Practical Implementation and Applications of DFT Methods

David J. Singh
Oak Ridge National Laboratory

Theory Winter School,
*Tallahassee, Florida*

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Blueberry Muffins

The blueberries change the taste, but the muffin is still basically a muffin.

The taste does not depend much on the distribution of berries.

The Electron Gas

D. Ceperley, Nature **397**, 386 (1999).
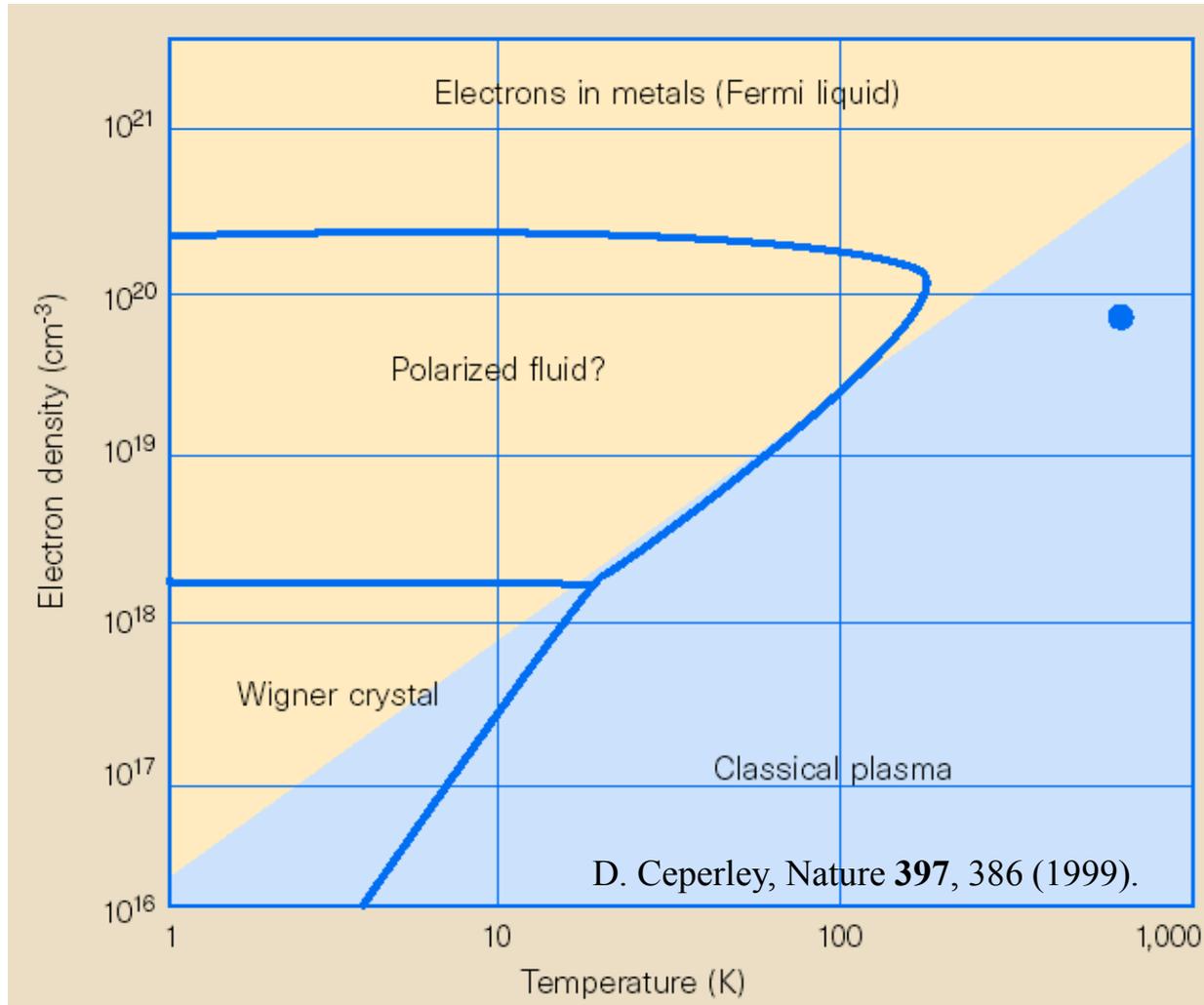
bcc **Fe:** $n_{av} = 2.2 \times 10^{24}$ e/cm^3 (total); $n_{av} = 6.8 \times 10^{23}$ e/cm^3 (valence)

Nothing Interesting Happens in the Uniform Electron Gas at Densities of Solids

The Electron Gas Now With Nuclei

He: liquid at 0 K
W: melts at 3695 K

First Principles Modeling

- Connect properties with atomic level structure.

- Sort out physical models.

- Ask "what if" questions.

- Microscopic mechanisms and **understanding.**

- Screen ideas for new/modified materials.

- Analyze failures.

Image courtesy of E. Wimmer

Pre-History

1902
P.A.M.
DIRAC OM
PHYSICIST
iℏ∂ψ=mψ
1984
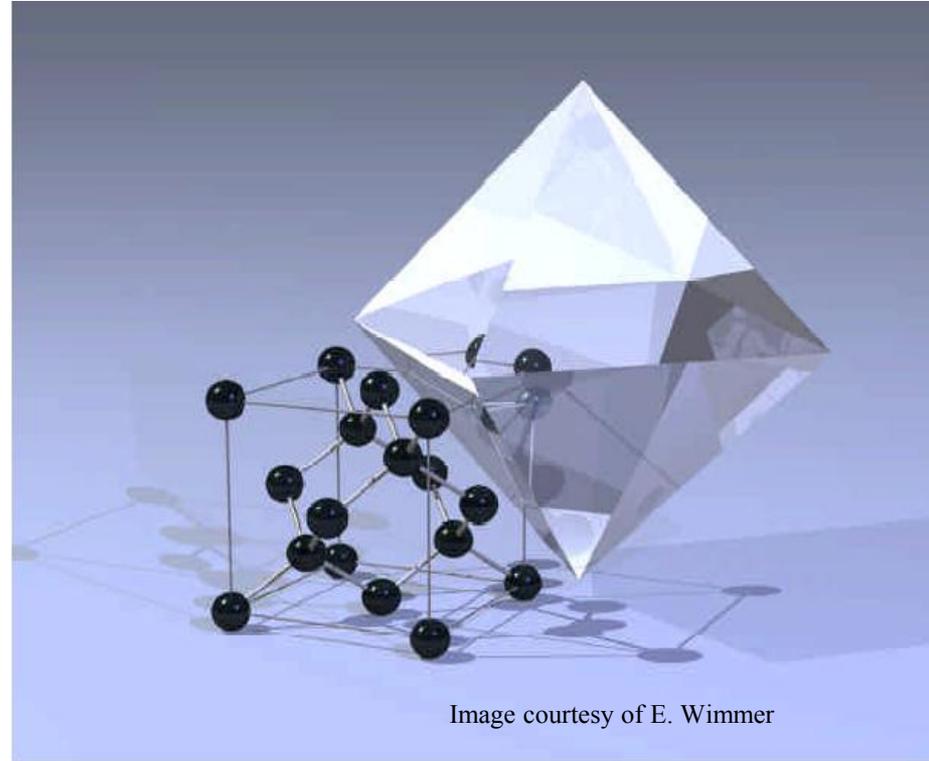
Westminster Abbey, London

"*The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations that are much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.*"

P.A.M. Dirac, *Proc. Roy. Soc. (Lond)* **123**, 714 (1929).

$H\psi = E\psi$: Many Body Problem, with correlated many-body wavefunctions ➜ Too hard.

Wigner and Seitz (1955)

"*If one had a great calculating machine, one might apply it to the problem of solving the Schrodinger equation for each metal and obtain thereby the interesting physical quantities, such as cohesive energy, the lattice constant, and similar parameters. Presumably, the results would agree with experimentally determined quantities and nothing vastly new would be gained from the calculation. **It would be preferable, instead, to have a vivid picture of the behavior of the wave functions, a simple description of the essence of the factors which determine cohesion, and an understanding of the origins** …*"

E.P. Wigner and F. Seitz, Solid State Physics, Vol. 1 (1955).

WARNING

If you do not ask questions, I will.

(corollary) If you do not contradict me, I will.
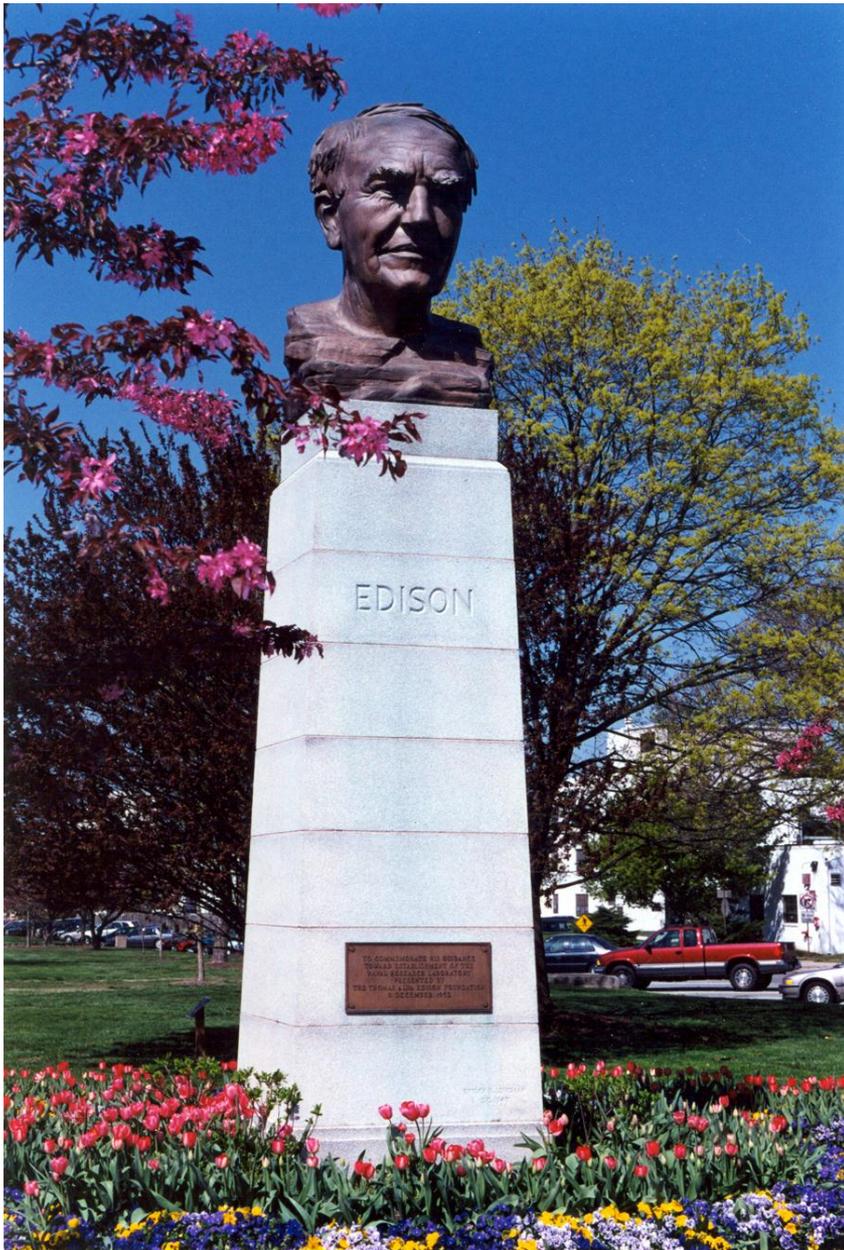
"Hell, there are no rules here - we're trying to accomplish something."

Thomas Edison

TODAY'S PLAN

- General Remarks about DFT and Applications.

- Magnetism and Superconductivity (Iron-Based Superconductors).

- Very Short Introduction to the LAPW Method and the ELK code for the Hand's-On.

Property Prediction and Surprises

$YBa_2Cu_3O_{6+x}$
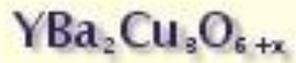
Y
Ba
Cu
O
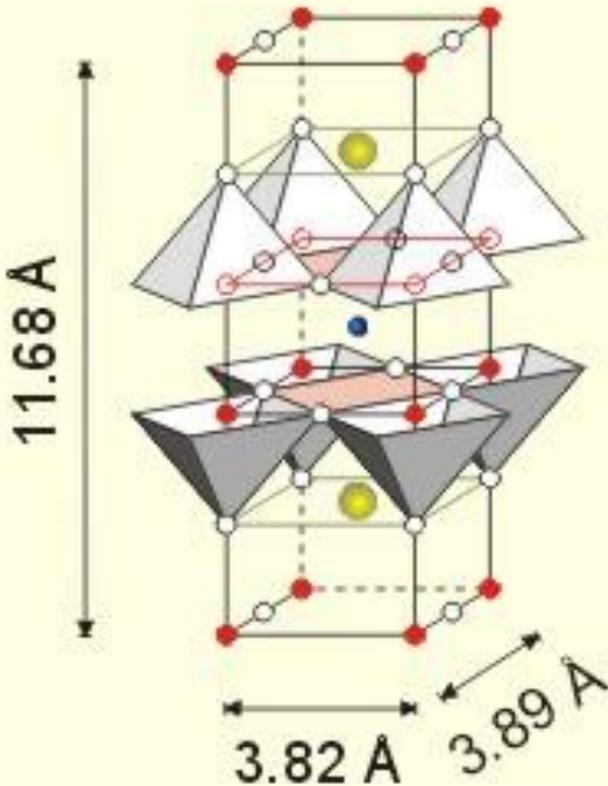
Cu(1), O(4)

Ba, O(1)

Cu(2), O(2), O(3)

Y

Cu(2), O(2), O(3)

Ba, O(1)

Cu(1), O(4)

11.68 Å

3.82 Å   3.89 Å

c
b
a
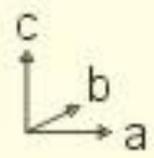
M. Opel

High-T_c Electronic Structures are 2D
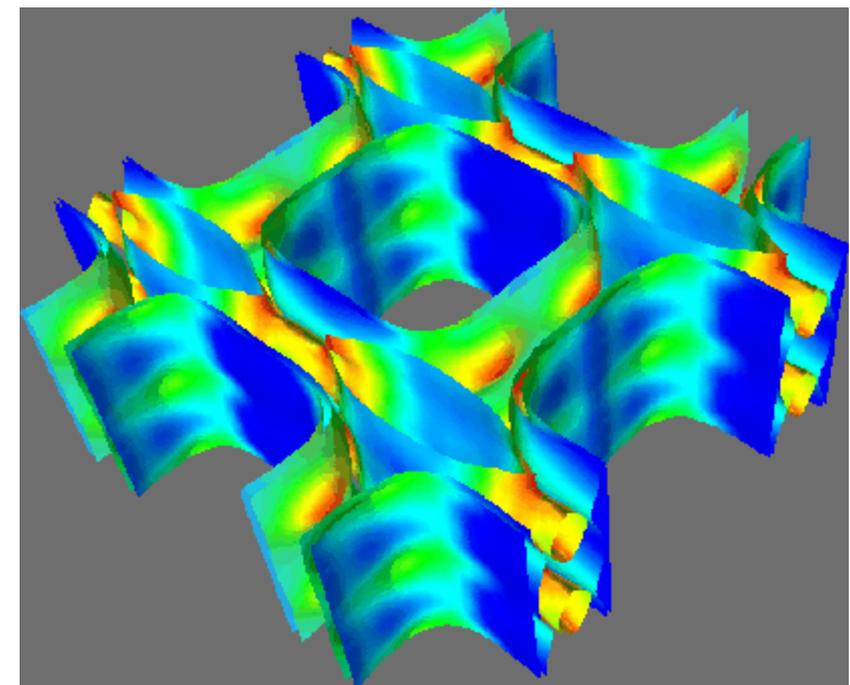
Pickett, Cohen, Krakauer, Singh

