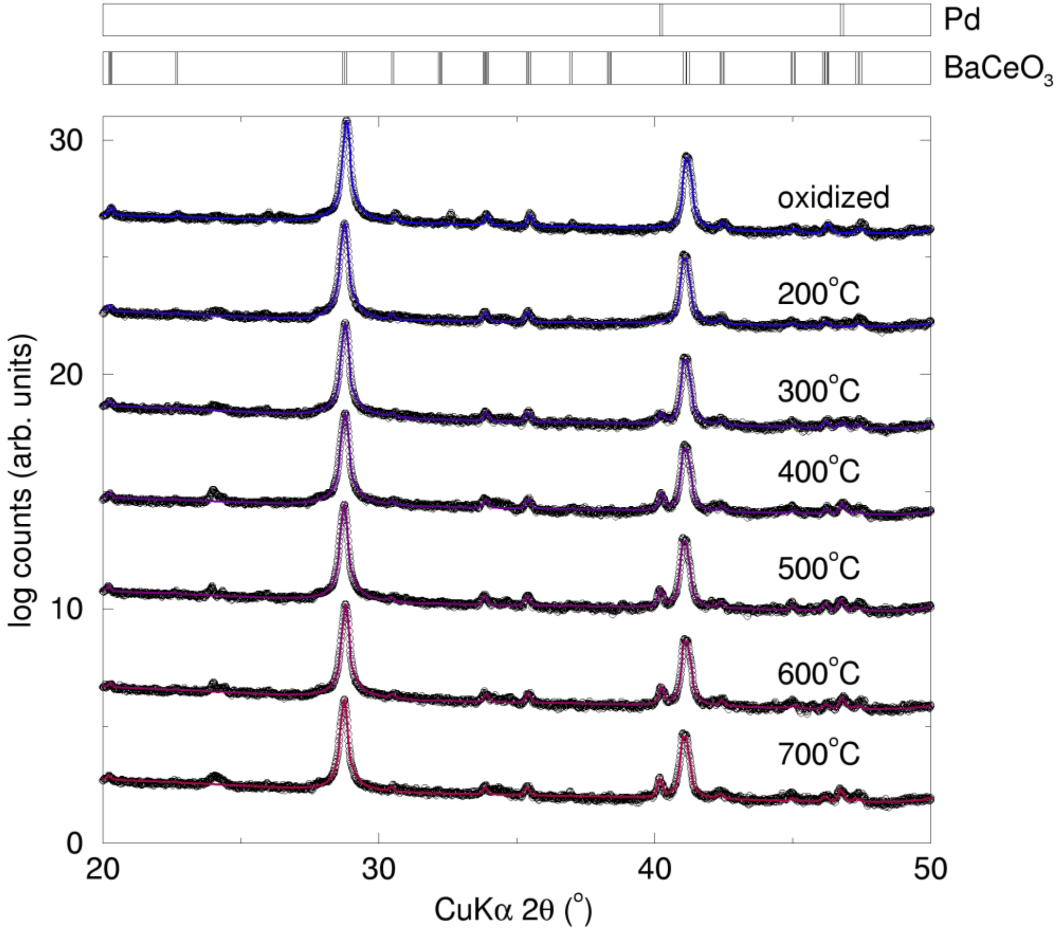
Pd^{2+}— substituted oxide catalysts

Egress of Pd as *fcc*-Pd upon H_2 reduction of $x = 0.10$ at different temperatures [5%-H_2/95%-N_2]



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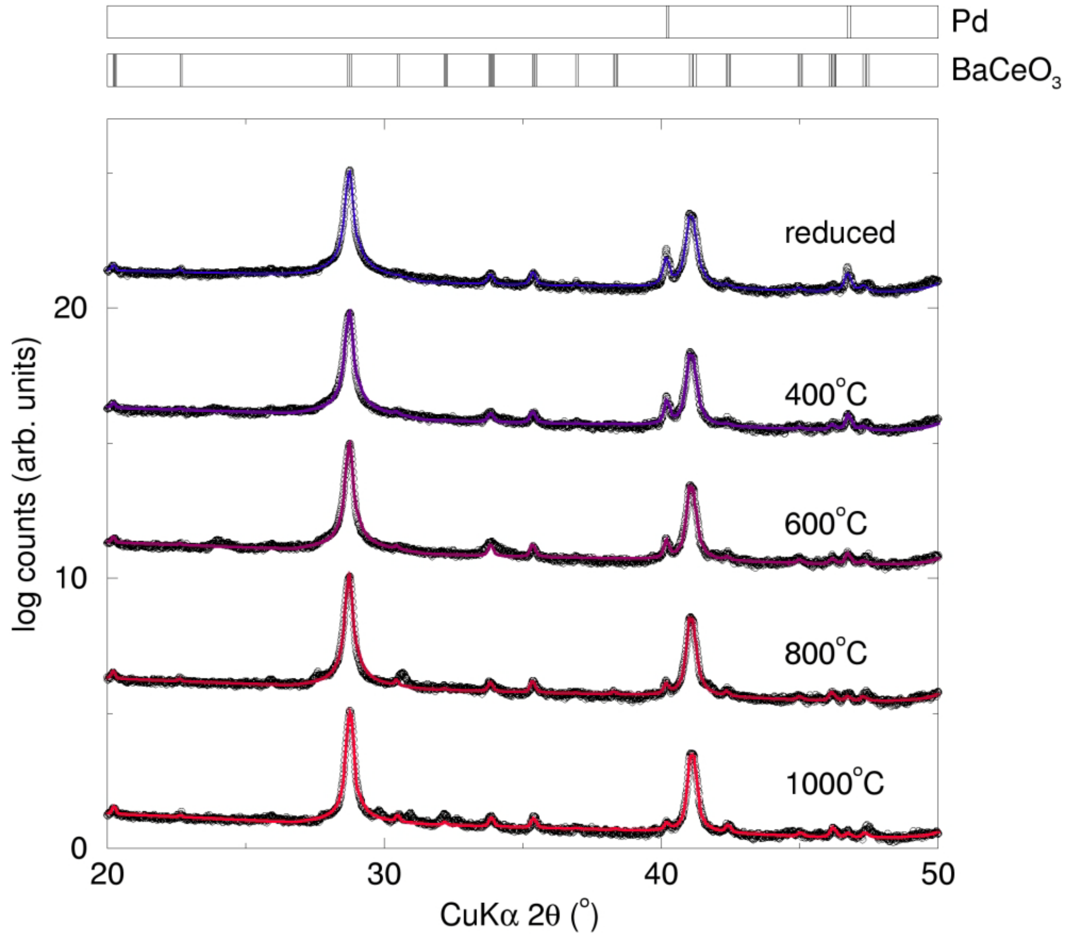
Pd²⁺— substituted oxide catalysts

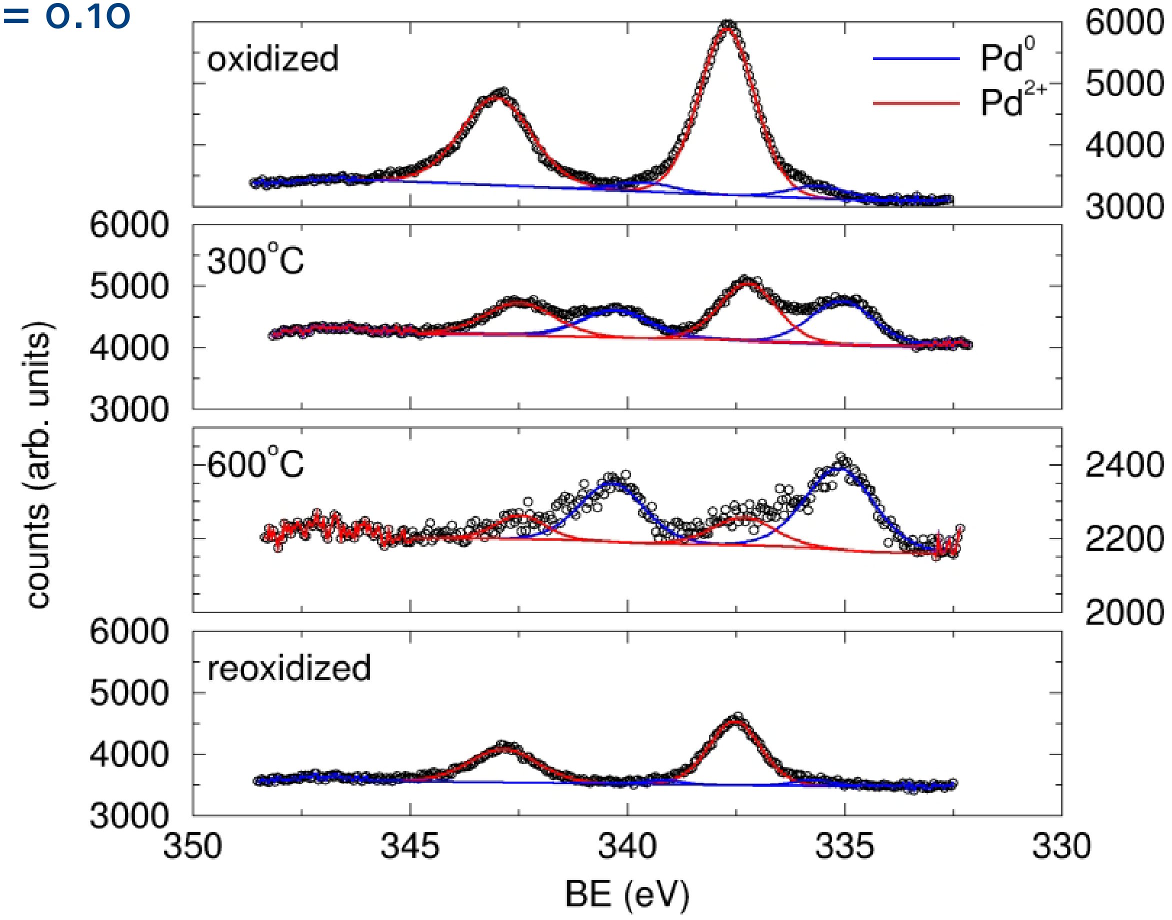
Ingress of Pd into the perovskite on heating the reduced two-phase sample in O_2 at different temperatures.