$Bi_2Sr_2(Ca_xY_{1-x})Cu_2O_{8+\delta}$

Y

Ca /Y
Cu, O(2,3)
Sr, O(1)
Bi, O(4)
Bi, O(4)
Sr, O(1)
Cu, O(2,3)
Ca /Y
Cu, O(2,3)
Sr, O(1)
Bi, O(4)
Bi, O(4)
Sr, O(1)
Cu, O(2,3)
Ca /Y

29 Å

5.5 Å

M. Opel

$La_3Ni_2B_2N_3$ (12K SC)
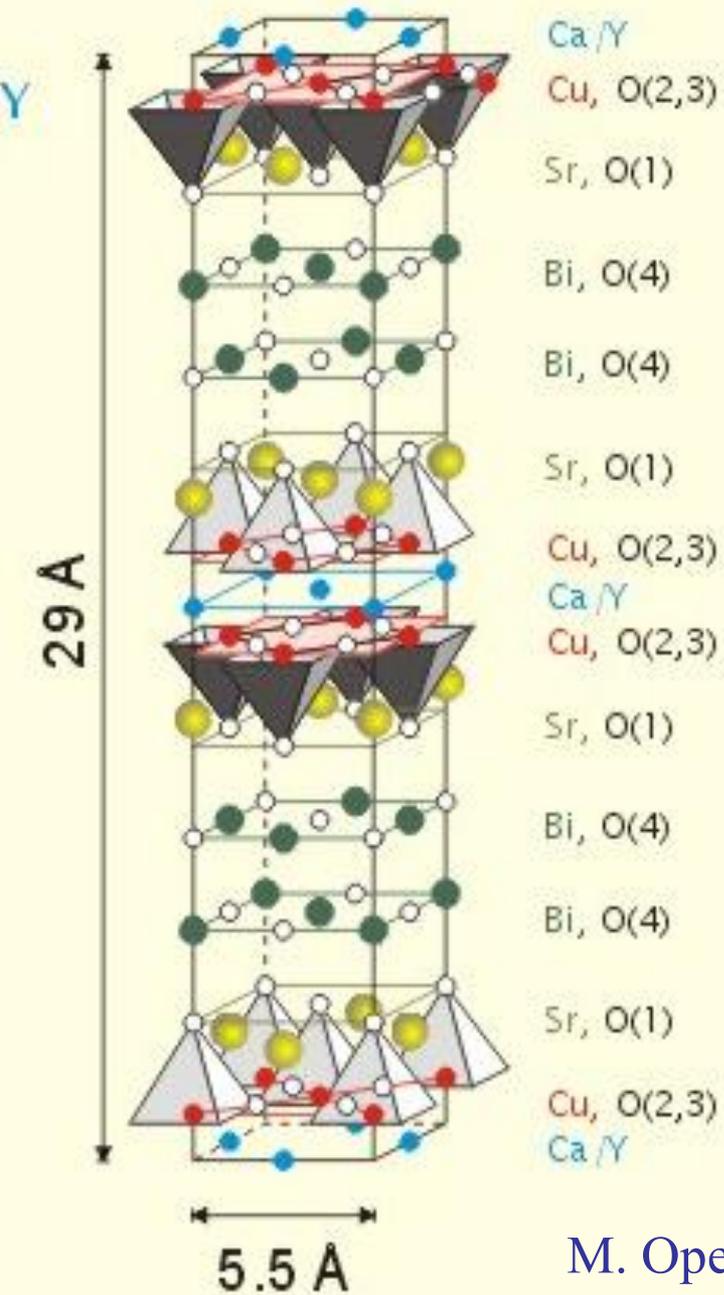
NEWS: 1994
(Nagarajan, PRL;
 Cava, Nature)

A new family of
superconductors
with T_c up to 23K

*Is 23K the tip of
the iceberg?*

LaN

Ni_2B_2

(Fig. by Huang et al.)
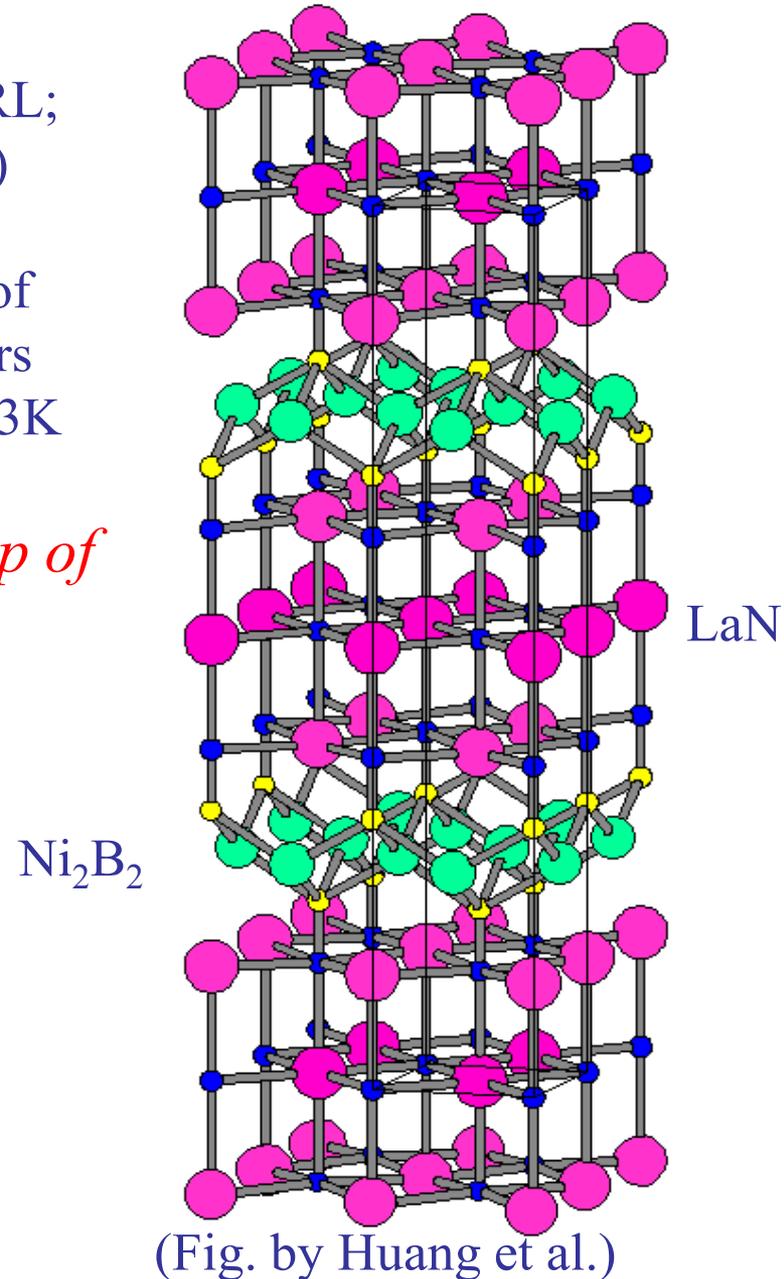
ANSWER: 1994 (Pickett and Singh, PRL) NO!

Fermi Surface of YNi_2B_2C ($T_c=16K$)
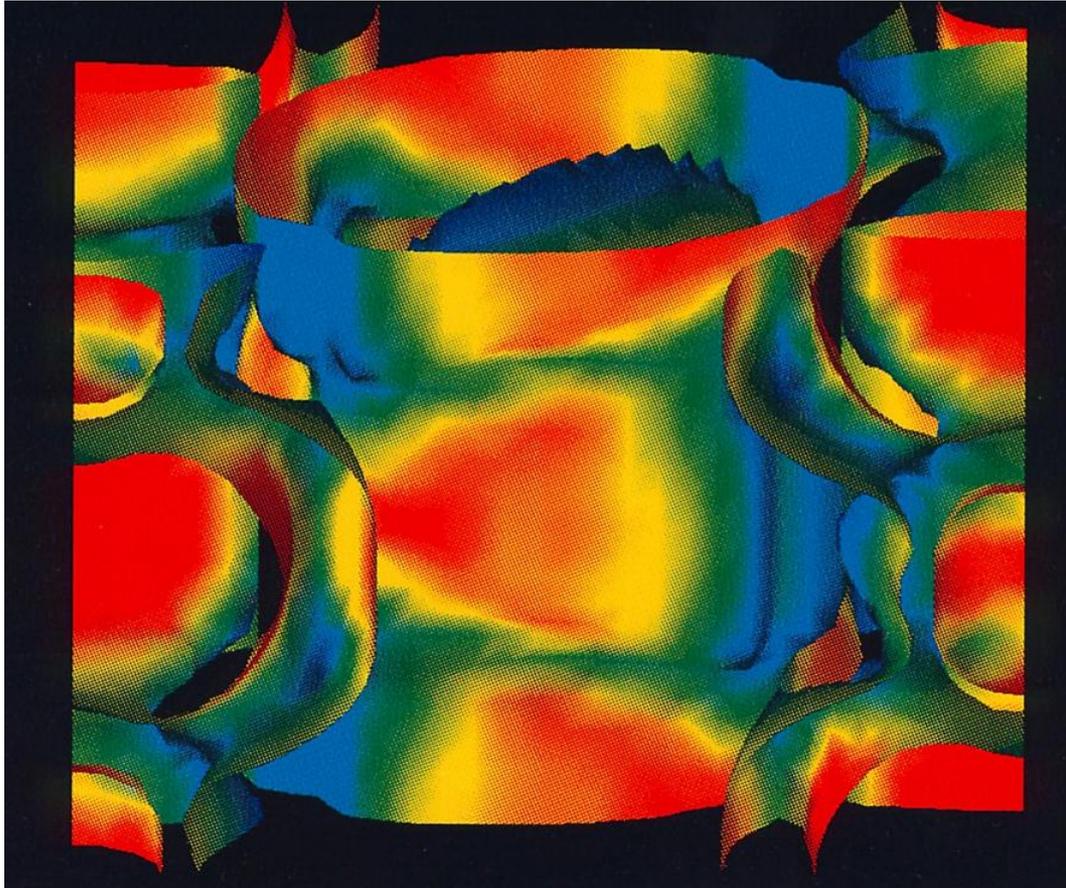
- Electronic structures are very three dimensional

- Due to strong B-C bonds

- Large electron phonon coupling is responsible for superconductivity (conventional mechanism).

- **NOT THE BASIS OF A NEW FAMILY OF HIGH TEMPERATURE SUPERCONDUCTORS**

Density Functional Theory

Standard approach: properties are governed by a wavefunction:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \; ; \; H\Psi = E\Psi$$

Given the Hamiltonian, we focus on solving for the wavefunction and extract observables as expectation values of operators with this wavefunction – for N electrons this is a $3N$ dimensional problem.

Density Functional Theory: Hohenberg-Kohn theorem tells us

- Energy and other observables of the ground state are given as functionals of the density $\rho(\mathbf{r})$ which exists in 3 dimensions only.
- The ground state density is unique and is the density that minimizes this functional.

$$E = E[\rho] \; ; \; \rho = \min_{E[\rho]}\{\rho\}$$

The functional E is proven to exist, but is not given by the theorem.

Kohn-Sham Approach

Any density N electron density can be written as the density corresponding to an N electron Slater determinant (never mind that the true wavefunction cannot).

$$\rho(\mathbf{r}) = \Sigma \; \varphi_i(\mathbf{r})^* \varphi_i(\mathbf{r}) \; ; \; i=1,2, \dots , N$$

Where the $\varphi_i(\mathbf{r})$ are the Kohn-Sham orbitals
➡ variational principle for ρ yields a variational principle for the $\varphi_i(\mathbf{r})$.

Kohn and Sham then separated terms that should be large in the functional leaving a (hopefully) small remainder as the unknown functional.

$$E[\rho] = T_s[\rho] + E_{ext}[\rho] + U_{Hartree}[\rho] + E_{xc}[\rho]$$

where, like E, E_{xc} is unknown. E_{xc} is defined by this equation.

Kohn-Sham Equations

Use the variational principle to write single particle equations for the Kohn-Sham orbitals.

$$\{T_s + V_{ext} + V_{Hartree} + V_{xc}\}\varphi_i = \varepsilon_i \varphi_i$$

$$\rho(\mathbf{r}) = \Sigma \, \varphi_i(\mathbf{r})^*\varphi_i(\mathbf{r}) \; ; \; i=1,2, \ldots , N$$

Here, V_{hartree} and V_{xc} are functionals of the density (functional derivatives of the energy terms with respect to density), so generally these equations must be solved self-consistently.

This is straightforwardly generalizable to magnetic systems via spin-density functional theory where instead of a single function one has spin-densities, $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$ for the collinear case and a four component spinor for non-collinear.

The Local Density Approximation

Generally one may write

$$E[\rho] = \int \rho(\mathbf{r}) \, \varepsilon_{xc}[\rho](\mathbf{r}) \, d^3\mathbf{r}$$

The local (spin) density approximation consists of taking $\varepsilon_{xc}[\rho]$ at each point $\mathbf{r}$ as the value for the uniform electron gas at the density for this $\mathbf{r}$.

This exceedingly simple approximation works remarkably well, especially considering that the electron gasses of solids are nothing close to the uniform electron gas.

Theory of static structural properties, crystal stability, and phase transformations: Application to Si and Ge

M. T. Yin* and Marvin L. Cohen

Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720
(Received 29 March 1982)

TABLE II. Comparison of calculated and measured static properties of Si and Ge.

	Lattice constant (Å)	Cohesive energy (eV/atom)	Bulk modulus (Mbar)
Si			
Calculation	5.451	4.84	0.98
Experiment	5.429[a]	4.63[b]	0.99[c]
Ge			
Calculation	5.655	4.26	0.73
Experiment	5.652[a]	3.85[b]	0.77[c]
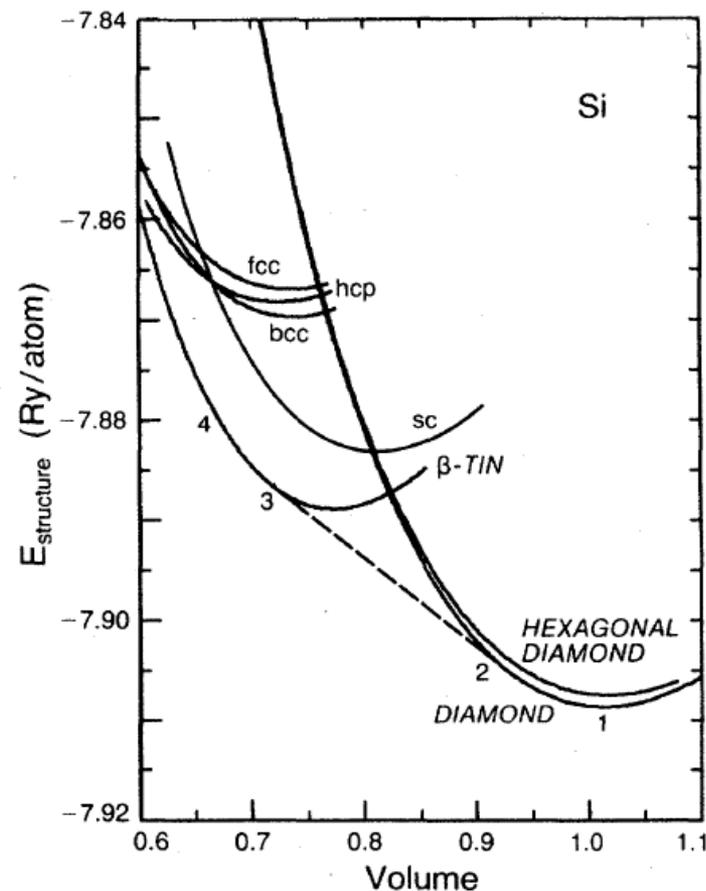
One of many early works of this type.