Pd^{2+}— substituted oxide catalysts

Pd core levels of the oxidized and reduced samples.

x = 0.10

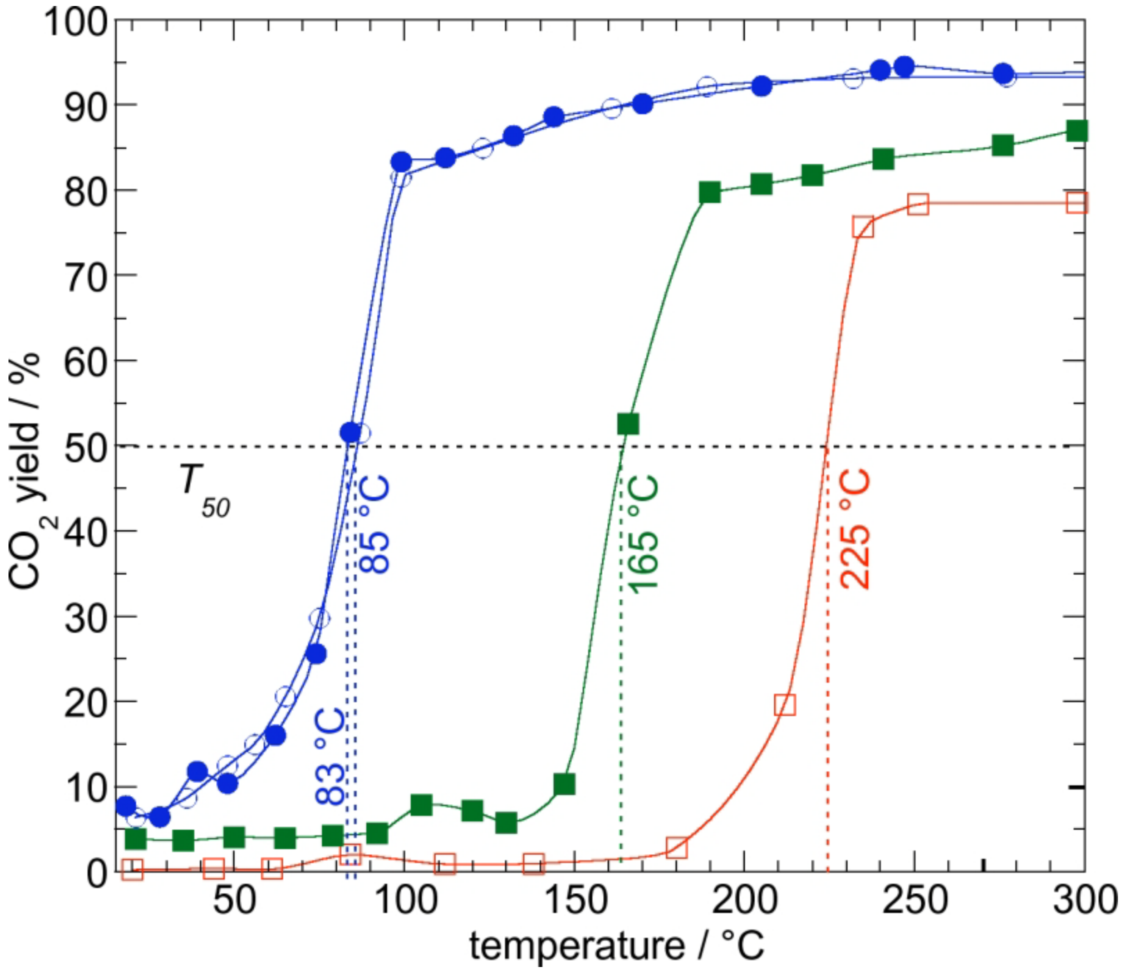


Note the drop in counts for the reduced samples.

Ce is always Ce^{4+}

Pd²⁺— substituted oxide catalysts

Good CO oxidation catalyst despite low surface area. The best catalyst is actually the as-prepared or re-oxidized sample with Pd^{2+}



Oxidized

Reduced

Activity is attributed to the presence of cationic Pd^{2+} in the perovskite Lattice

Also works for Suzuki coupling.

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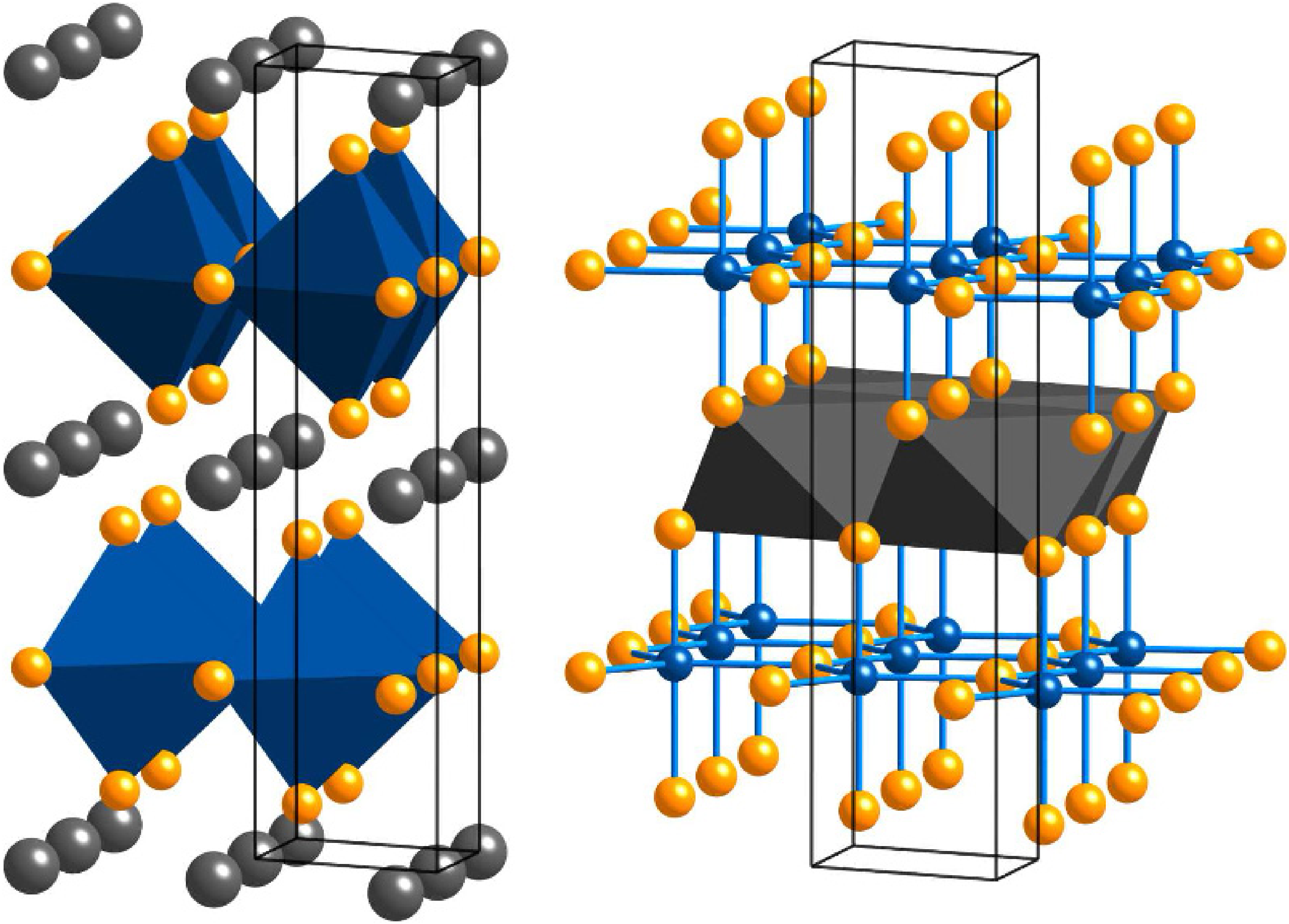
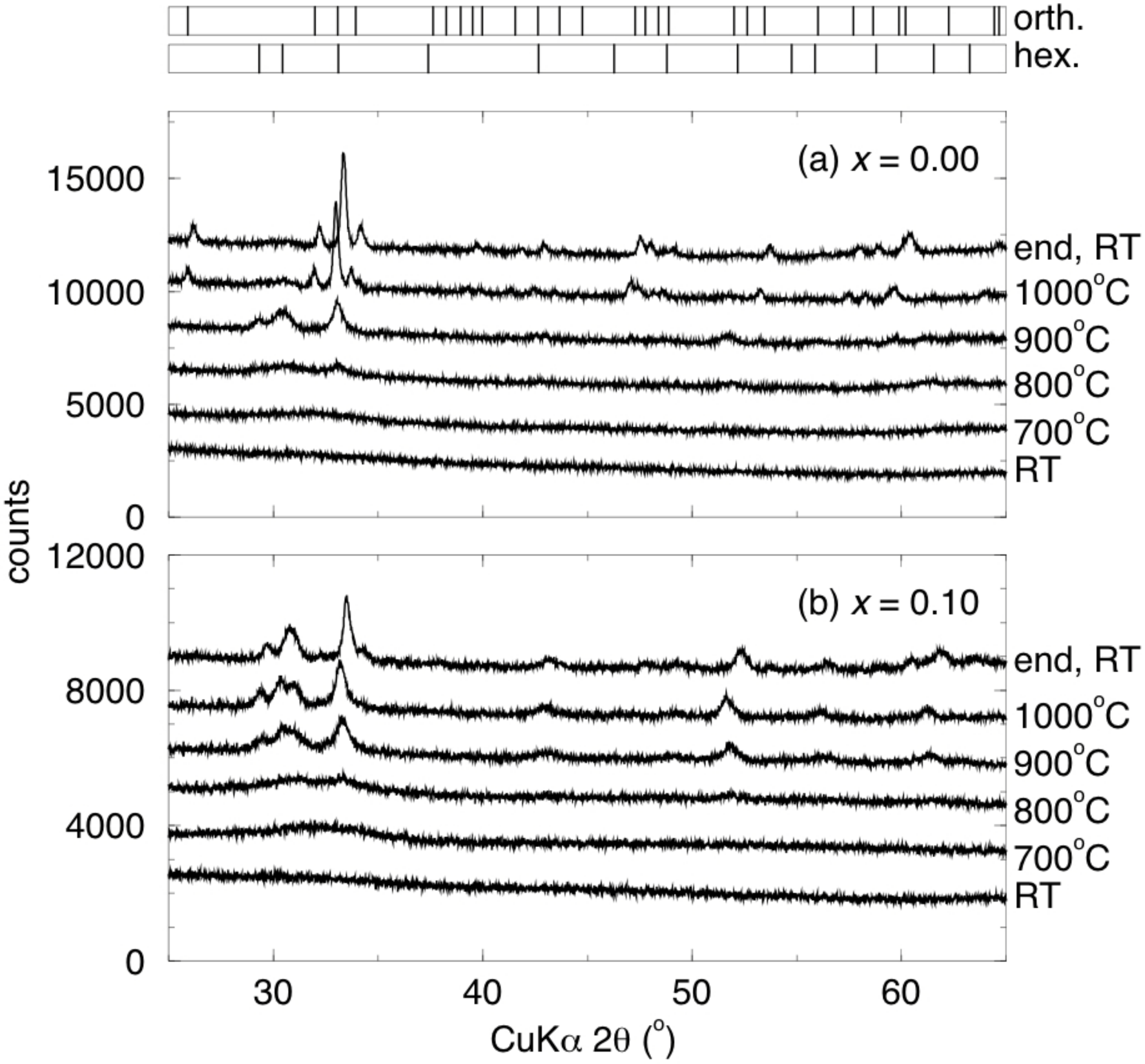
Pd^{2+}— substituted oxide catalysts



$YFeO_3$ exists as a stable perovskite or a metastable (sol-gel prep.) hexagonal compound with the $YAlO_3$ structure. 5-coordinate Fe^{3+} in the hexagonal structure.