Modern Density Functionals

$$E[\rho] = \int \rho(\mathbf{r})\, \varepsilon_{xc}[\rho](\mathbf{r})\, d^3\mathbf{r}$$

(1) Local (spin) density approximation: $\varepsilon_{xc}[\rho](\mathbf{r}) = \varepsilon_{local}(\rho(\mathbf{r}))$

- Widely used, especially for metals.

(2) Generalized gradient approximations (GGA, Langreth, Perdew):
$$\varepsilon_{xc}[\rho](\mathbf{r}) = \varepsilon_{gga}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|)$$

- Much improved binding energies compared to LDA (chemical accuracy).

- Not gradient expansions, but sophisticated functionals based on exact scaling relations for the inhomogeneous electron gas (electron gas in solids is very non-uniform – can't use gradient expansions).

- New versions, e.g. PBE-SOL, Wu-Cohen, give almost uniform improvement over LDA in structural properties.

Modern Density Functionals

(3) Hybrid functionals (Becke and others):

- Mixture of GGA and Hartree-Fock exchange on the Kohn-Sham orbitals.

- Common in chemistry and semiconductor physics (band gaps are better than standard LDA or GGA's).

(4) Van der Waal's Functionals (Langreth, Lundqvist):

- Non-local functionals that incorporate dispersion interactions.

- Surface science, molecular systems, water, DNA, carbon materials, etc.

Salt

NaCl:

Halides (Cl, Br, I)

- Structures generally show cations in locally symmetric anion cages, but the overall lattice structures of halides are often very non-isotropic (Pauling Rules).
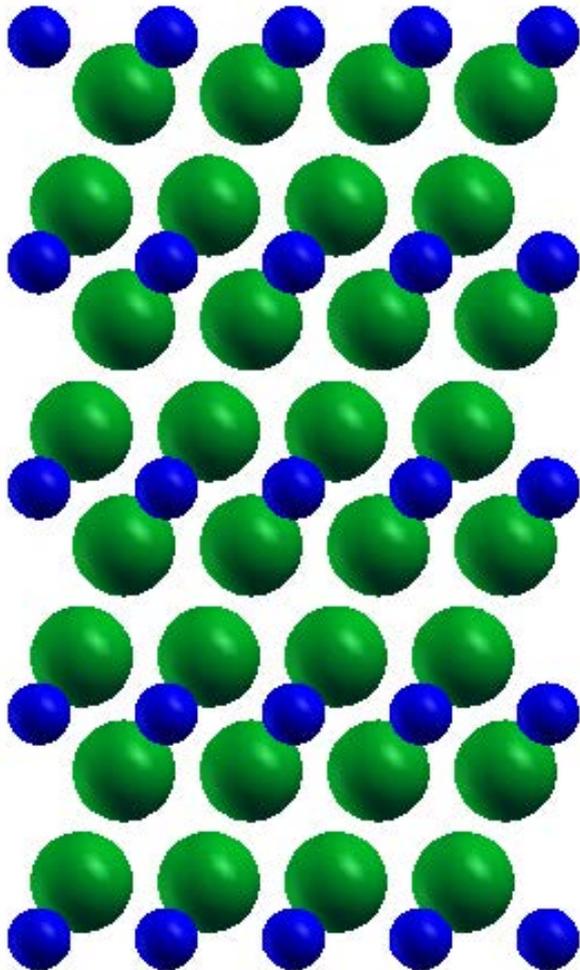
CaI$_2$ – light yield is >100,000 ph/MeV with Eu^{2+} activators (Hofstadter, 1964, Cherepy, 2008), but this has not proven useful because of ***difficulties with crystal growth*** – very anisotropic , micaceous, rhombohedral material that invariably cracks.

Optical Properties of CaI$_2$
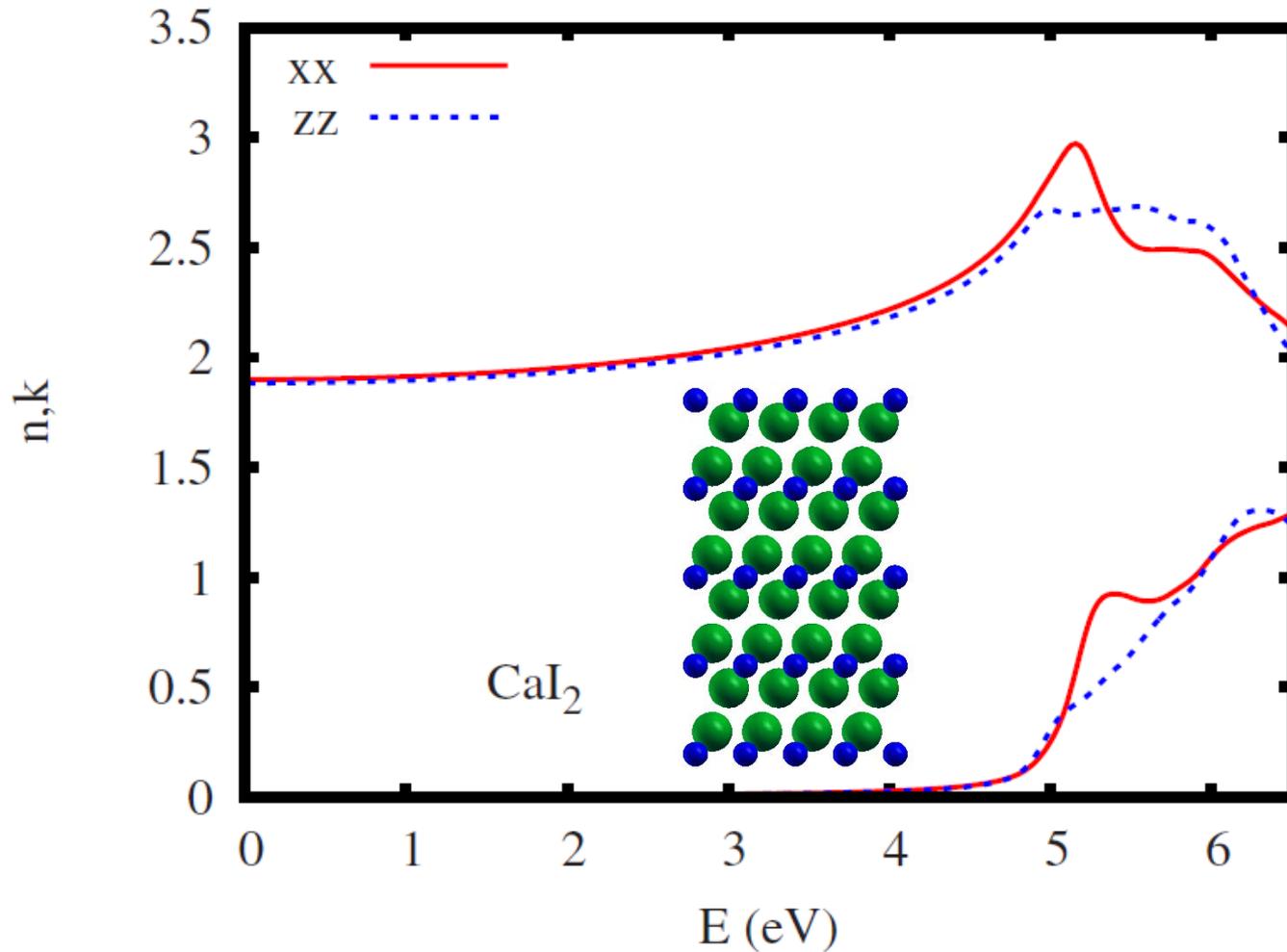
Low energy limit: $n_{zz}/n_{xx}=0.991$

Not the expected result

Not All Halides Are Near Isotropic

1.6 eV:
$n_{zz}/n_{xx}=0.956$

BiI_3
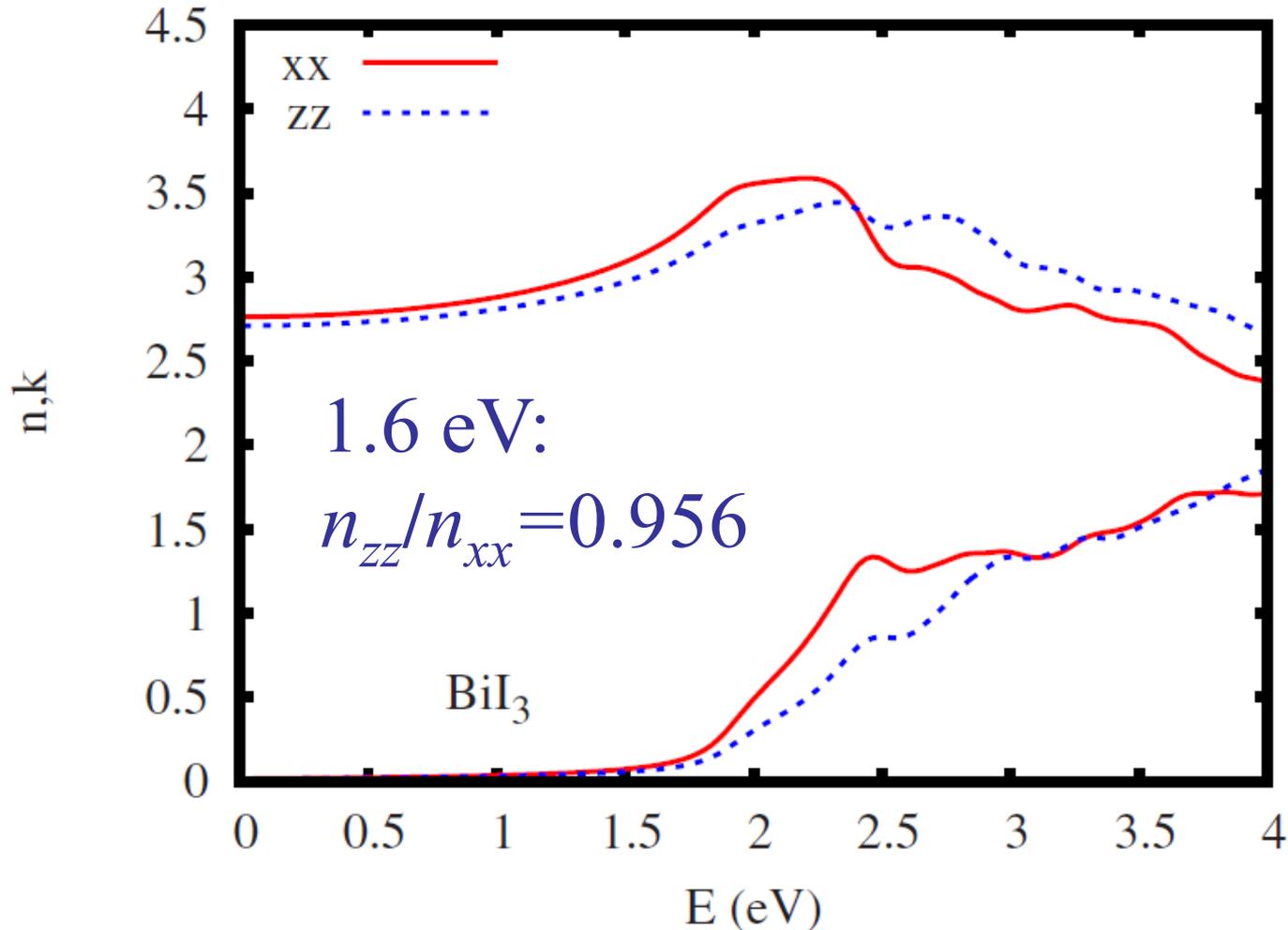
Measurements (G.E. Jellison, Jr., et al.): $n_{AV}(1.6\ eV)=3.1$
First principles: $n_{AV}(1.6\ eV)=3.11$ *in excellent agreement*

But we found that many are: BaIBr

Orthorhombic:
L.Y. > 80,000 ph/MeV with Eu^{2+}
Energy resolution better than 5%
(Bourret-Courchesne, et al., 2010).

BaIBr
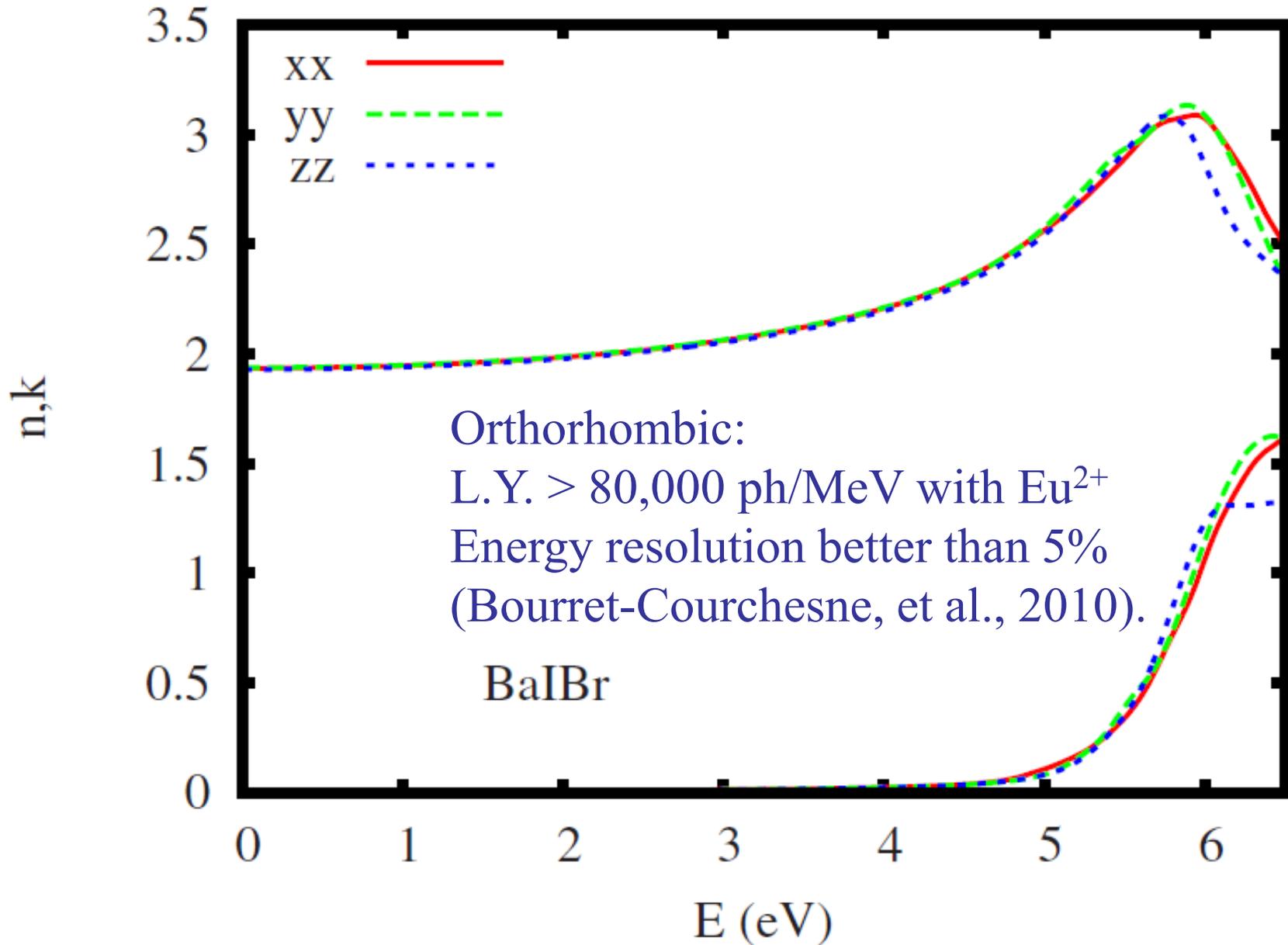
Transparent Ceramics

Key:

High density ceramic.