Pd^{2+}— substituted oxide catalysts



Even small Pd substitution strongly stabilizes the hexagonal compound, in keeping with the nature of d^8 Pd^{2+}.

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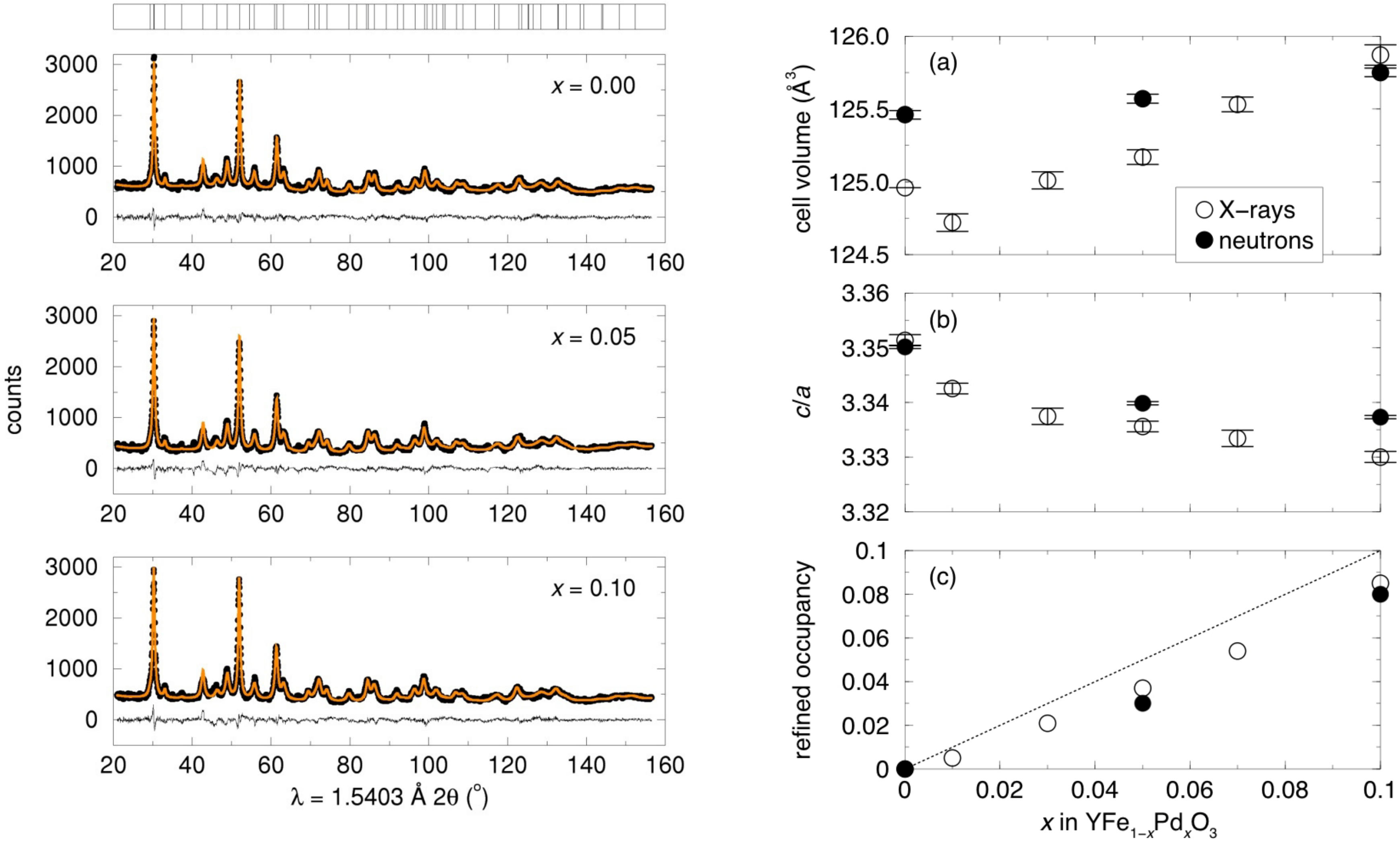
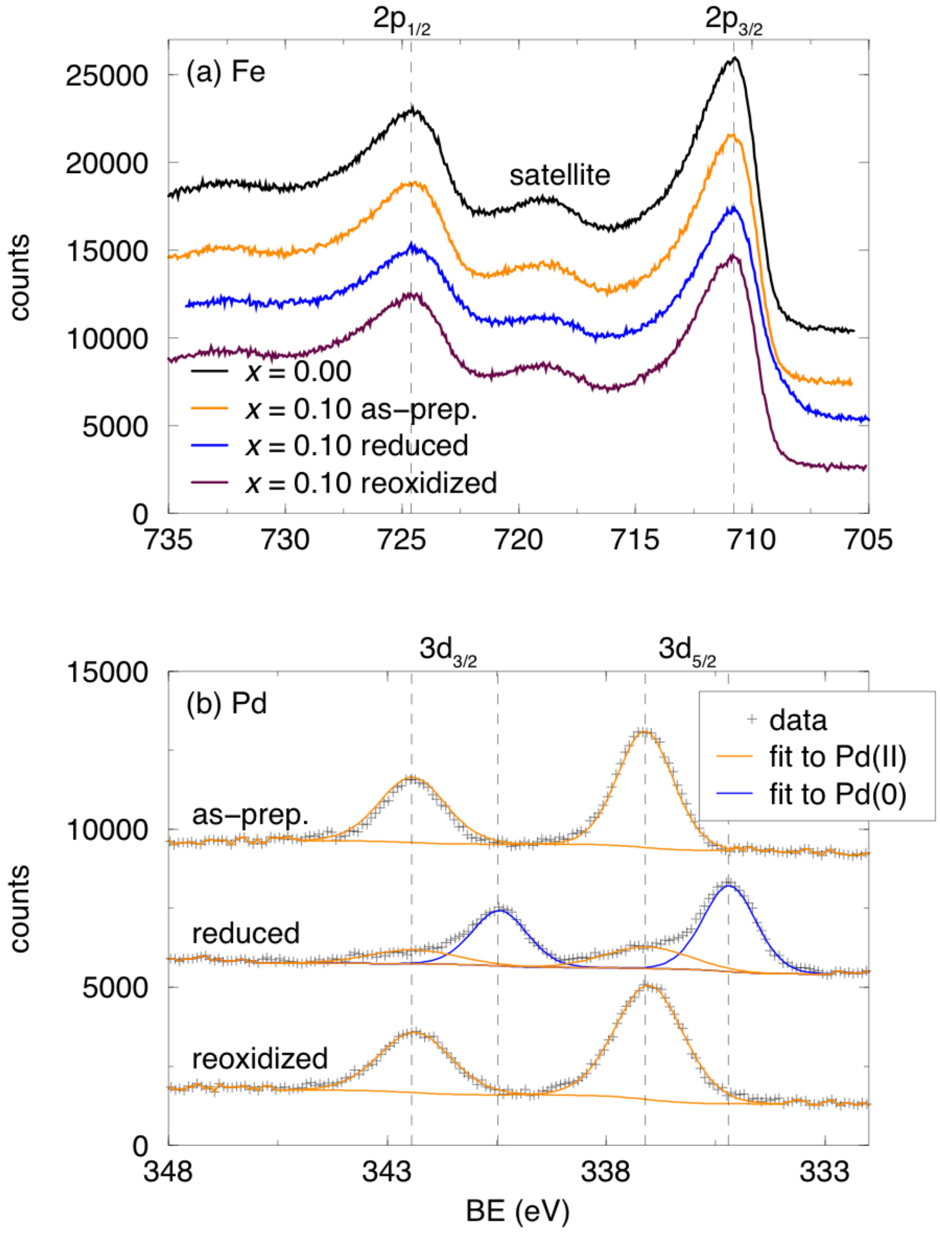
Pd^{2+}— substituted oxide catalysts



Neutron diffraction [NIST, BT-1] confirms the substitution.

Pd^{2+}— substituted oxide catalysts



Fe core levels unchanged with oxidation/reduction.

Pd core levels suggest ingress and egress under redox. Not all Pd^{2+} reduced.

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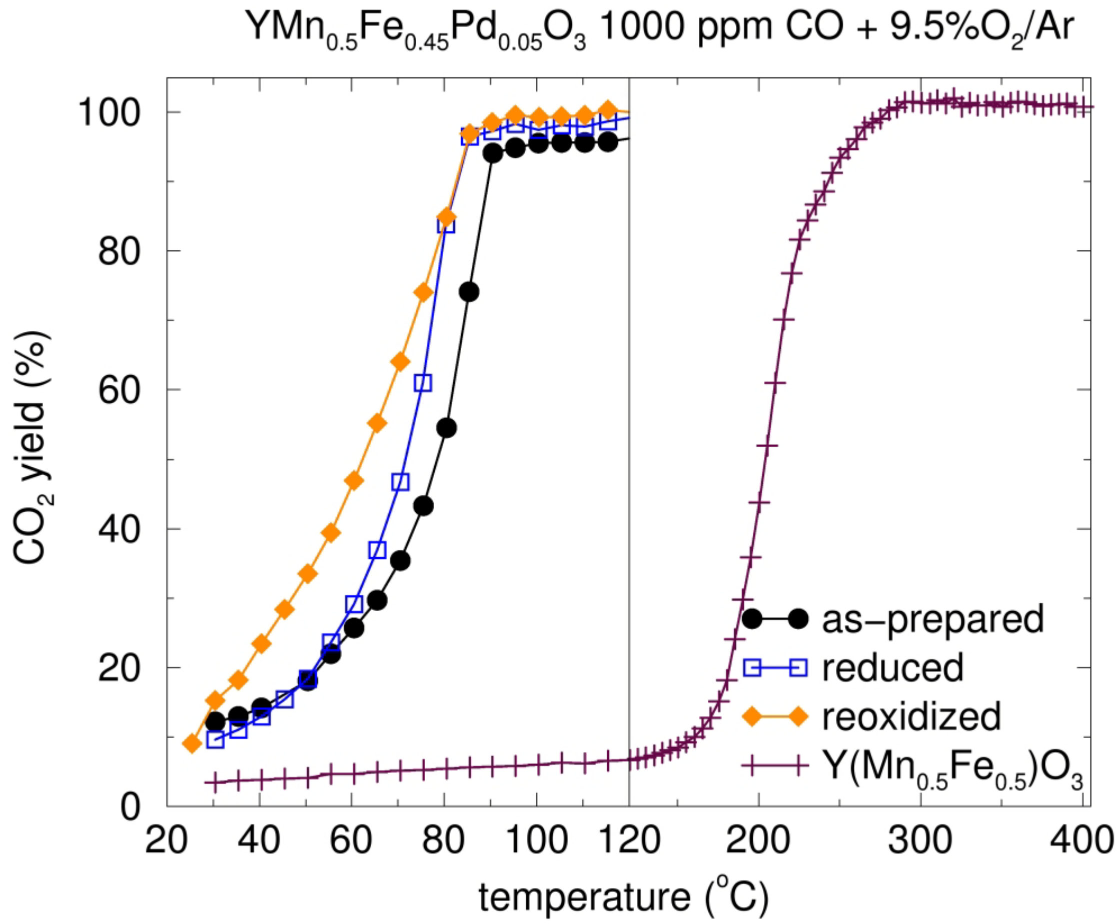
Pd²⁺— substituted oxide catalysts

Oxidized compound, and even better catalyst



Low light-off temperature. Effective catalyst despite low surface areas.

Spinel magnets

Why spinels (or pyrochlores) ?

Postulate: Two cationic sites are the minimal requirement for many interesting electronic properties (polar behavior, magnetism, electronic instabilities ...) ⇨ ternary compounds !

Postulate: Interesting properties arise when structures possess covalent networks, associated with somewhat disperse bands whose widths are controllable ⇨ simple topologies !

Many different ternary families: Most are boring from the electronic properties viewpoint

ABX_3: $CaCO_3$, Perovskite, Hexagonal, Pyroxene, Corundum
ABX_4: Zircon, Scheelite, Barite, Ordered SiO_2
A_2BX_4: K_2NiF_4, b-K_2SO_4, Olivine, Spinel, $CaFe_2O_4$
Others: ABX_2, $A_2B_2X_7$, A_2BX_5, A_2BX_6, A_3BX_5

O. Muller and R. Roy, *The major ternary structural families*, Springer-Verlag 1974.

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Perovskites in contrast to spinels and pyrochlores:

Large *A* cation results in an oxidizing environment.

Near 180° bond angle (tuned by the tolerance factor) imply broad bands, particularly for e_g perovskites because of metal e_g – anion *p* covalency.

Illustrations:

- Mn is usually +2 or +3 in spinels, but is often +3 or +4 is perovskites
- There are numerous metallic oxide perovskites, but all of the metallic oxide spinels are marginal, with some unusual ground state: $LiTi_2O_4$, LiV_2O_4, Fe_3O_4.

The metal-anion network in spinels and pyrochlores *do not* result in disperse bands.

Spinel magnets

In $A_2B_2O_7$ pyrochlores, a covalent AO network leads to metallic behavior: $Tl_2Mn_2O_7$ displays CMR, and is FMM [Subramanian *et al. Science* **272** (1996) 81; Singh *Phys. Rev. B* **55** (1997) 313]

In $RE_2Mo_2O_7$, a 4*d* TM on the B site results in broad bands and ferromagnetism [Ali *et al. J. Solid State Chem.* **83** (1989) 178; Moritomo *et al. Phys. Rev. B.* **63** (2001) 144425]

In AOs_2O_6, a 5*d* TM and the high oxidation state broadens bands leading to metals/superconductors [Yonezawa *et al. J. Phys. Soc. Jpn.* **73** (2004) 819]

In spinels, when S or Se are the anion (rather than O), the band width is recovered: $CuCr_2S_4$ is FMM and $Cu_{0.5}Fe_{0.5}Cr_2S_4$ shows CMR [Ramirez *et al. Nature* **386** (1997) 156]

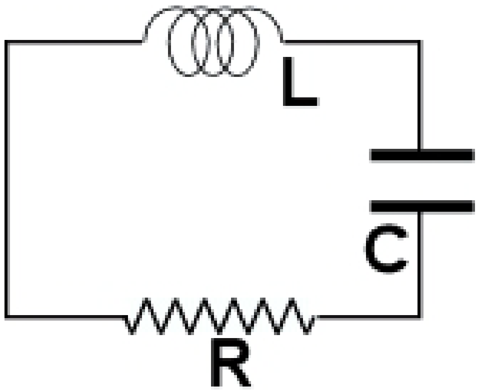
Spinel magnets

Frustration: The topologies of these two structures result in certain ground states being geometrically frustrated ⇨ rich magnetic phase behavior can ensue. *Sketch frustration.*

Two *d* cation sites in spinel: The possibility of ferrimagnetism. Also non-collinear structures in Cr spinels.

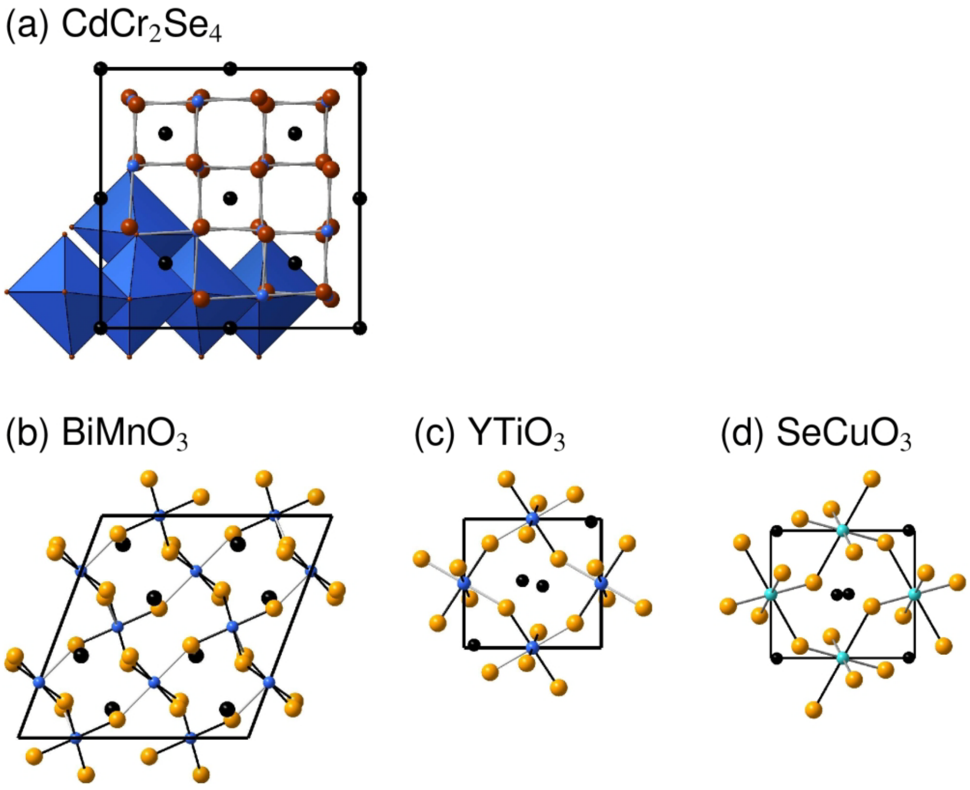
Spinel magnets

Why magnetic insulators ?

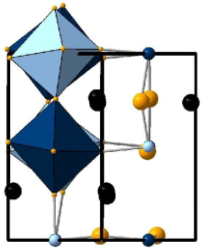


- High k and high m materials
- Materials with magnetic field tunable capacitance
- Multiferroics

Require magnetic insulators !



(e) La_2NiMnO_6



All low T_c materials except (e)

Spinel magnets

Driven by antiferromagnetic interactions, can be insulating

The AB_2O_4 palette: Almost all ions are closed magnetic shells.

A	Magn.	JT	B	Magn.	JT	Aniso.
Mn^{2+}	Y	N	V^{3+}(s)	Y	Y	N/Y
Fe^{3+}	Y	N	Cr^{3+}(s)	Y	N	N
Co^{2+}	Y	N	Mn^{3+}(s)	Y	Y	N/Y
Ni^{2+}	Y	Y	Fe^{2+}	Y	N	N
Cu^{1+}	N	N	Fe^{3+}	Y	N	N
Cu^{2+}	Y	Y	Co^{2+}	Y	N	Y
Zn^{2+}	N	N	Co^{3+}	N	N	N
Ga^{3+}	N	N	Rh^{3+}(s)	N	N	N
			Ni^{2+}	Y	N	N
			Cu^{2+}	Y	N	N
			Al^{3+}	N	N	N

Spinel magnets

$CoCr_2O_4$: A new magnetoelectric

Lawes, Melot, Page, Ederer, Proffen, Hayward, Seshadri, *Phys. Rev. B* **74** (2006) 024413(1-6).

Mn_3O_4: A new magnetoelectric material

Tackett, Lawes, Melot, Grossman, Toberer, Seshadri, *Phys. Rev. B* **76** (2007) 024409(1-6).

Complex (conical) magnetic ordering

1. Dilution of the A-site in $CoCr_2O_4$:
   $Zn_{1-x}Co_xCr_2O_4$

2. Dilution of the A-site in Mn_3O_4:
   $Mn_{3-x}Zn_xO_4$

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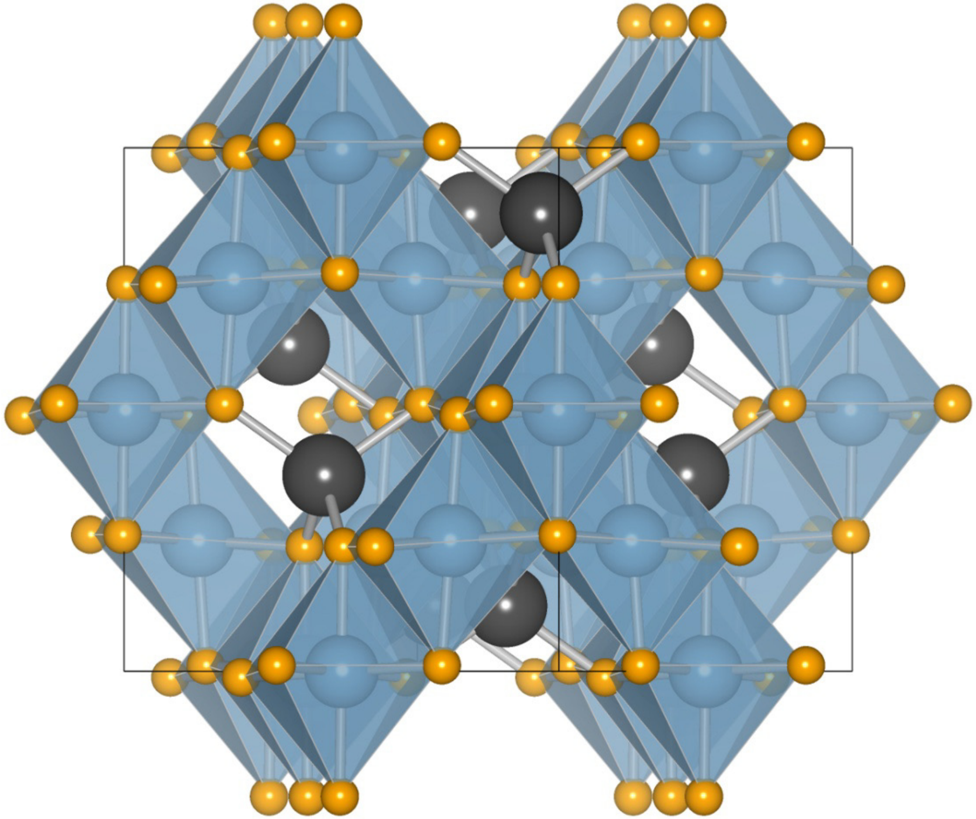
Spinel magnets