Low light scattering due to use of cubic (isotropic) materials.

Crystal growth is not part of the process.

Casio transparent ceramic camera lens (2004).

Opportunity for lower-cost manufactured scintillators with uniform characteristics.

Predictive Theory

Near optical isotropy in noncubic SrI$_2$: Density functional calculations

D. J. Singh[a]

Materials Science and Technology Division and Center for Radiation Detection Materials and Systems, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114, USA

Fabrication and Properties of Translucent SrI$_2$ and Eu:SrI$_2$ Scintillator Ceramics

Stephen R. Podowitz, Romain M. Gaumé, Wesley T. Hong, Atlal Laouar, and Robert S. Feigelson
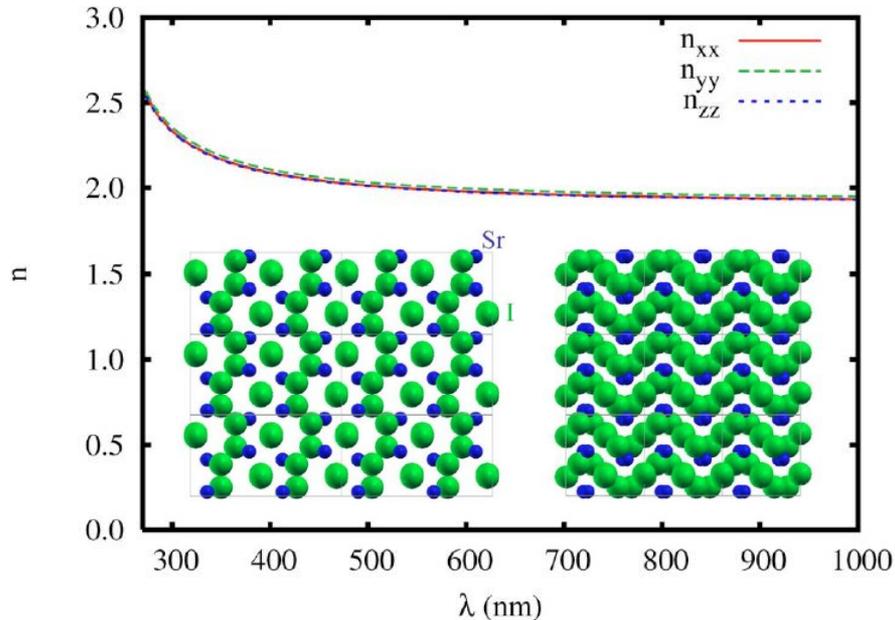
FIG. 4. (Color online) Wavelength dependent refractive index of SrI$_2$ as obtained with the Engel–Vosko GGA.
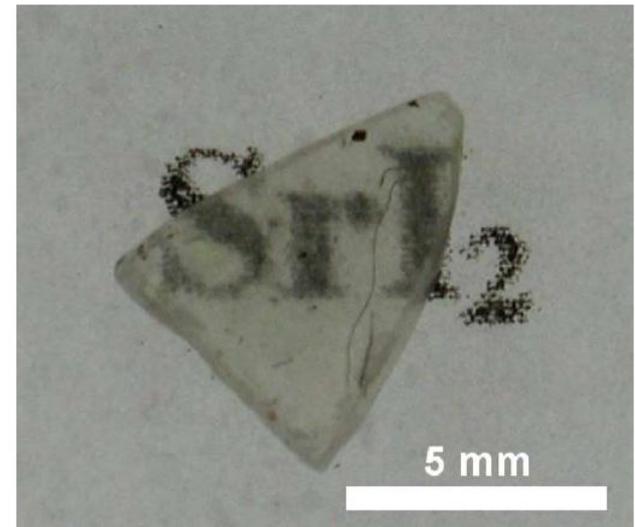
Fig. 5. Translucent ceramic sample of 0.77 mm-thick Eu:SrI$_2$ backlit.

First principles theory, not fit to experiment ➔ results that can point in unanticipated directions.

Dynamics

Giant anharmonic phonon scattering in PbTe

O. Delaire[1]*, J. Ma[1], K. Marty[1], A. F. May[2], M. A. McGuire[2], M-H. Du[2], D. J. Singh[2], A. Podlesnyak[1], G. Ehlers[1], M. D. Lumsden[1] and B. C. Sales[2]
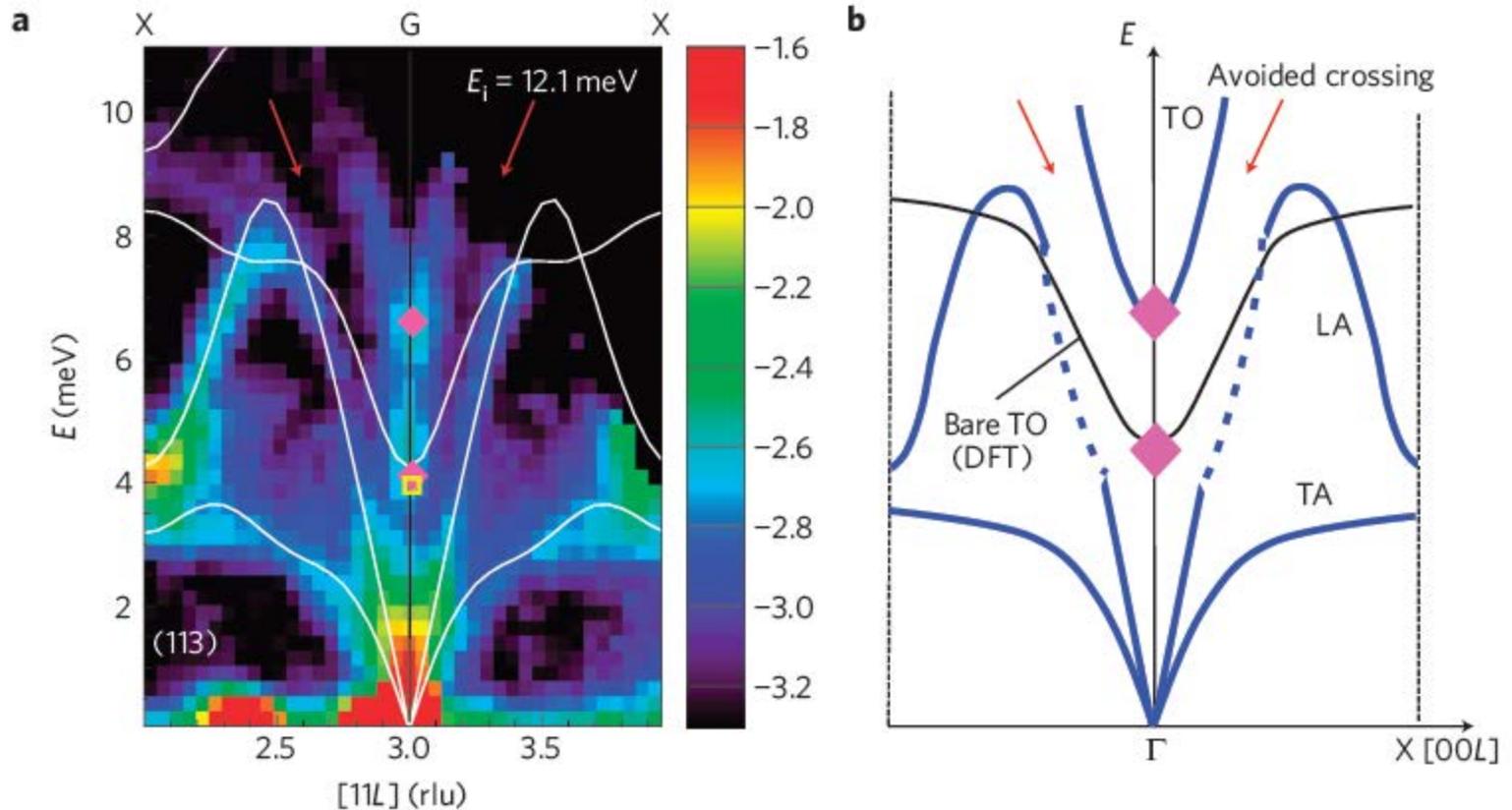
Magnetism
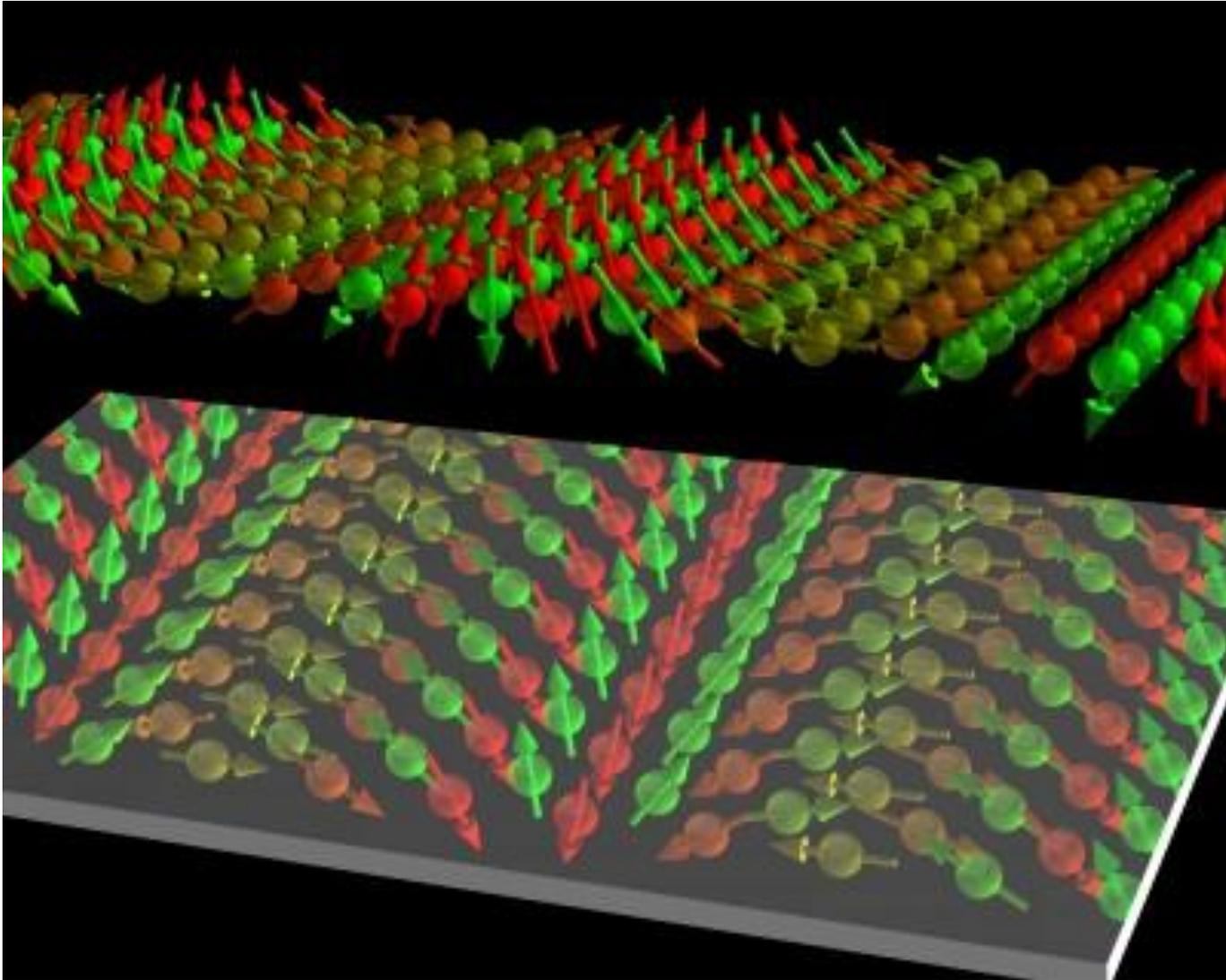
S. Blugel, Julich, Germany: Non-collinear magnetism on a thin film.

Fermi Surfaces
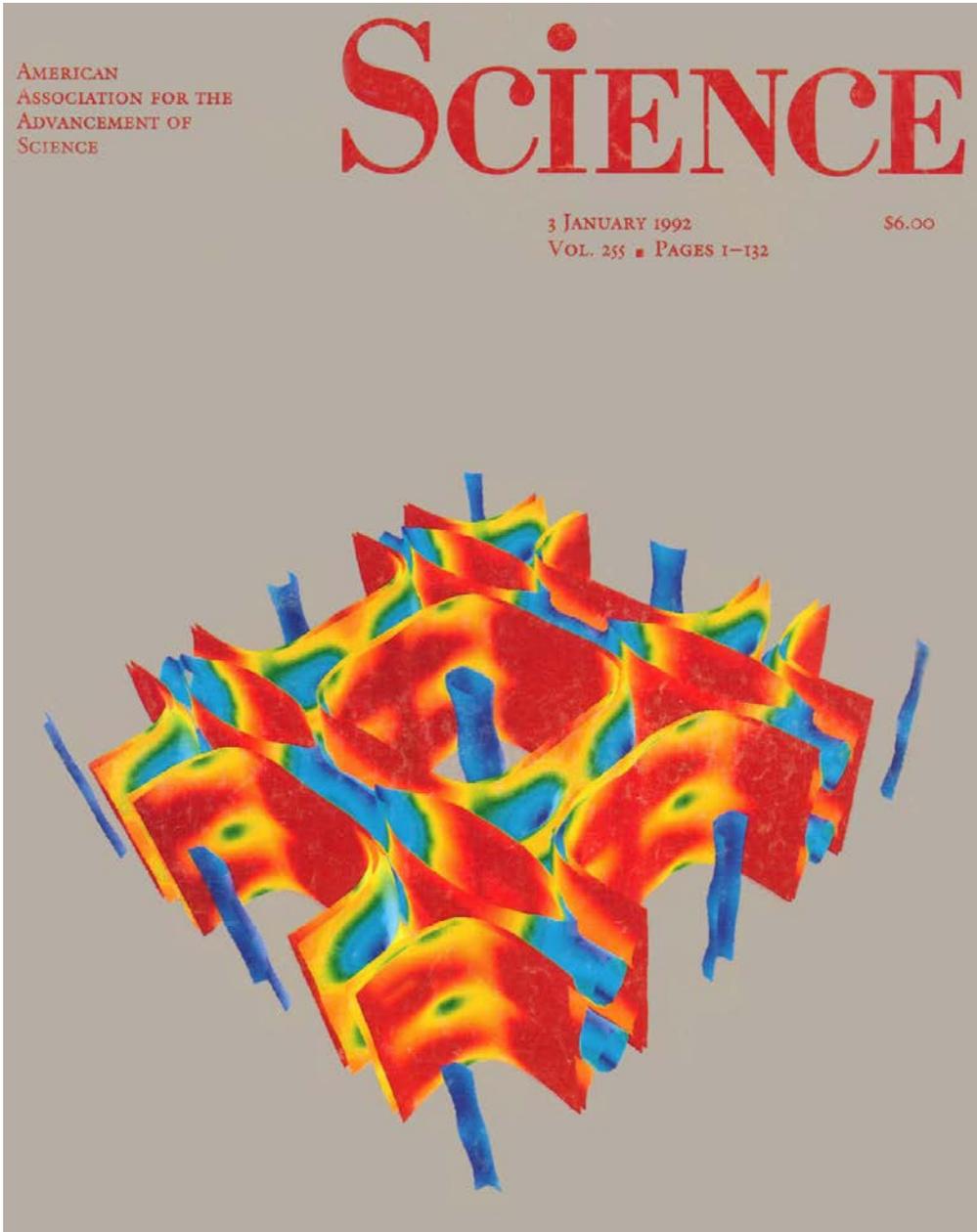
Based on Kohn-Sham eigenvalues, which are not fundamentally related to excitation energies in exact DFT – but this is known to be predictive and useful based on experience.

Band Structures
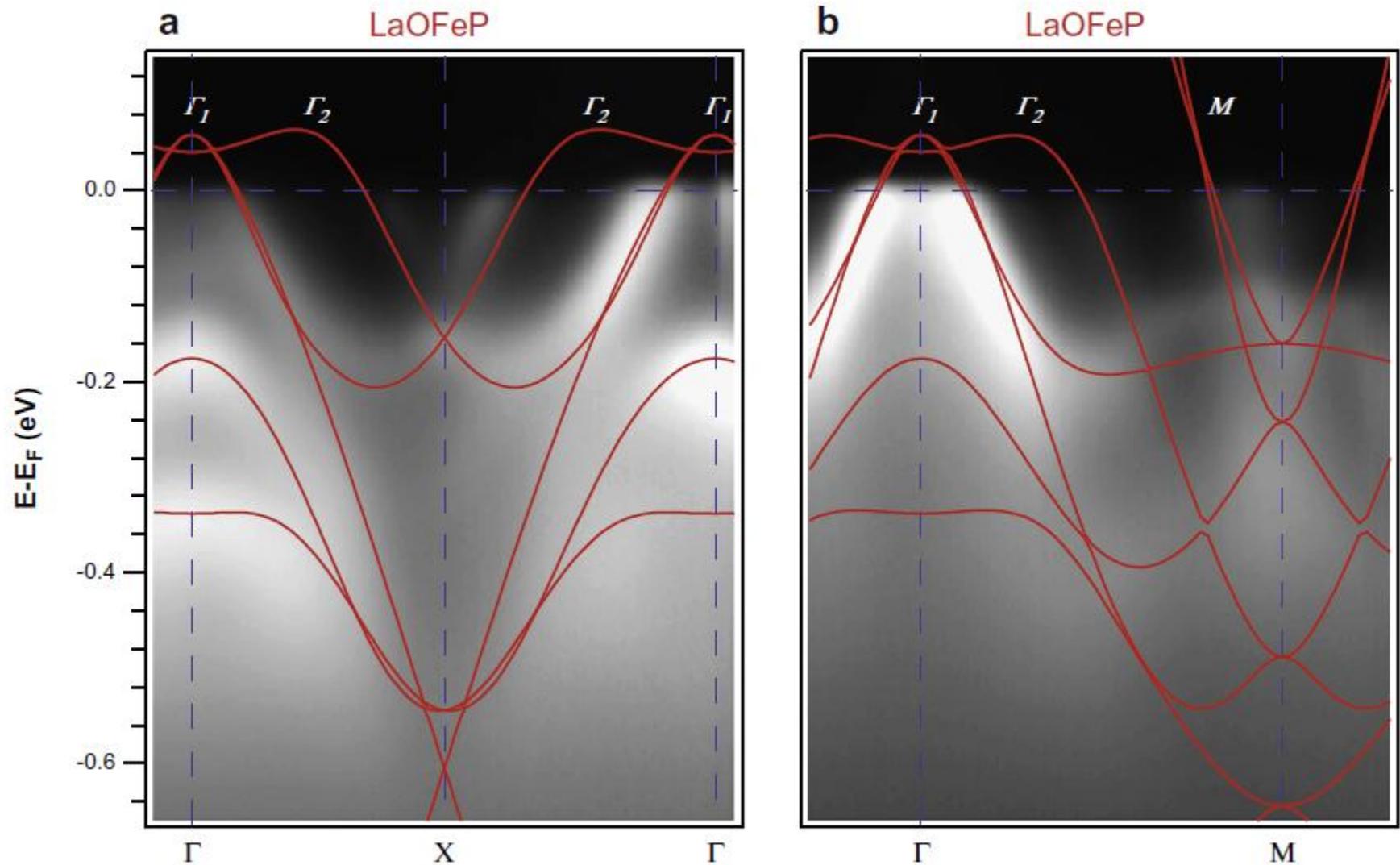
D.H Lu (2009)

Band Structure Related Quantities

- Optical properties.

- Excitation energies.

- Electronic transport.

- Electron-Phonon interactions.

- etc.

None of these are fundamental in DFT, but they are often quite accurate, and the inaccuracies are well established from much experience.

This is very useful because DFT is tractable, microscopic and predictive.

Hartree-Fock vs. Approximate DFT

- Hartree-Fock is a controlled approximation. Approximate DFT is not.

  - ➢ We can systematically improve Hartree-Fock, but with DFT we always have to "guess" about what is / is not already included. LDA+x need not be better than LDA (but it may very well be). *Be Judicious.*

- Hartree-Fock gives poor results for materials. Modern approximate DFT is typically excellent for structures, energies etc.

- There are no metals, no stable Fermi surfaces and no Fermi liquids in Hartree-Fock. There are in DFT, perhaps too many.

Never equate DFT calculations with Hartree-Fock.

bcc Iron

- Ferromagnetic metal: m_{spin}=2.13μ_B, m_{orb}=0.09 μ_B.
- LAPW calculations with GGA (PBE) and spin-orbit.
- LDA+U with SIC double counting.
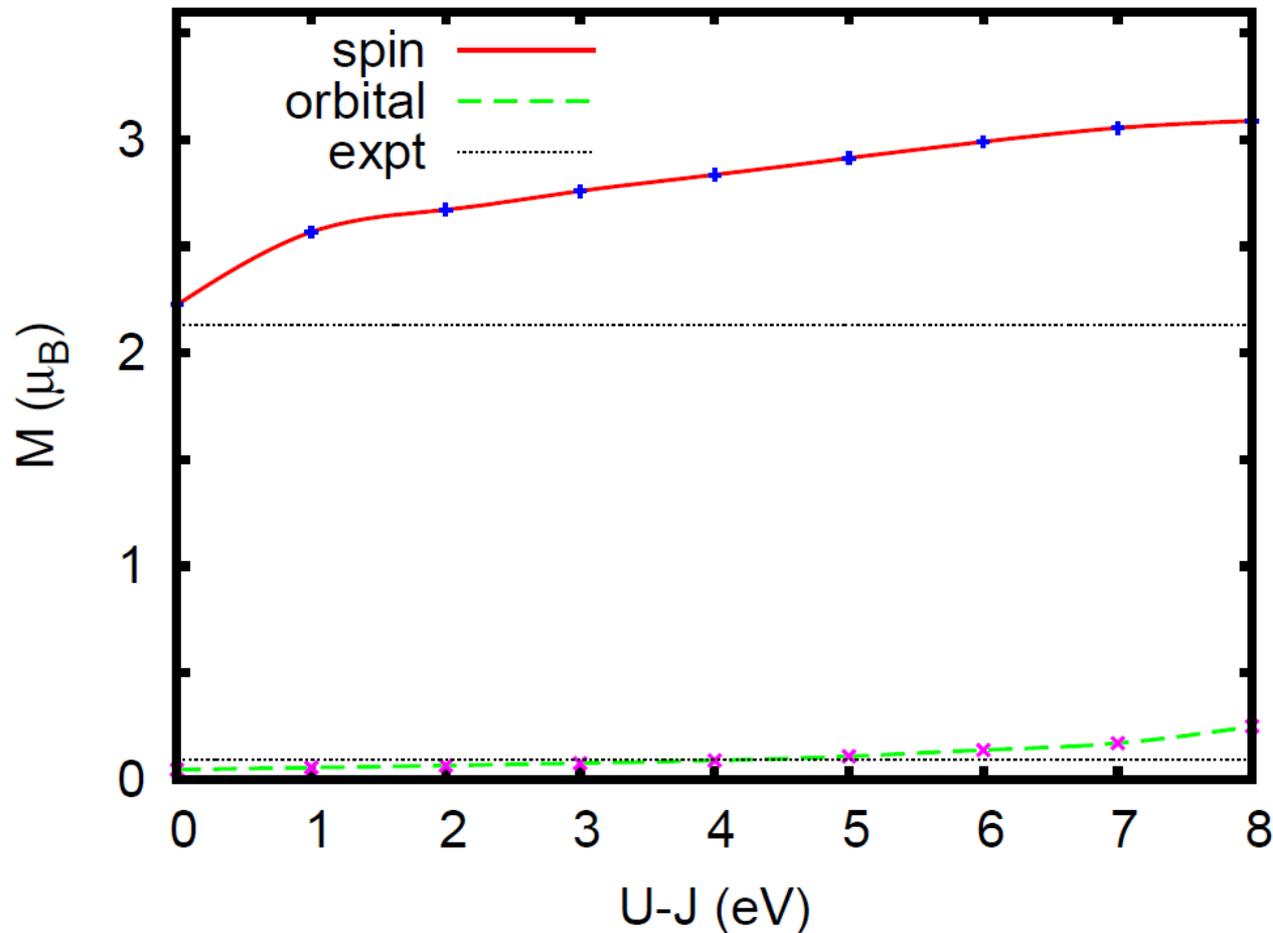
	PBE	Expt.
m_{spin}	2.21	2.13
m_{orb}	0.05	0.09

bcc Iron (Ferromagnetic) Density of States
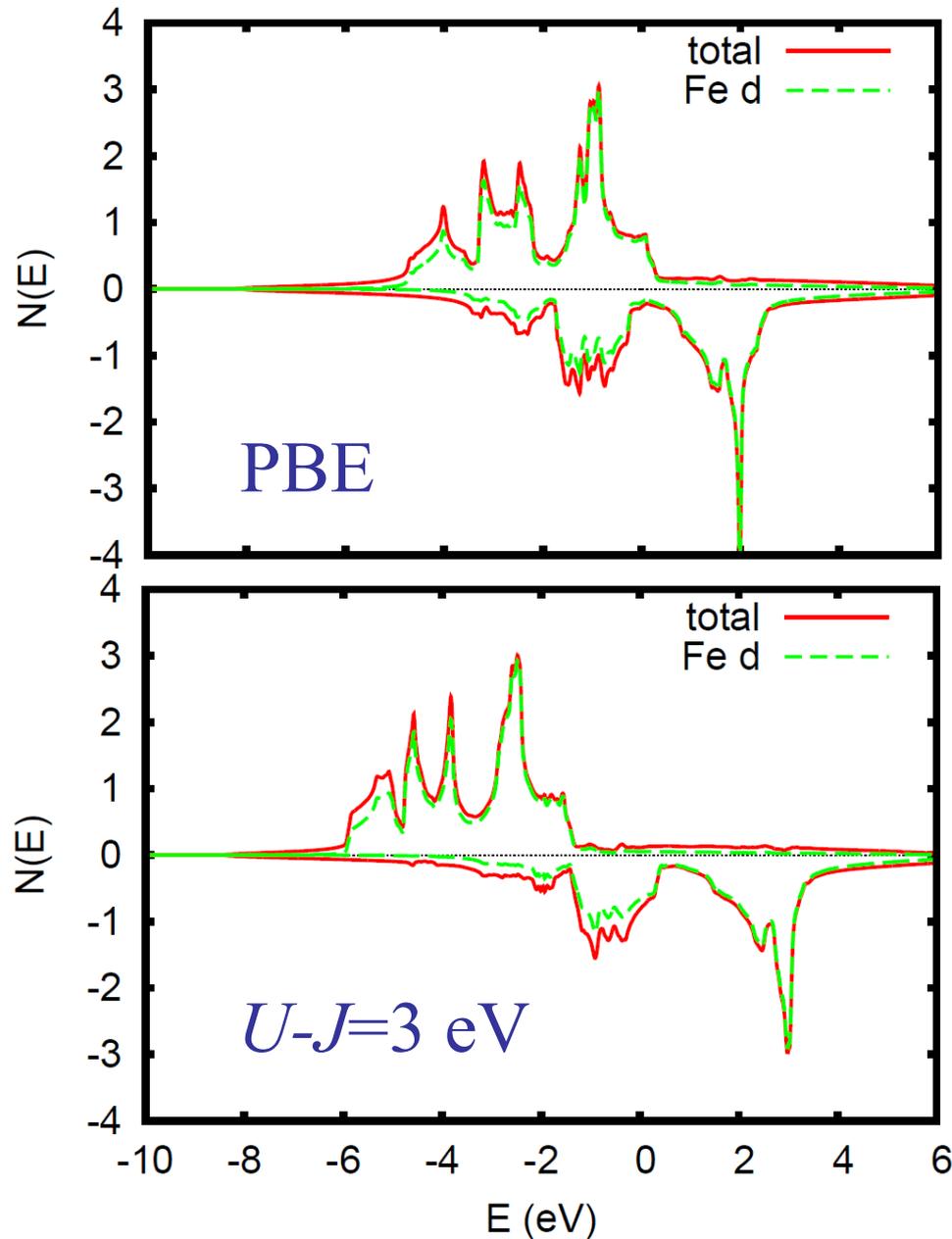
As U is increased go from metallic partially polarized $3d$ metal to a fully polarized metal with 5 electrons in the t_{2g} manifold ➡ expected ground state will become orbital ordered antiferromagnetic insulator.

References: DFT and Methods

1. H. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L.J. Sham, *Phys. Rev.* **140**, A1133 (1965). *Foundation Papers for DFT.*

2. S. Lundqvist and N.H. March, *Theory of the Inhomogeneous Electron Gas* (Plenum, N.Y., 1983). *Excellent book on DFT.*

3. R.G. Parr and W. Yang, *Density functional theory of atoms and molecules* (Oxford, 1994). *Book with a chemical viewpoint.*

4. G.B. Bachelet, D.R. Hamann and M. Schluter, *Phys. Rev. B* **46**, 4199 (1982). *Norm conserving pseudopotentials and their use.*

5. J. Ihm, A. Zunger and M.L. Cohen, *J. Phys. C* **12**, 4409 (1979). Total energy formalism for norm conserving pseudopotentials.

6. D.J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials and the LAPW Method, 2nd Ed.* (Springer, 2006). *Book about the LAPW method with some discussion of pseudopotentials.*

7. V. Eyert, *The Augmented Spherical Wave Method* (Springer, Berlin, 2007). *A detailed description of the ASW (closely related to LMTO) method.*

8. Richard M. Martin, *Electronic Structure of Matter* (Cambridge University Press, 2004). *Excellent overview of electronic structure methods and calculations.*

Magnetism and Superconductivity

[4] P. W. Anderson and A. H. Dayem, Phys. Rev. Letters 13, 195 (1964). See also J. Lambe, A H. Silver, J. E. Mercereau, and R. C. Jaklevic, Phys. Letters 11, 16 (1964).

[5] A. H. Dayem and C. C. Grimes, Appl. Phys. Letters 9, 47 (1966).

[6] P. L. Richards, J. Opt. Soc. Am. 54, 1474 (1964).

[7] E. Riedel, Z. Naturforsch. 19a, 1634 (1964).

[8] N. R. Werthamer, Phys. Rev. 147, 255 (1966).