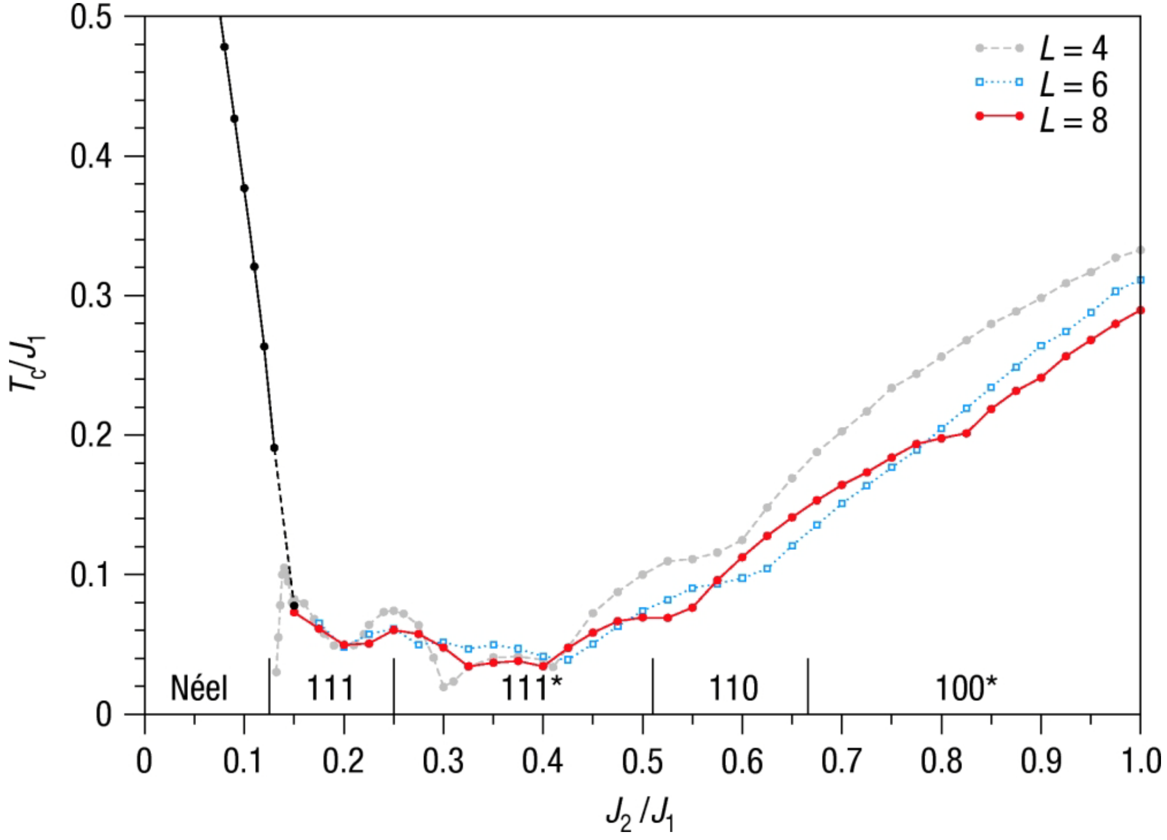


Importance of A-A couplings hinted in $CoCr_2O_4$

The A sites form a diamond lattice: two interpenetrating *fcc* lattices. All couplings are antiferromagnetic. *fcc* lattices can be frustrated.

Tristran, Hemberger, Krimmel, Krug von Nidda, Tsurkan, Loidl, *Phys. Rev. B* **72** (2005) 174404.

Spinel magnets



Magnetic ordering and frustration decided by the ratio of the next-near-neighbor (J_2) and near neighbor (J_1) couplings.

Interest in the 111 spiral structures

Bergman, Alicea, Gull, Trebst, and Balents, *Nature Phys.* 3 (2007) 487-491.

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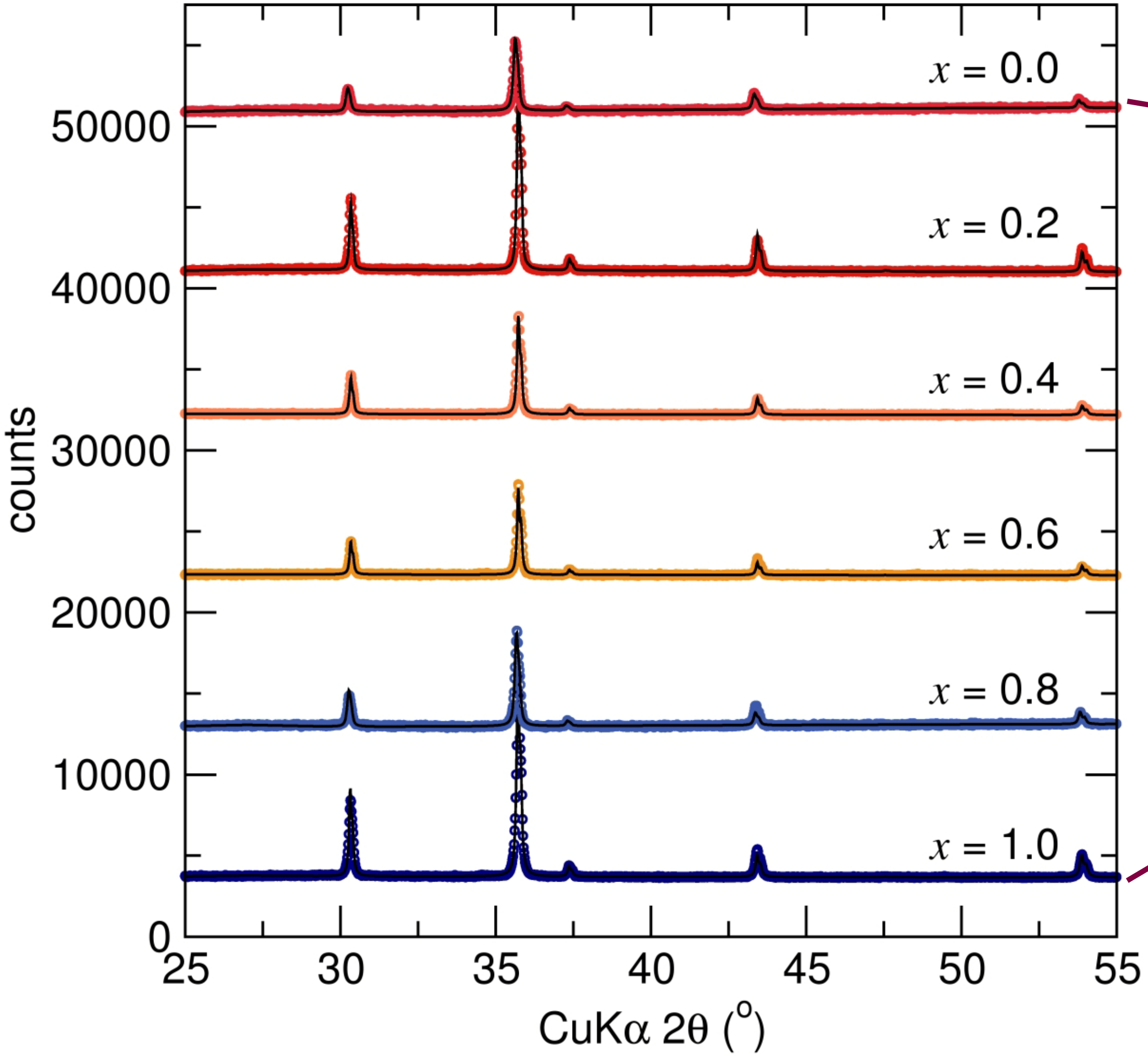

$ZnCr_2O_4$: Famously distorts to escape frustration [spin Jahn-Teller].

$CoCr_2O_4$: Conical ground state, magnetoelectric.

Fully ordered Cr^{3+} on the B site.