[9] I. K. Yanson, V. M. Svistunov, and I. M. Dmitrenko, Zh. Eksperim. i Teor. Fiz. 48, 976 (1965) [translation: Soviet Phys.—JETP 21, 650 (1965)]; D. N. Langenberg, D. J. Scalapino, B. N. Taylor, and R. E. Eck, Phys. Rev. Letters 15, 294, 842(E) (1965); D. N. Langenberg, D. J. Scalapino, and B. N. Taylor, Proc. IEEE 54, 560 (1966).

EFFECT OF FERROMAGNETIC SPIN CORRELATIONS ON SUPERCONDUCTIVITY*

N. F. Berk and J. R. Schrieffer

Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania

(Received 24 June 1966)

Pd is not a superconductor because of nearness to ferromagnetism.

Bardeen Cooper Schrieffer - 1957

Singlet (*s,d*)
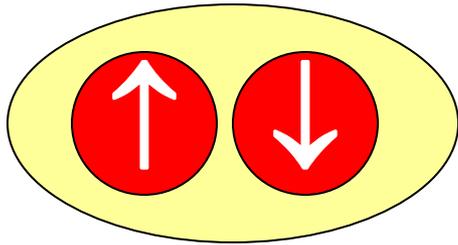
Hg, Pb, Cuprates

electron - polarization - electron

Singlet Channel:
Charge fluctuations (phonons) are attractive.
Ferromagnetic fluctuations are pair breaking
Spin fluctuations in general are repulsive.

Since electron phonon is always attractive the *s*-wave channel is most favored by it.

Inferred Phase Diagram

Competition of superconductivity and magnetism.

Ferromagnet

Paramagnetic metal

T

S.C.

$N(E_F)I$

1.0
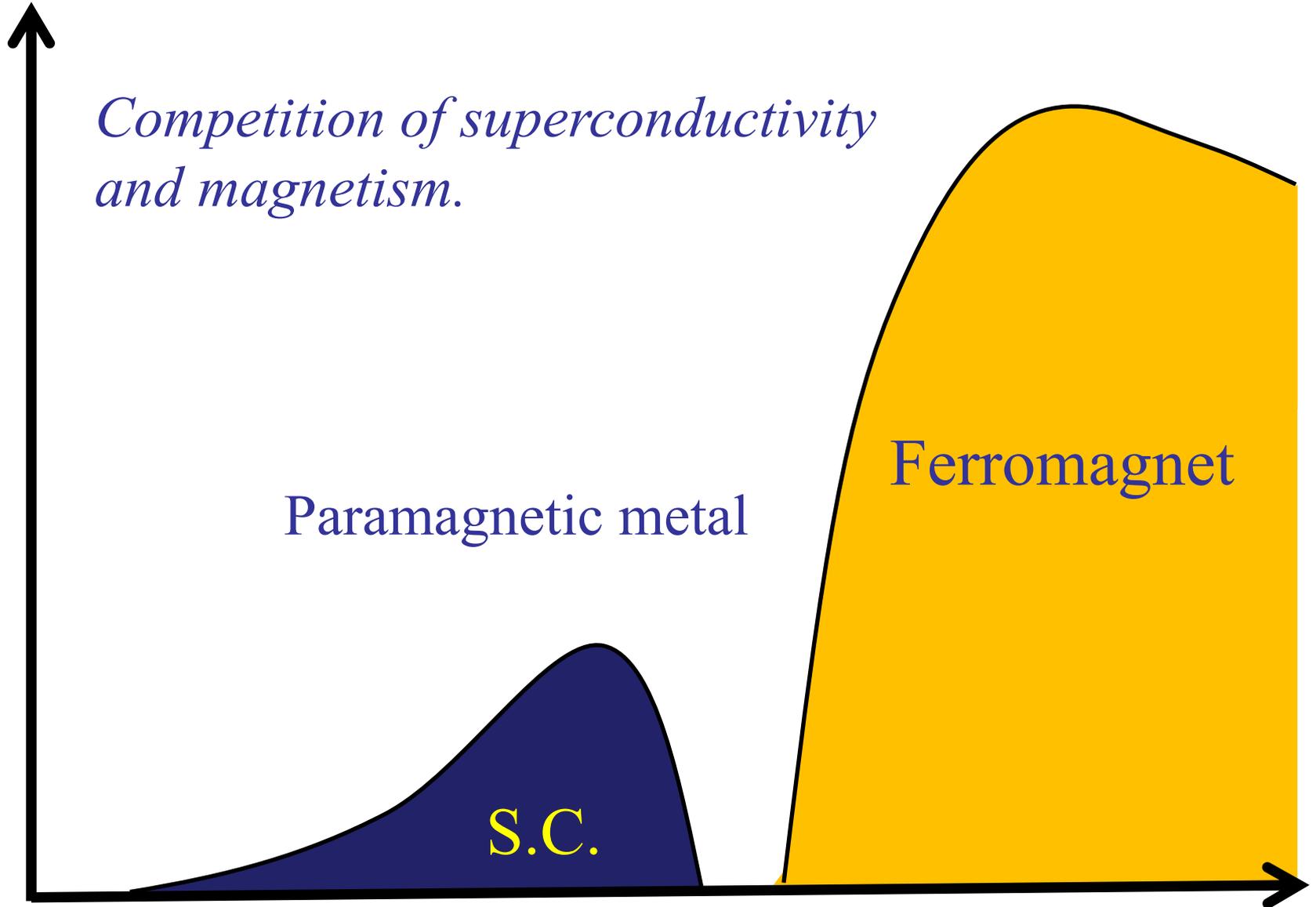
Metals Near Quantum Critical Points
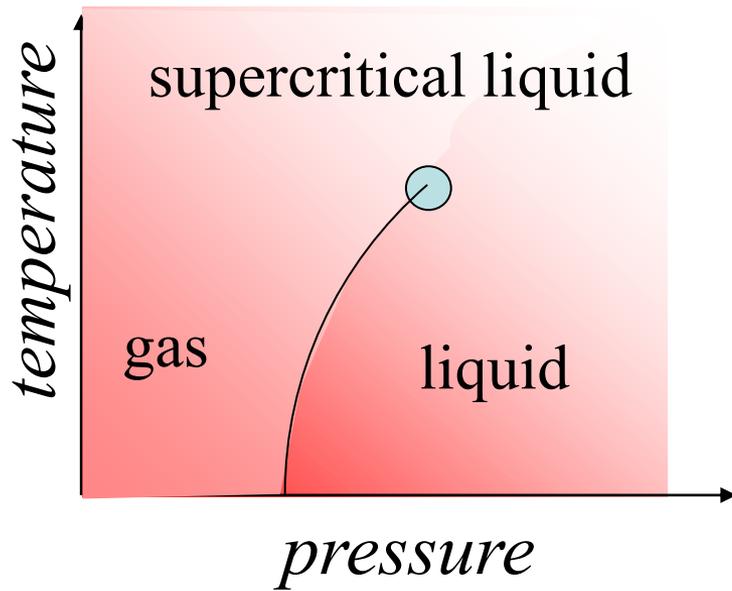
Classical criticality: Thermal density fluctuations grow indefinitely close to the Critical Point (CP).
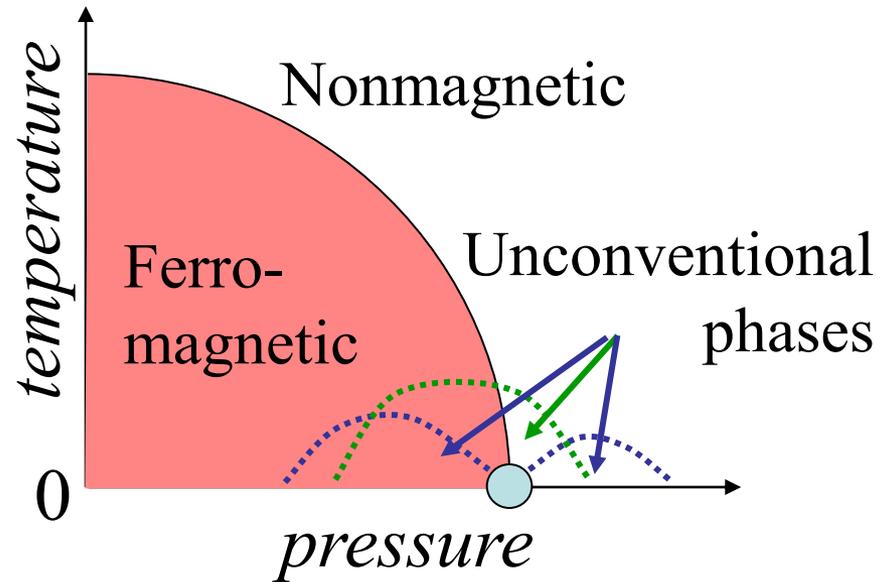
Quantum criticality: Quantum density fluctuations grow indefinitely close to the Quantum Critical Point (QCP).

Interesting things happen near critical points: In this region fluctuations are important and DFT does badly.

Something Different?

CePd$_2$Si$_2$, after Mathur et al, 1998
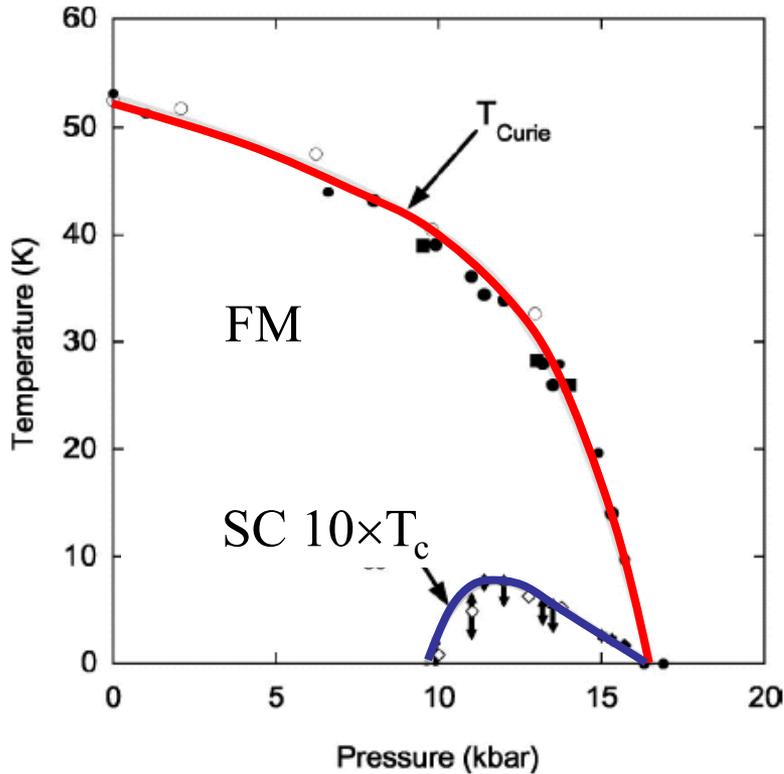
UGe$_2$, after Huxley et al, 2001 and Saxena et al, 2000
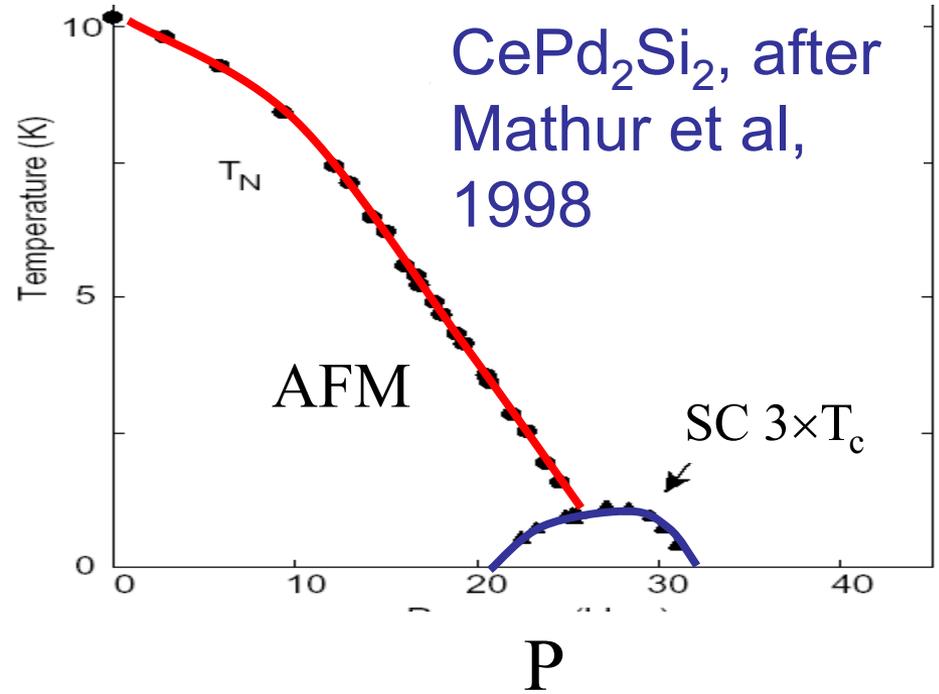
Interesting things may happen near critical points: In this region fluctuations are important and DFT does badly.

"Strontium Ruthenate"

$Sr_{n+1}Ru_nO_{3n+1}$

Ru^{4+} (4 d-electrons)
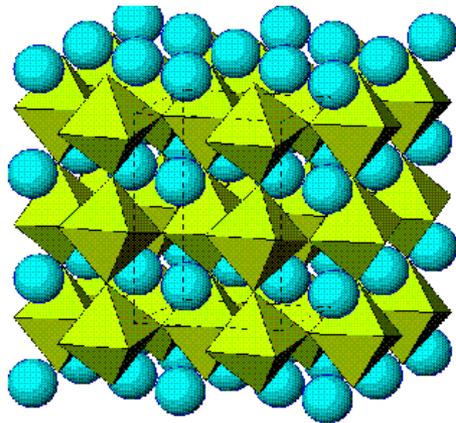
$n = \infty$

Ferromagnet
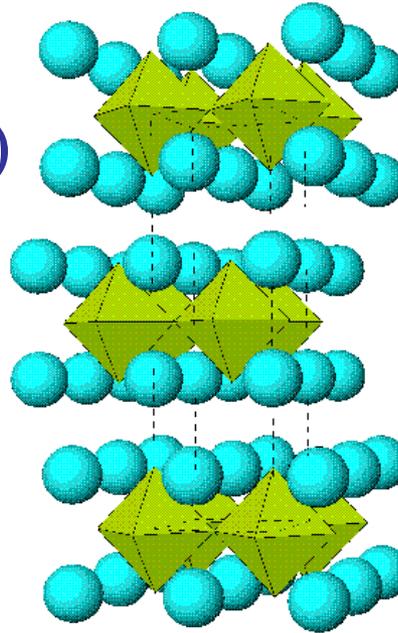
$n = 1$

Triplet superconductor
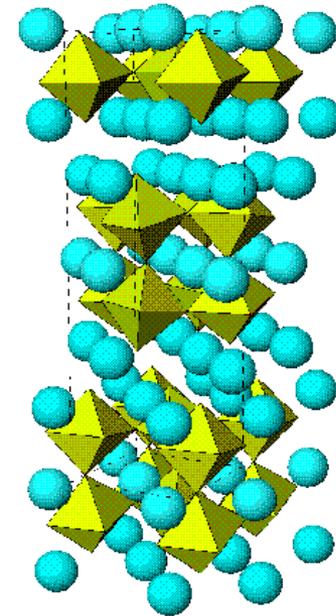
$n = 2$

Metamagnetic quantum critical point

Magnetic Order in $Sr_{1-x}Ca_xRuO_3$

Experiment:

- $SrRuO_3$ is FM $T_C \sim 165K$.
- T_C fall smoothly with x, reaching 0 near x=1.
- $CaRuO_3$ was reported AFM, but now thought PM.

LSDA: Octahedral Tilt Broadens DOS.