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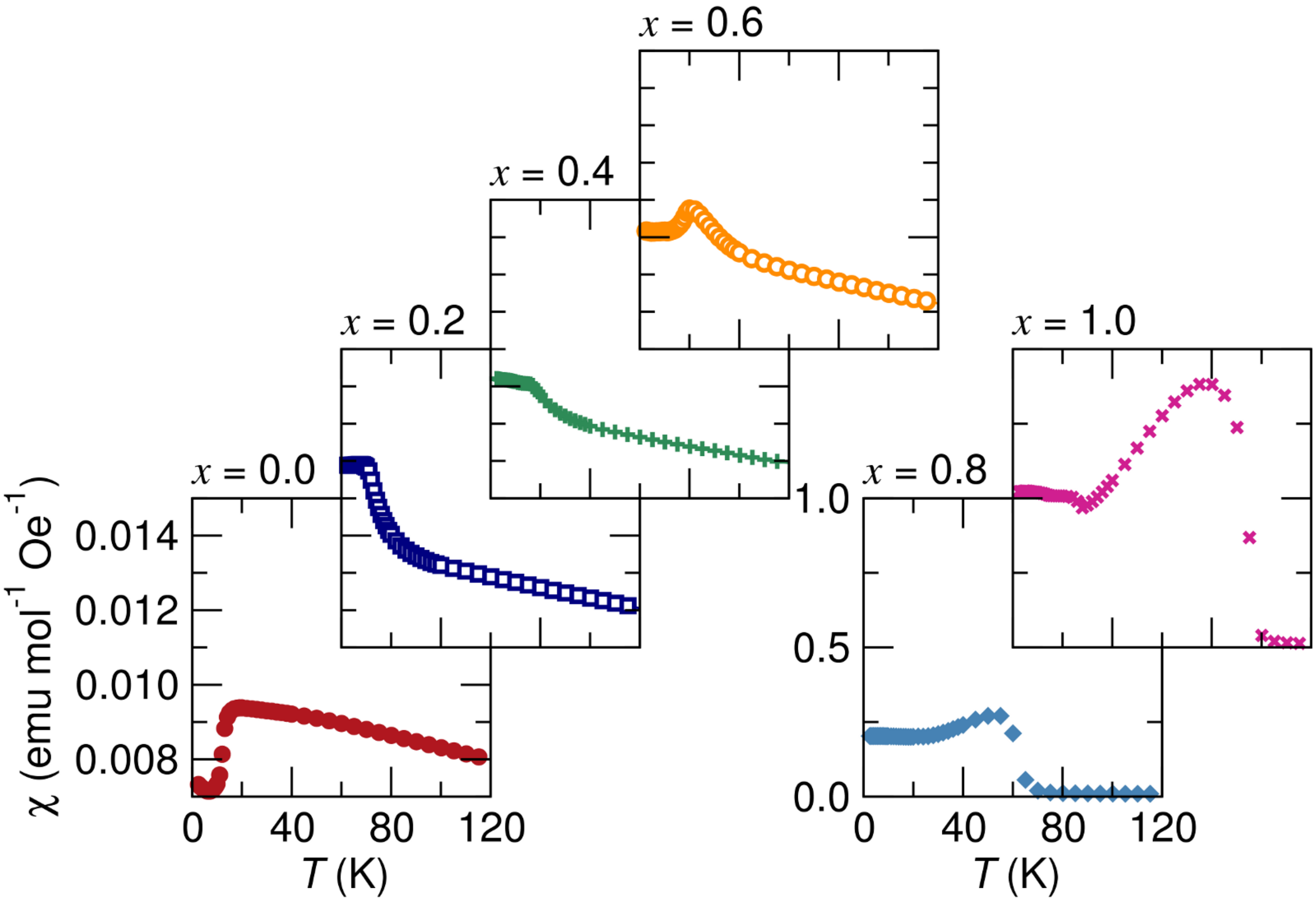
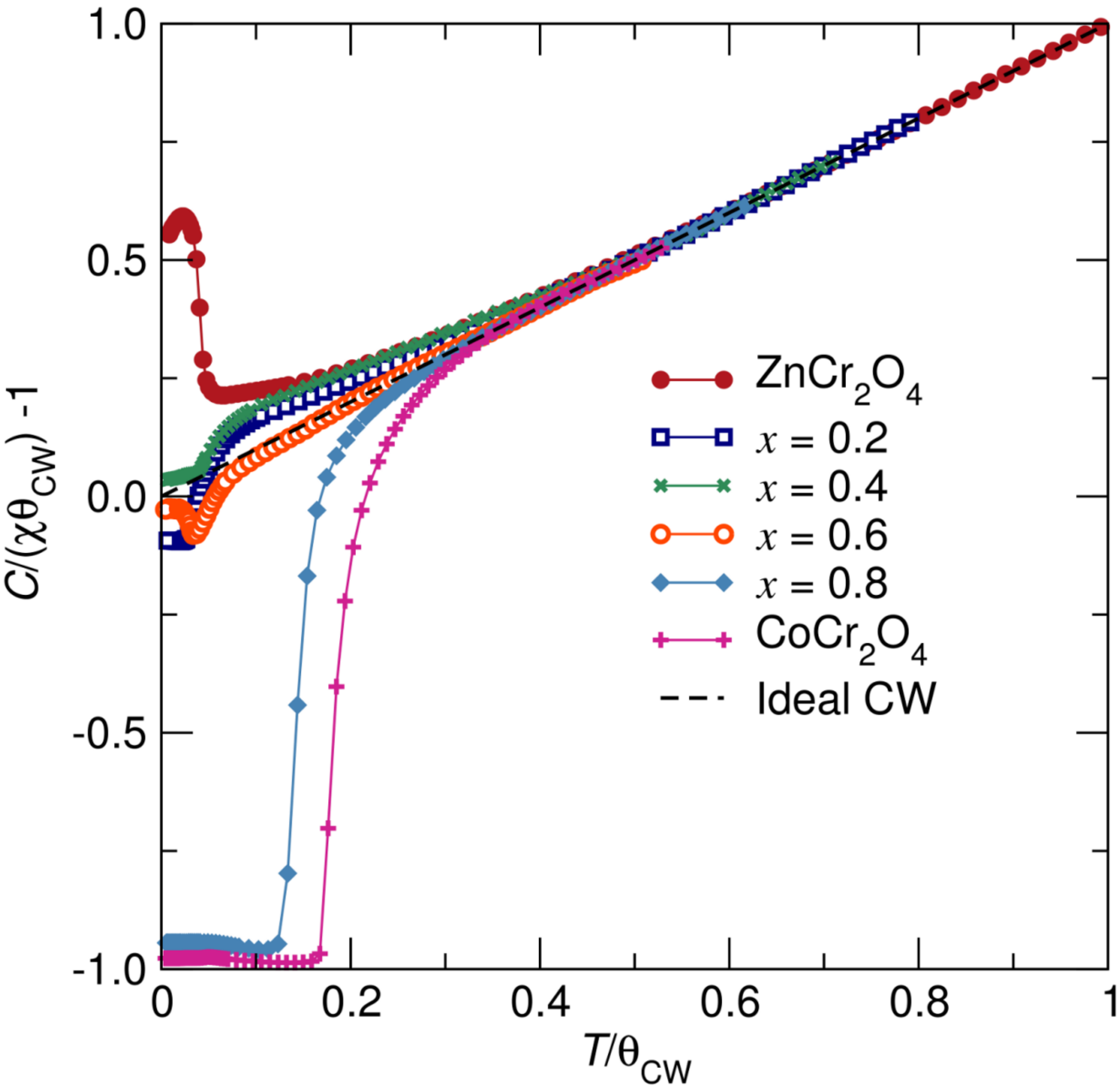
All the samples transition below 100 K, with the nature of the transition widely varying:



Spinel magnets



All compounds are frustrated.

Notable switch in the nature of the deviation from Curie-Weiss behavior on Co substitution: Ferrimagnetism

Analogy with metal-insulator transitions.

Curie-Weiss:

$\chi = C/(T-\Theta_w)$

$C/\chi\Theta_w = T/\Theta_w - 1$

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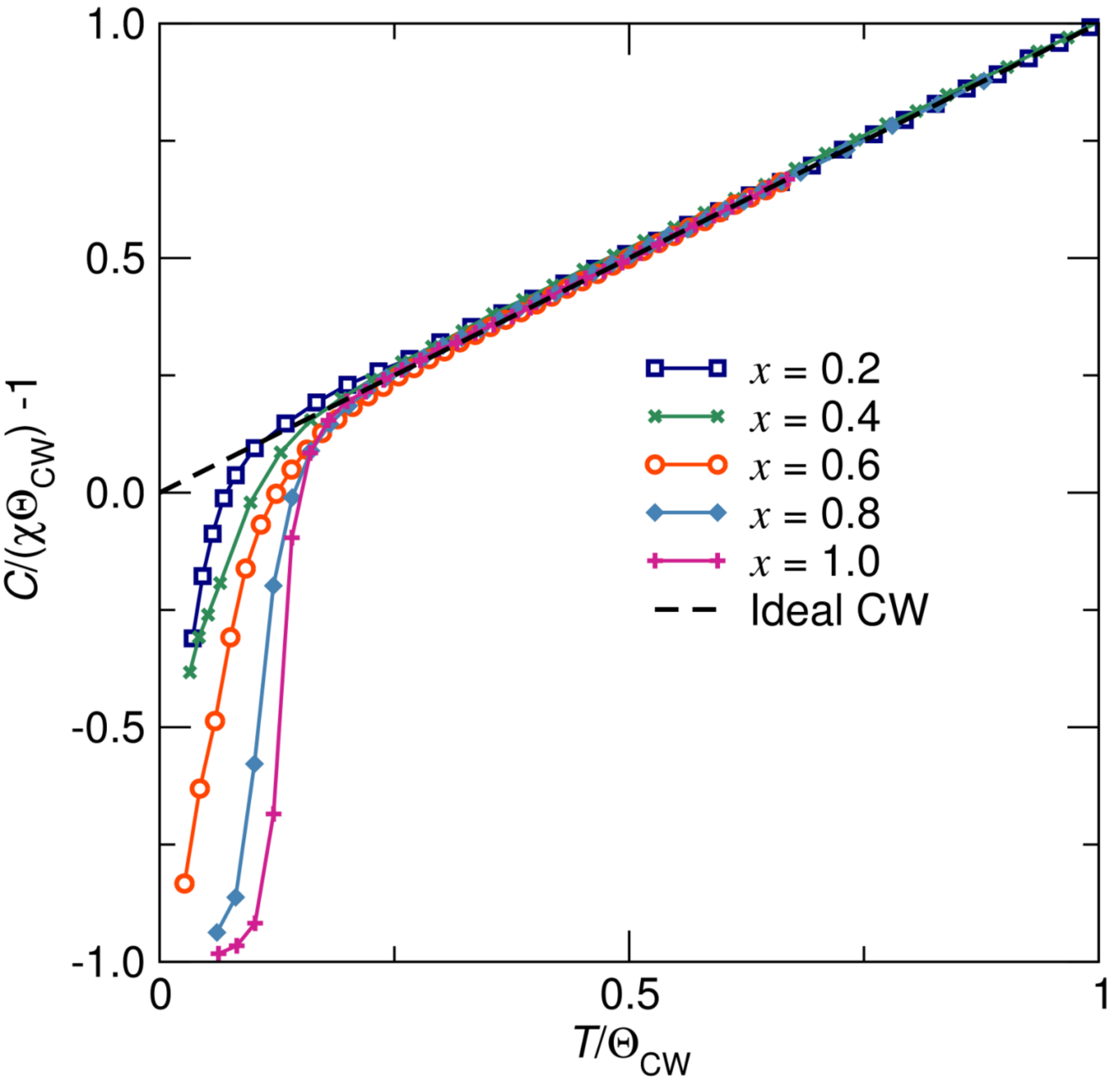

Monte-Carlo simulations (Miles Stoudenmire) do a good job of reproducing the gross features.

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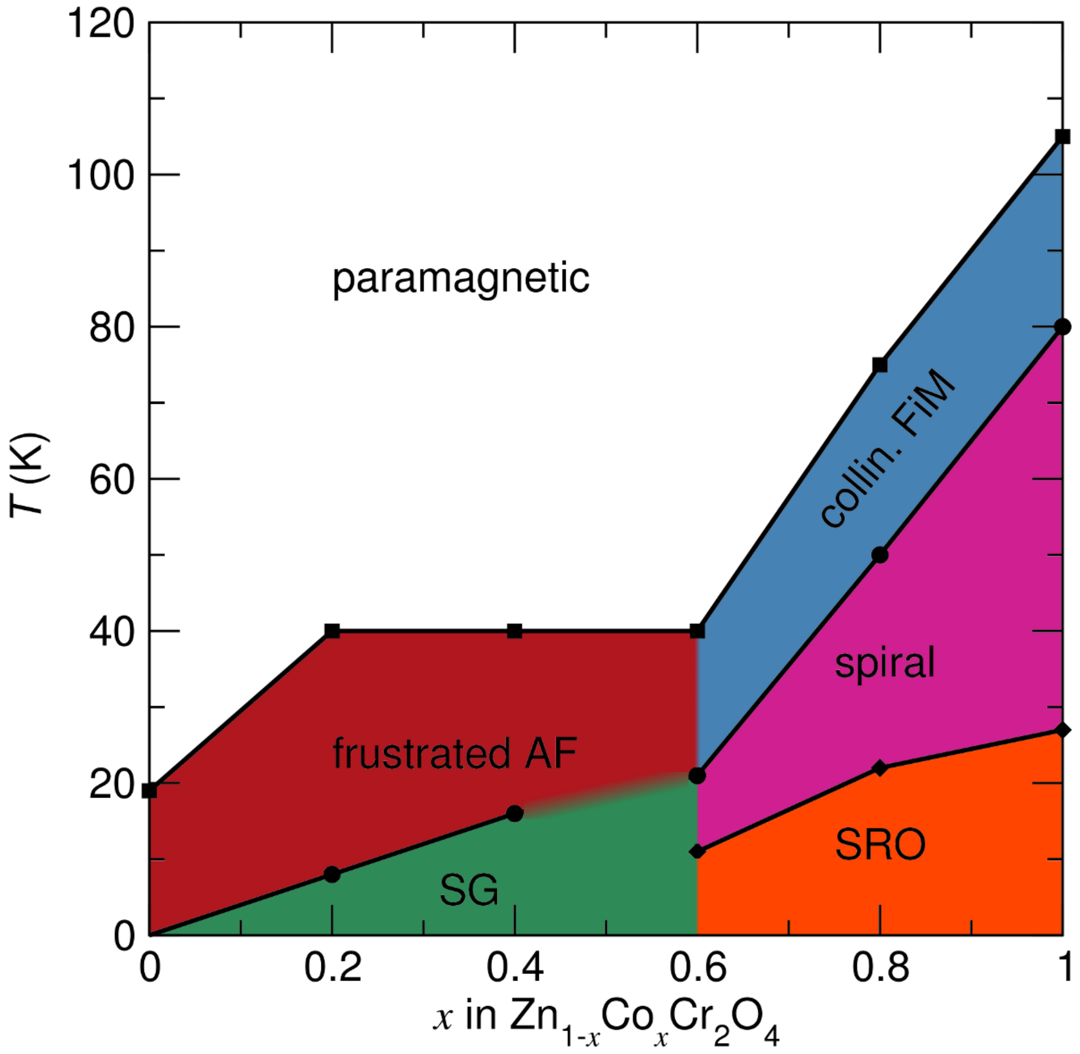
Rich phase experimental phase diagram, extrapolated from end-members.

Awaits direct verification.



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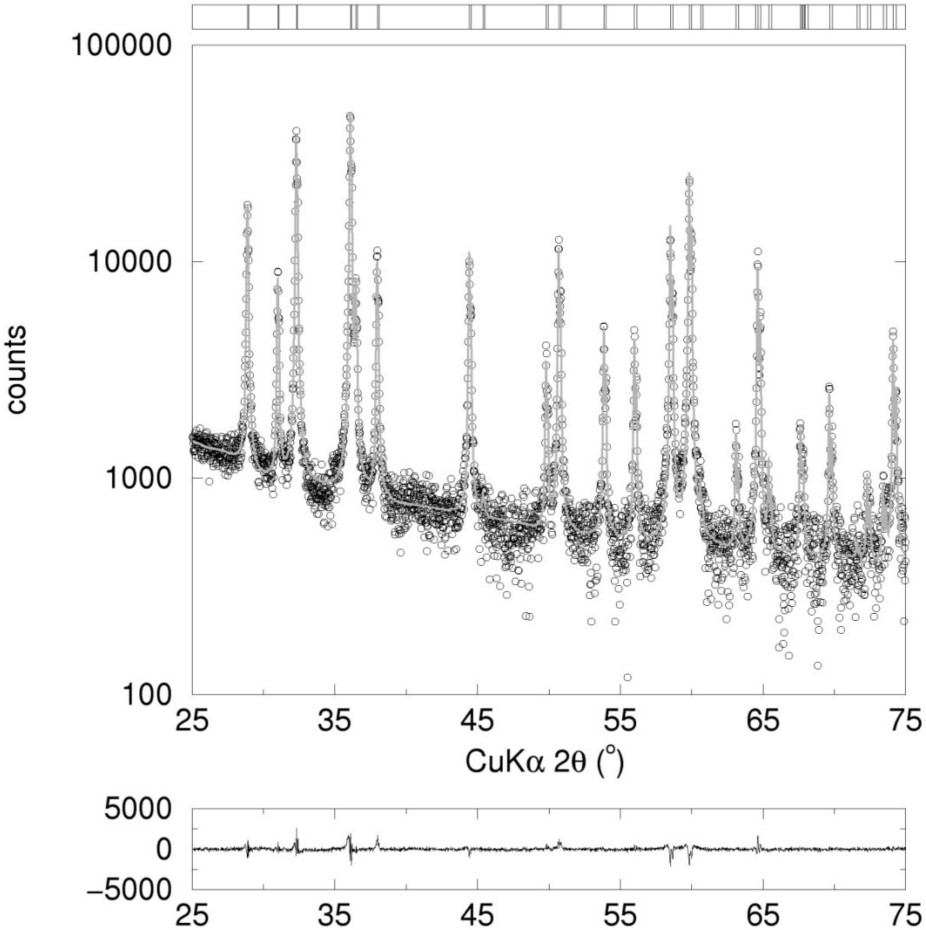
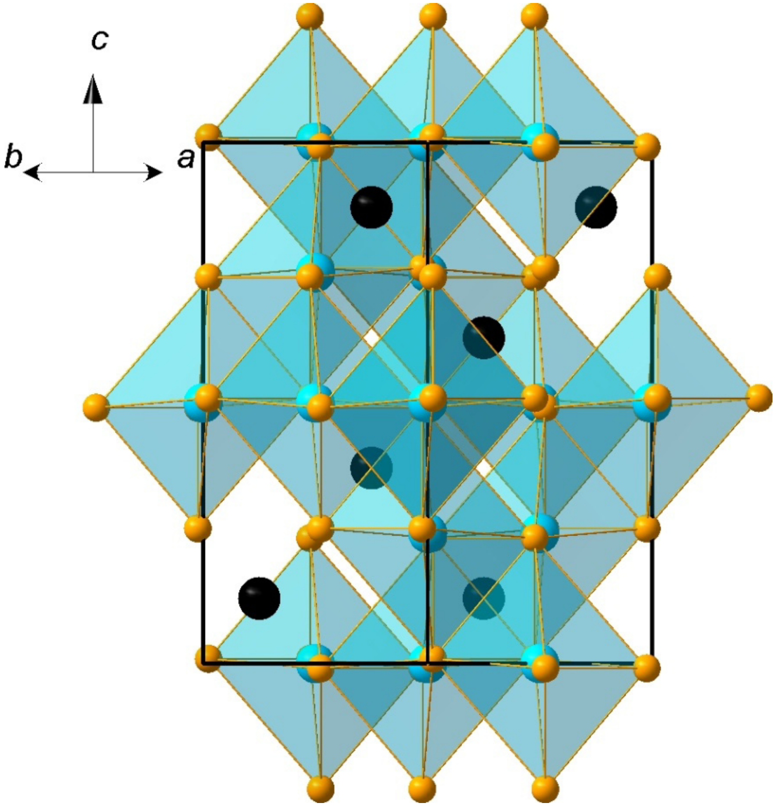
Hausmanite: Jahn-Teller distorted spinel: $Mn^{2+}Mn^{3+}{}_2O_4$





Clean samples obtained by quenching from high temperatures.

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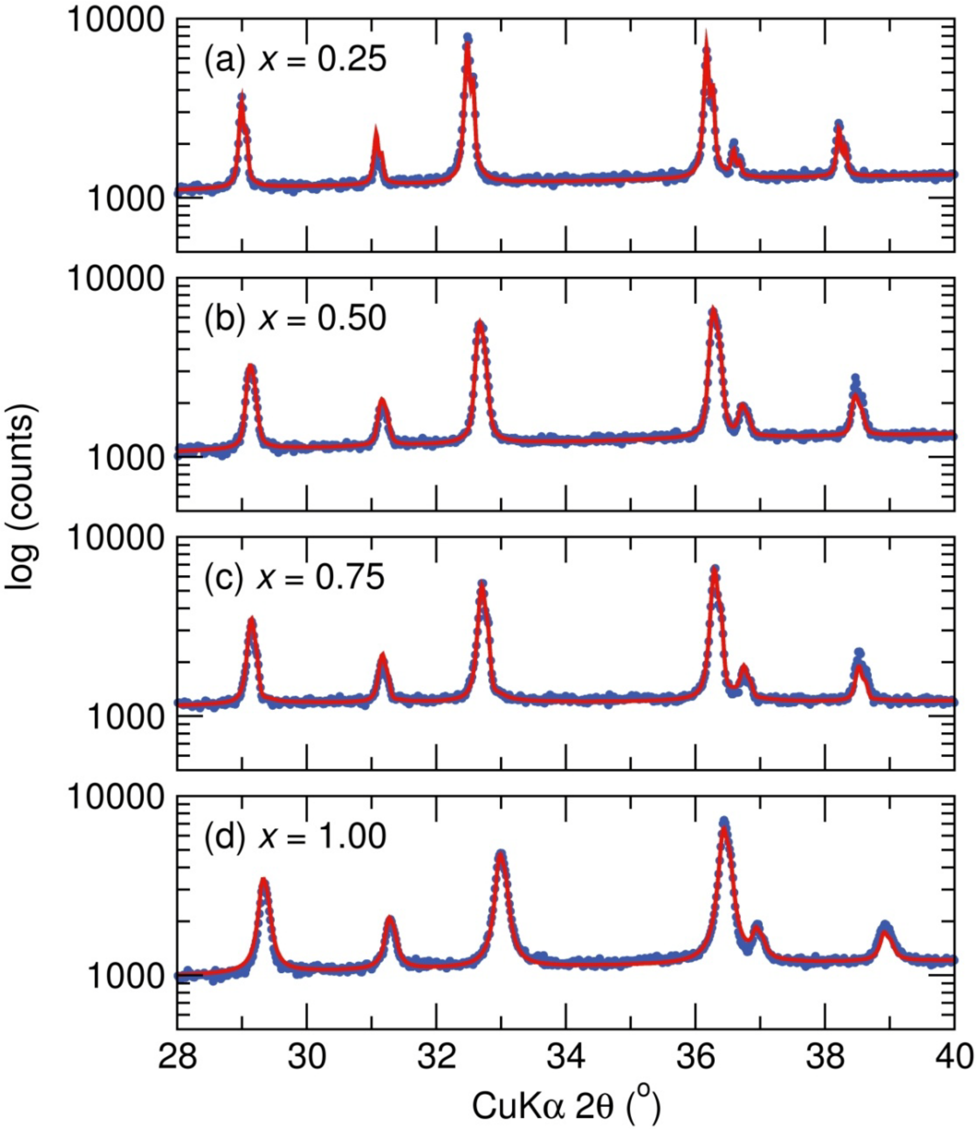
Hausmanite to haeterolite, clean phases, with no evidence from peak broadening for inhomogeneiety.