Fixed Spin Moment
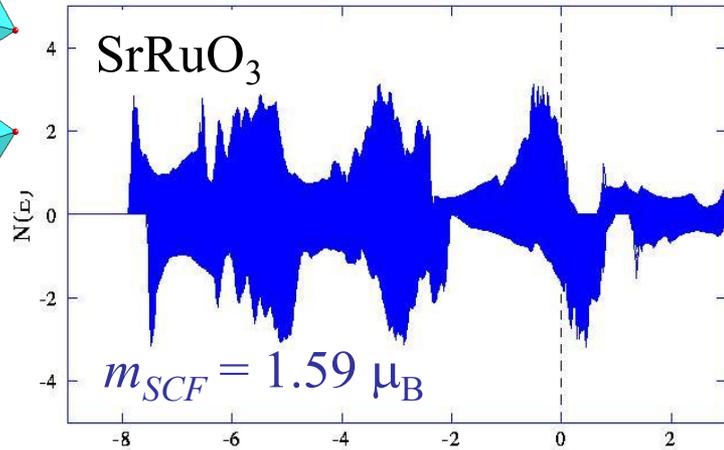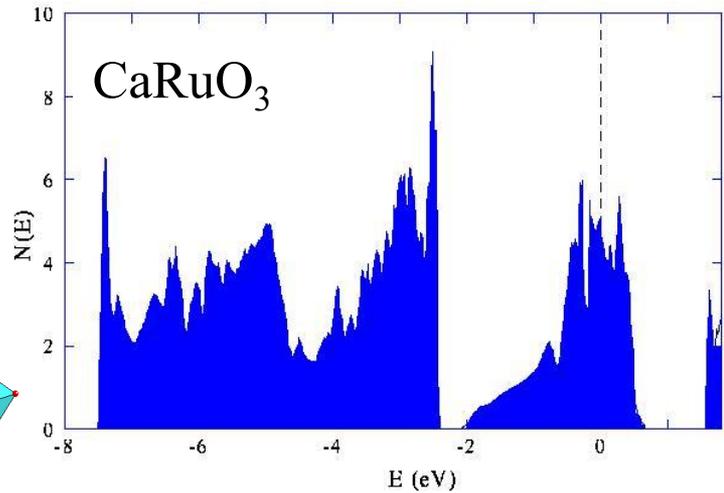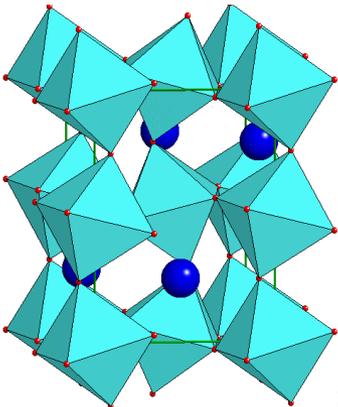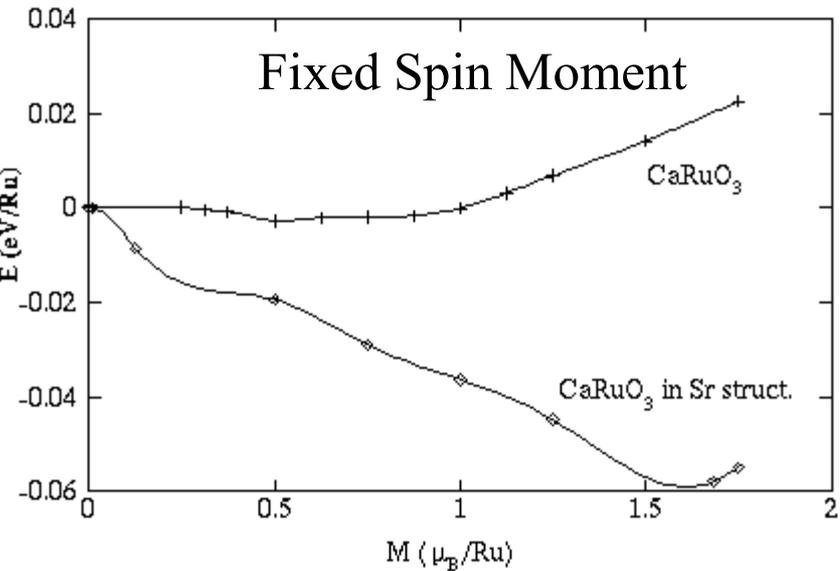
Itinerant Stoner Explanation

$CaRuO_3$

$SrRuO_3$

$m_{SCF} = 1.59\ \mu_B$

STONER PICTURE

$$\Delta E = \frac{1}{2} \int_0^m [m'\,dm' / N(m')] - I_{TOT}m^2/4 \qquad \text{with } I_{TOT} = \sum_\alpha I_\alpha \nu_\alpha^2$$

$$\Delta E = -I_{TOT}m^2/4 = -\sum_\alpha I_\alpha m_\alpha^2 /4 \qquad \text{and } N = \sum_\alpha N_\alpha \nu_\alpha$$

For SrRuO$_3$

- $I_{TOT} = 0.41$eV
- $I_{Ru} = 0.35$eV

➔ Significant on-site O contribution

- Favors Ferromagnetism.
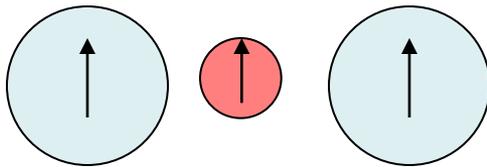
- Over Antiferromagnetism.
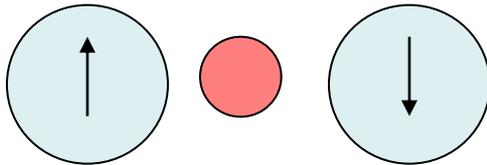
Also band KE.
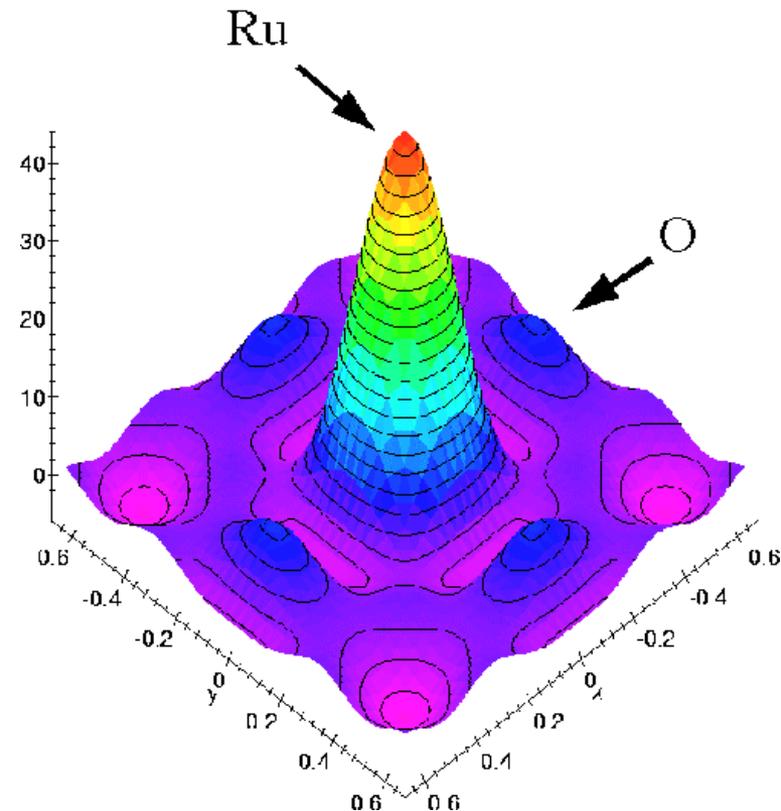
Nagler and Chakoumakos, ORNL

Quantum Critical Points and the LDA

Density Functional Theory: LDA & GGA are widely used for first principles calculations but have problems:

- Mott-Hubbard: Well known poor treatment of on-site Coulomb correlations.

- Based on uniform electron gas. Give mean field treatment of magnetism: Fluctuations missing (generally small, but important near quantum critical points)

Resistivity exponent in $Sr_3Ru_2O_7$
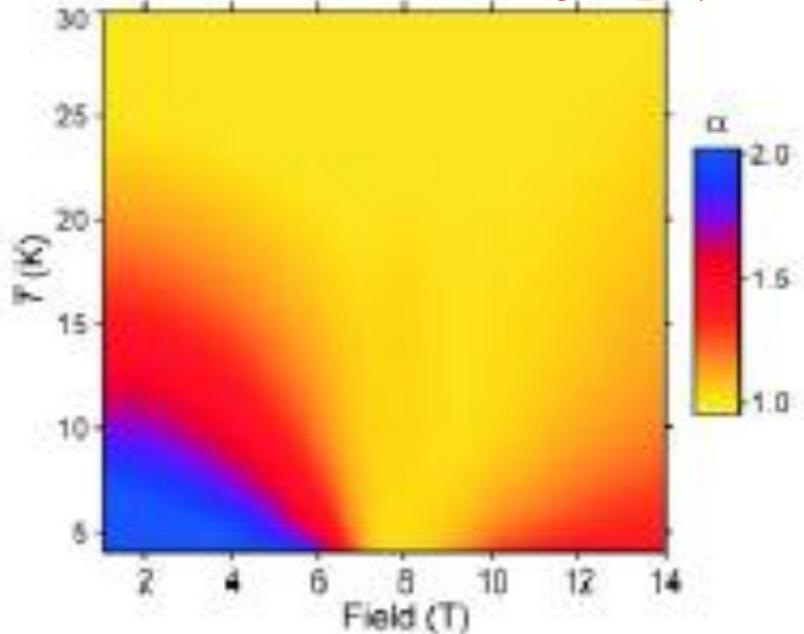
Grigera *et al.*, Science (2001).

LDA Fixed spin moment:
- For $Sr_3Ru_2O_7$ predicts weak itinerant ferromagnetism
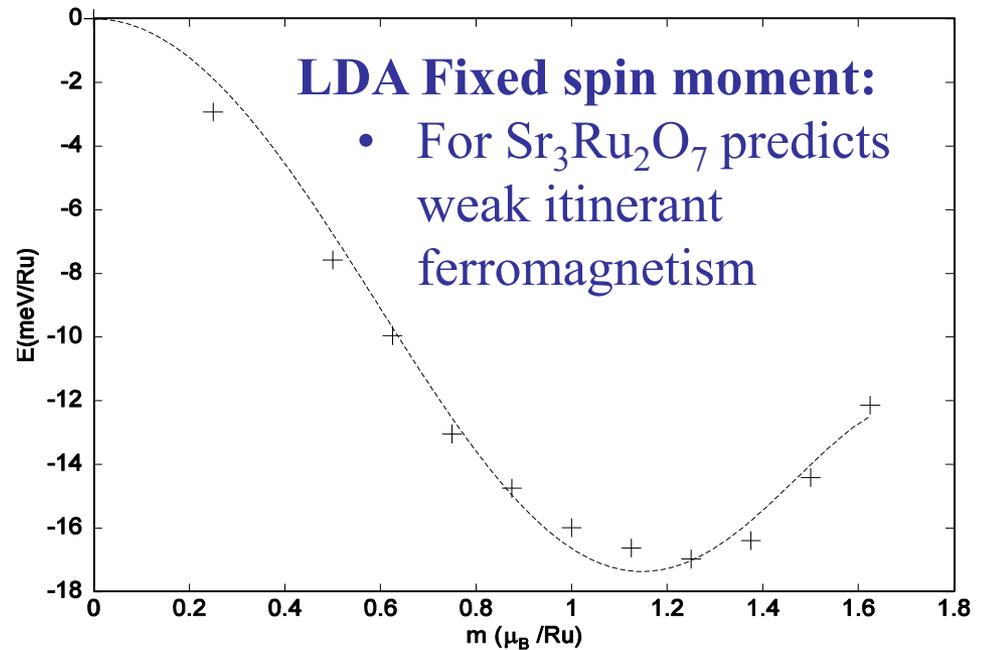
LDA overestimate of ferromagnetic tendency is a signature of quantum critical fluctuations – neglected fluctuations suppress magnetism

Electronic Structure of Sr$_2$RuO$_4$

Sr$_2$RuO$_4$ - I4/mmm
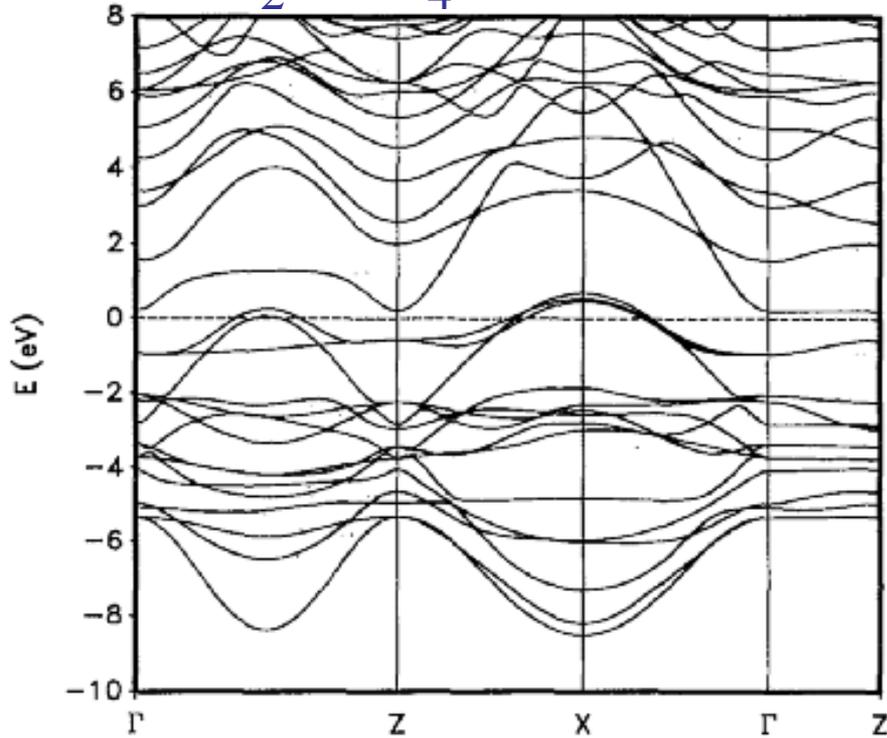
•3 t_{2g} derived bands at E_F: d_{xy}, d_{xz}, d_{yz}.
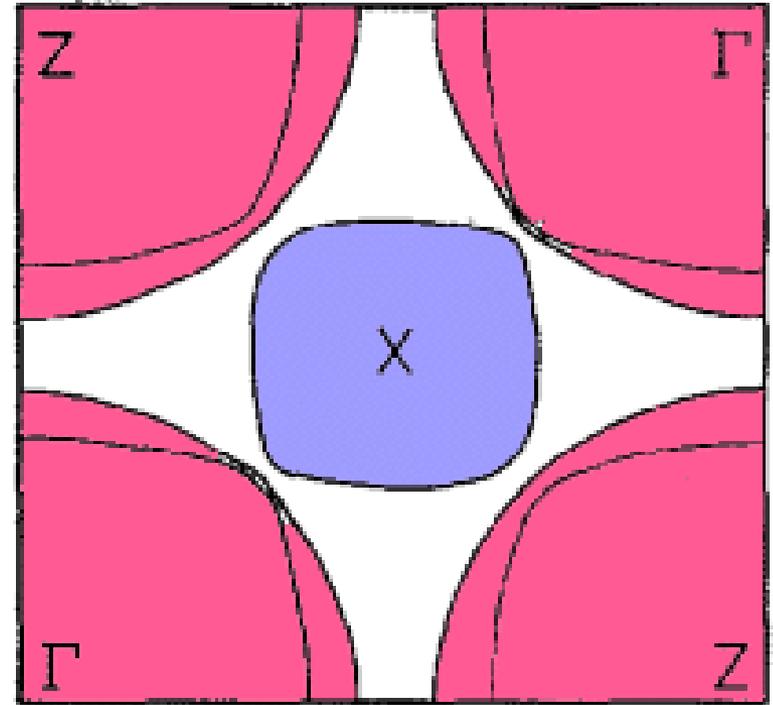
•Highly 2D electronic structure.