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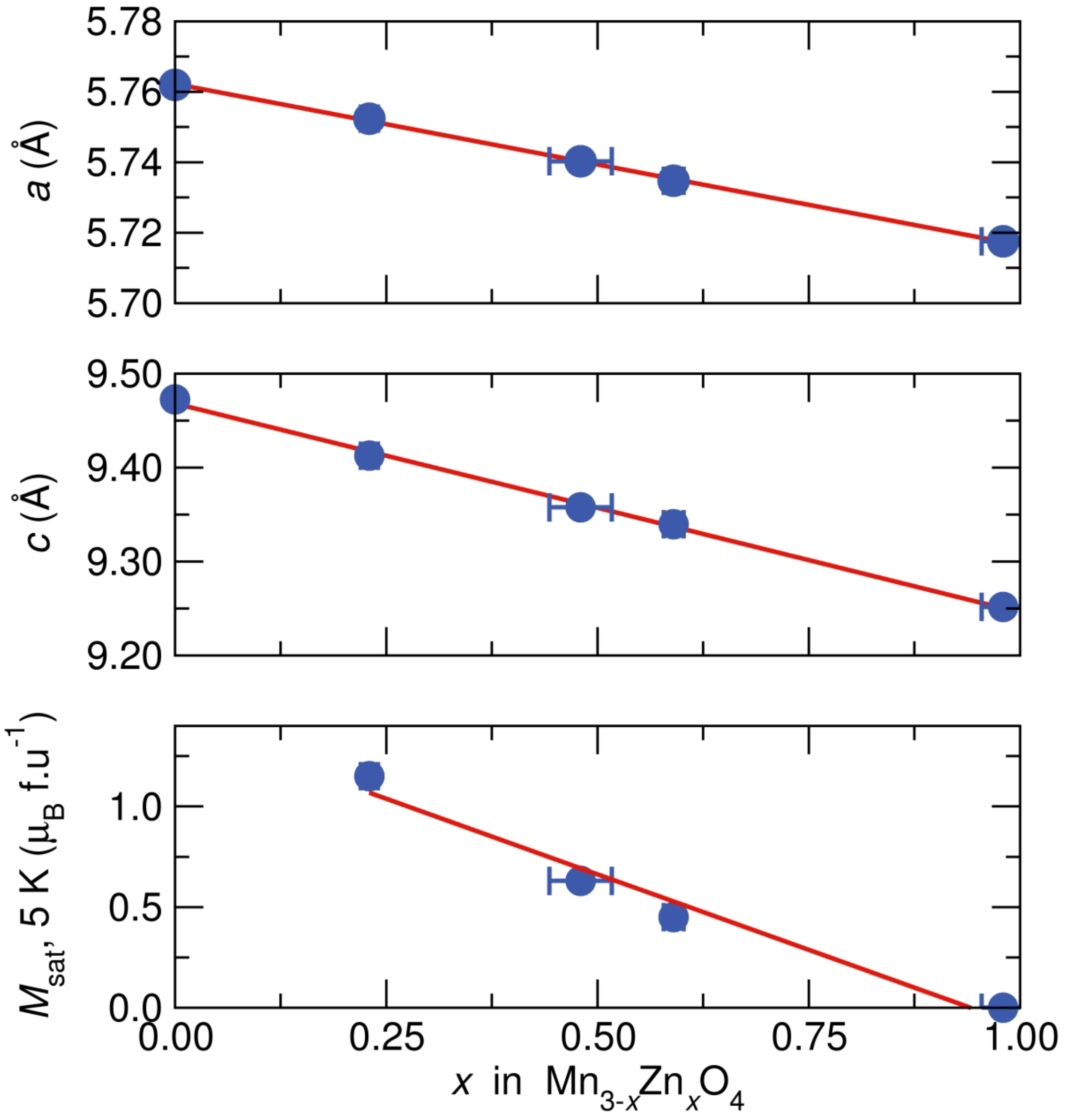

Cell parameter evolution obeys Vegard law.

TEM studies in progress.

Composition from electron microprobe analysis suggests homogeneity . Some deviation in the 0.75 sample from starting stoichiometry.

Saturation magnetization (5 K) is also well-behaved.

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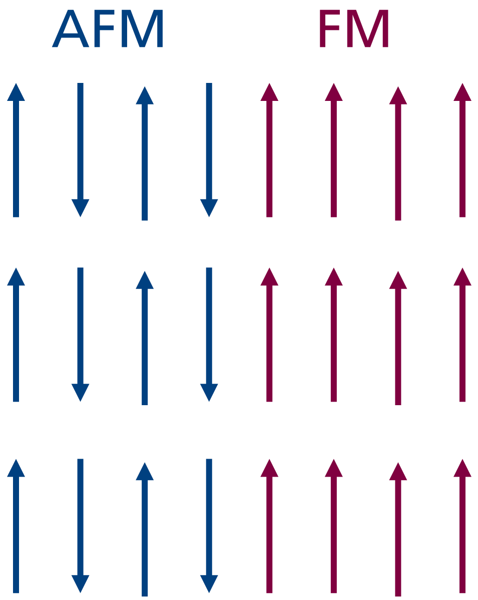
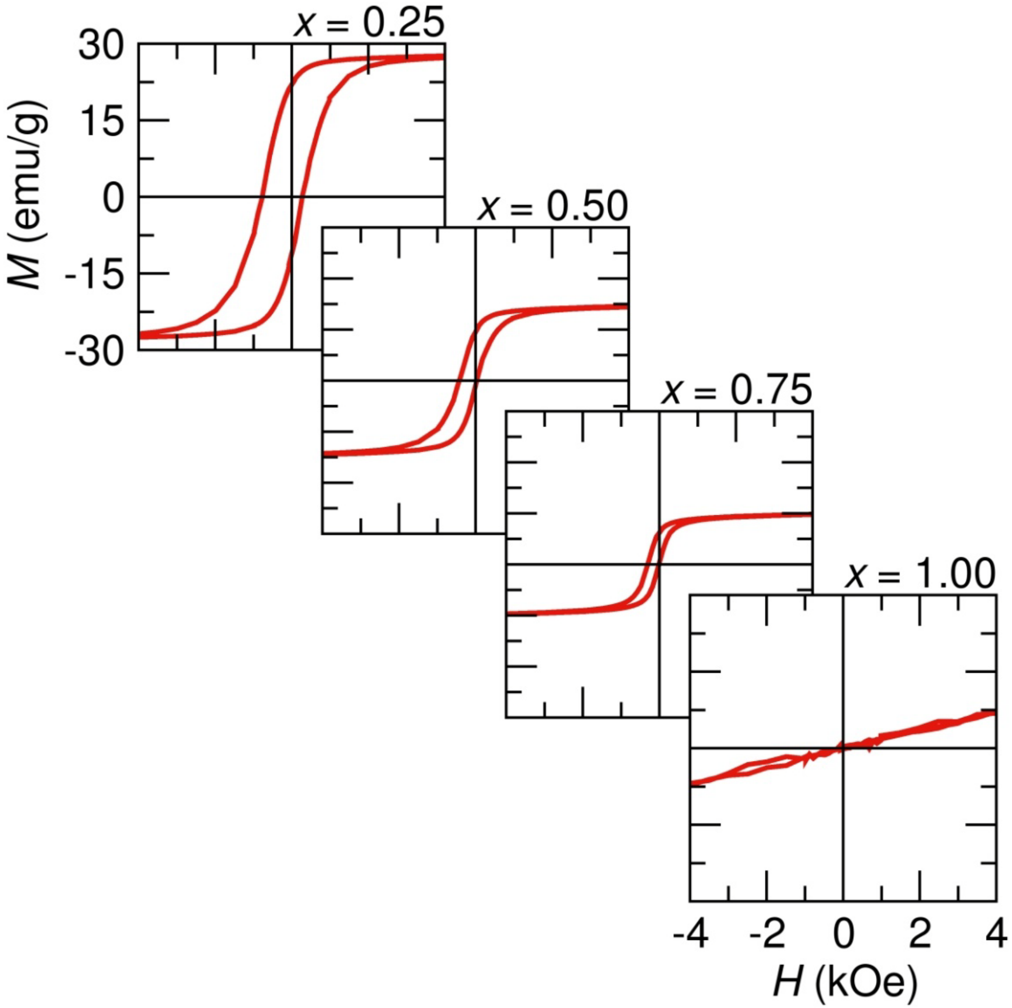
Hysteresis loops after field cooling display a puzzling shift. Exchange bias ?





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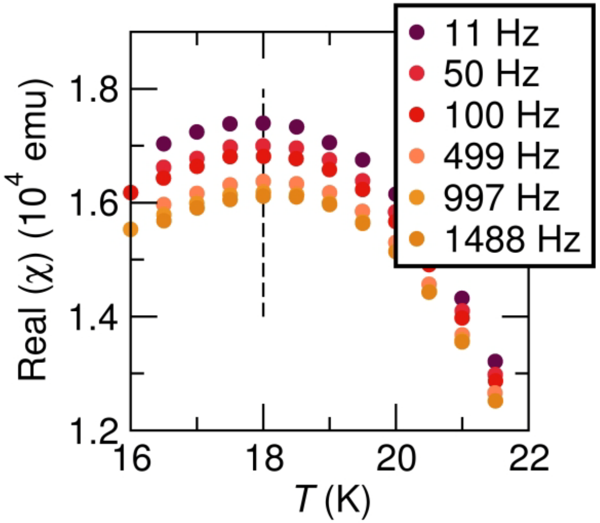
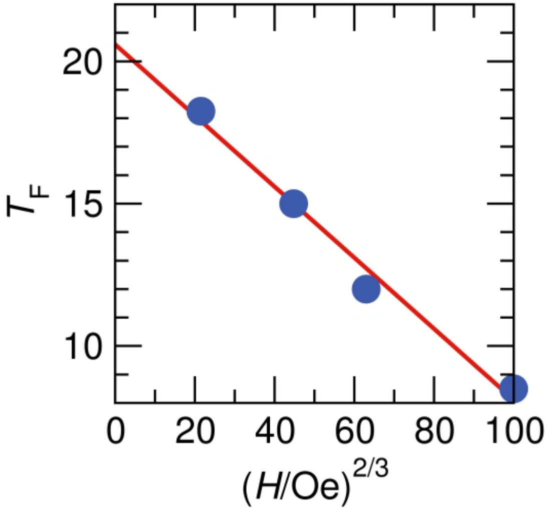
Spinel magnets

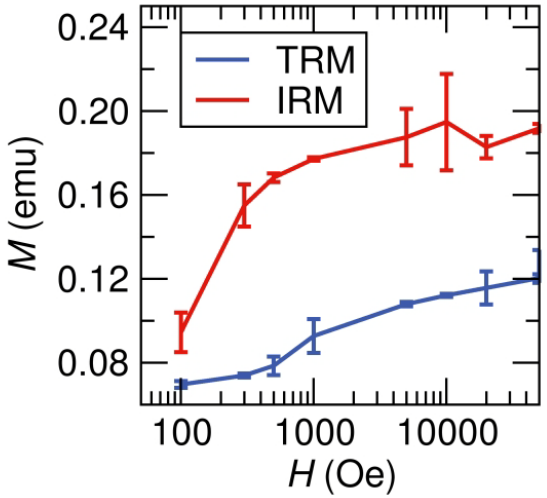
Hysteresis loops after field cooling display a puzzling shift.

Exchange bias, or a consequence of glassy magnetism ?

Some tests for a spin glass fulfilled, not others.







Thank you !