•FS agrees in detail with dHvA.

•Mass renormalizations ~ 4

What are the pairing interactions on the FS? Unconventional symmetry ➔ not electron-phonon.

➔ Spin-fluctuations?

SPIN-FLUCTUATIONS

Ingredients:

1. On-Site Stoner (O) - Ru-O hybridization

Sr_2YRuO_6 - no shared O
Sr_2RuYO_6 → AFM

$SrRuO_3$ - shared O
→ FM

Sr_2RuO_4 - shared O
→ FM flucts.

Ru

Y
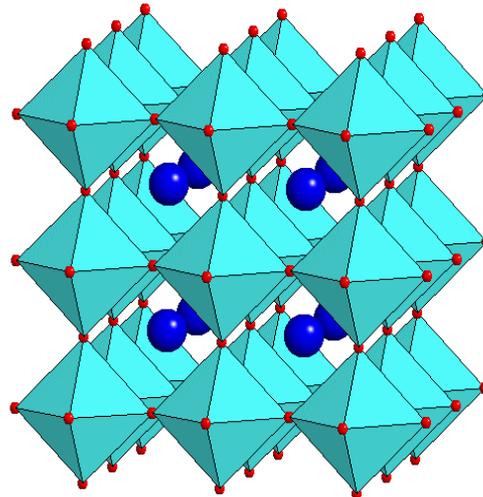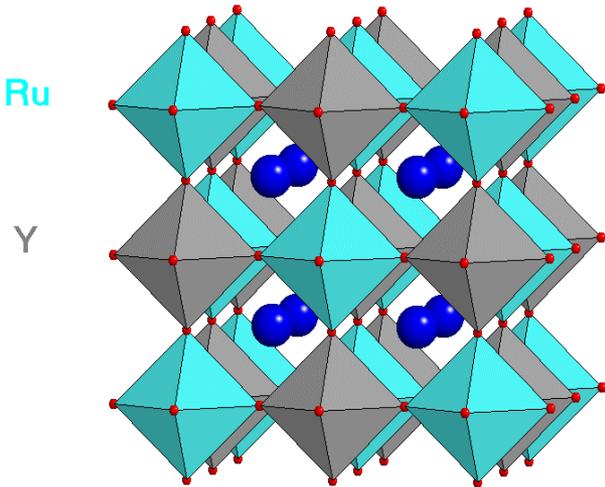
- Shared O in RuO_2 planes will favor FM fluctuations.

- Can model by smooth background using calculations of
  - I_{Ru} and I_O.
  - Projections of $N(E_F)$.
  - Taking full O contribution at **k**=(0,0) and no O contribution at **k**=(½,½).

Ferromagnetic Part

FM: with O

AFM: no O
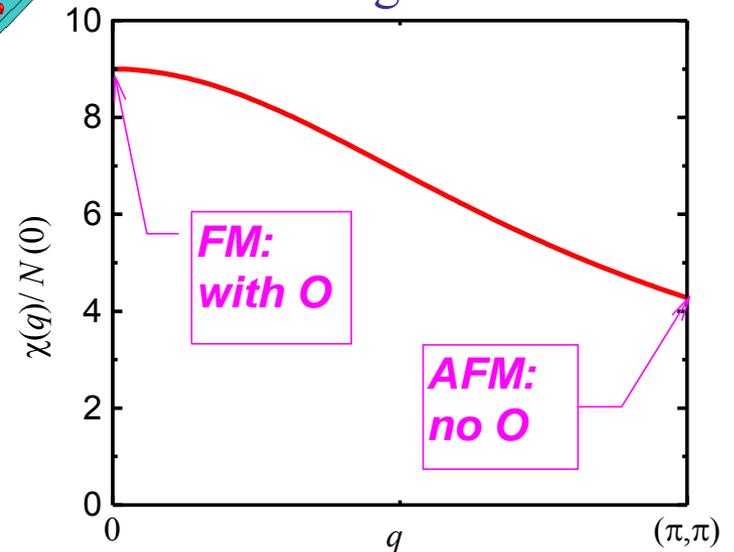
SPIN-FLUCTUATIONS (CON'T)

2. Nesting:

$$\chi(\mathbf{q}) = \frac{\chi_0(\mathbf{q})}{1 - I(\mathbf{q})\chi_0(\mathbf{q})}$$

Previous slide had $I(q)$ from Stoner but no $\mathbf{q}$ dependence in χ_0

Fermi Surfaces: Simple and 2-dimensional ➔ strong nesting.

Sidis *et al.* - Neutrons (1999).
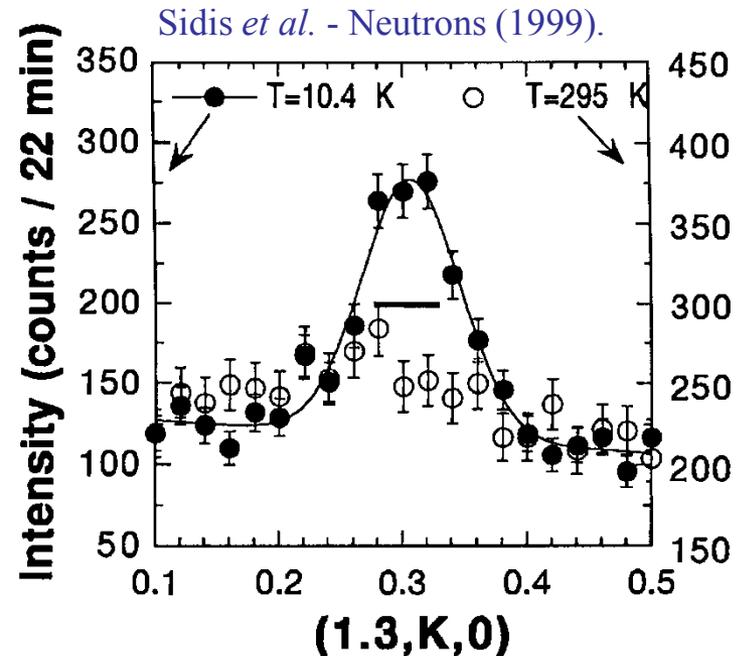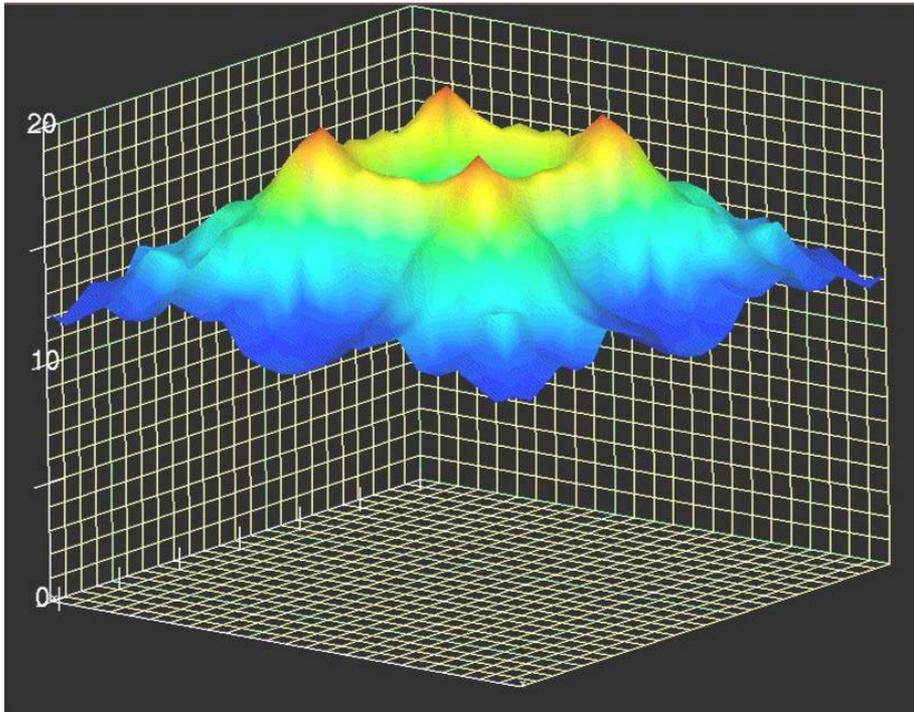
SUPERCONDUCTIVITY

e.g.

$q=k\text{-}k'$
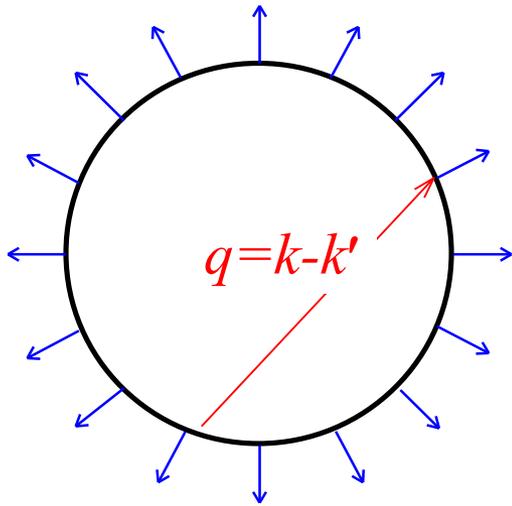
Triplet works in BCS gap equation provided that the pairing at small **q** is dominant (s.f. are attractive for triplet).

- Non-*s* depends on q dependence in $V(q)$.
- Generally higher ℓ needs more structure in $V(q)$.
- The details of the Fermi surface and $V(q)$ are crucial.

Singlet:
$$V(\mathbf{q}) = -\; \frac{I^2(q)\chi_0(\mathbf{q})}{1 - I^2(\mathbf{q})\chi_0(\mathbf{q})}$$

Triplet:
$$V(\mathbf{q}) = \frac{I^2(q)\chi_0(\mathbf{q})}{1 - I^2(\mathbf{q})\chi_0(\mathbf{q})}$$

Note signs

SUPERCONDUCTIVITY (Con't)

What we did:

- Calculate matrix elements $V_{k,k'}$ for a set of k,k' on the FS.
- Set-up gap equation -- diagonalize V.
- Use $\chi_0(q) = N(0) + \alpha\chi_{nesting}(q)$. -- *i.e.* FM Stoner + adjustable strength nesting -- $\alpha = 0$ means no nesting; $\alpha = 0.98$ is AFM.

Result:

- Triplet wins over a wide range ($\alpha < .85$)

$d(x^2\text{-}y^2)$

Note lack of pairing on α sheet.
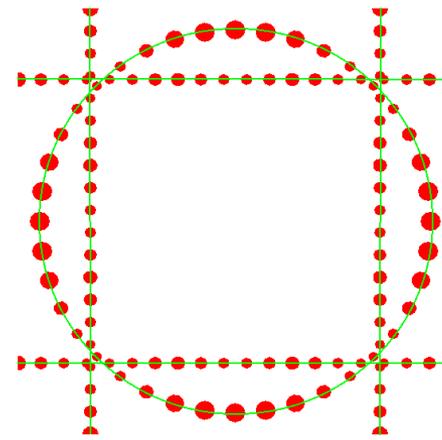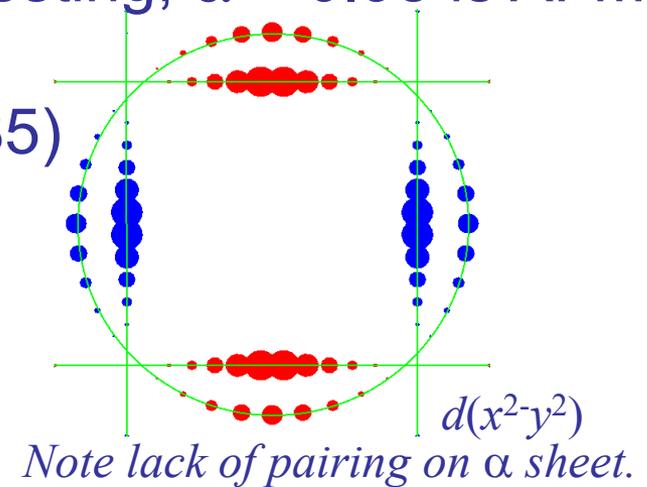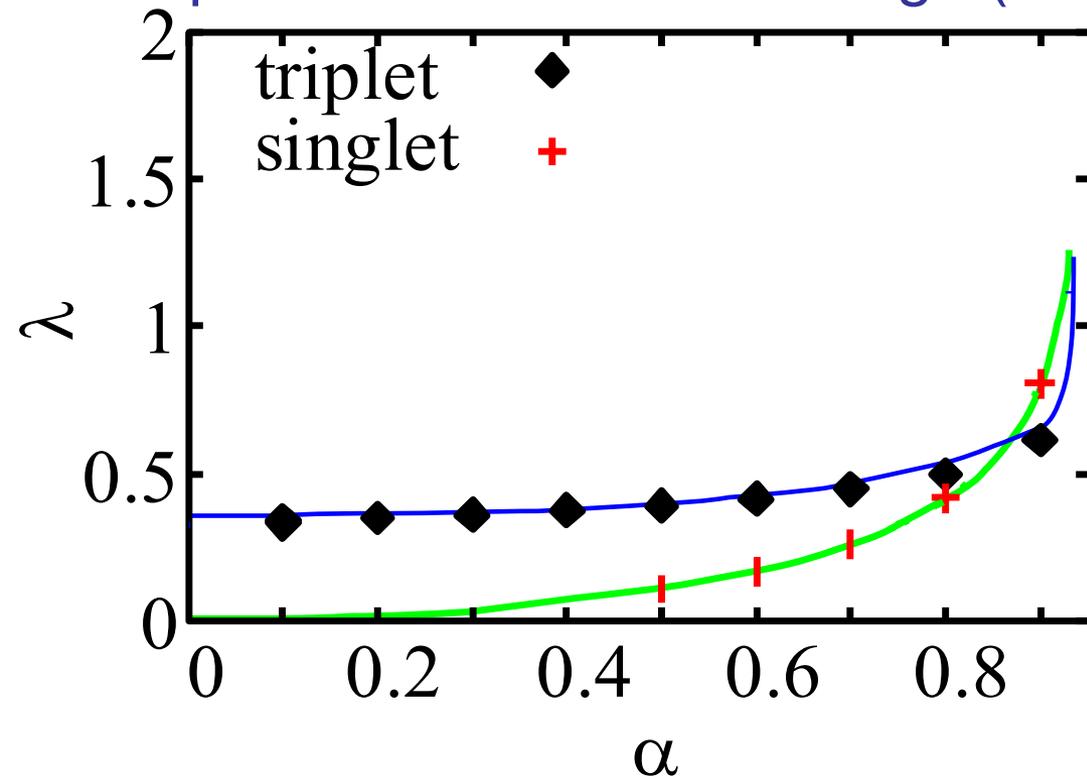
A Brief Introduction to Cuprates

- Prominent Mott Insulating Phases (not described in band structure)
- Structural complexity (perovskite)
- Doping is essential
- Copper is essential (e.g. Zn alloying destroys superconductivity)

Insulator

T

Pseudo-gap Metal

AF Mott Insulator

Metal

Superconductor

Doping Level
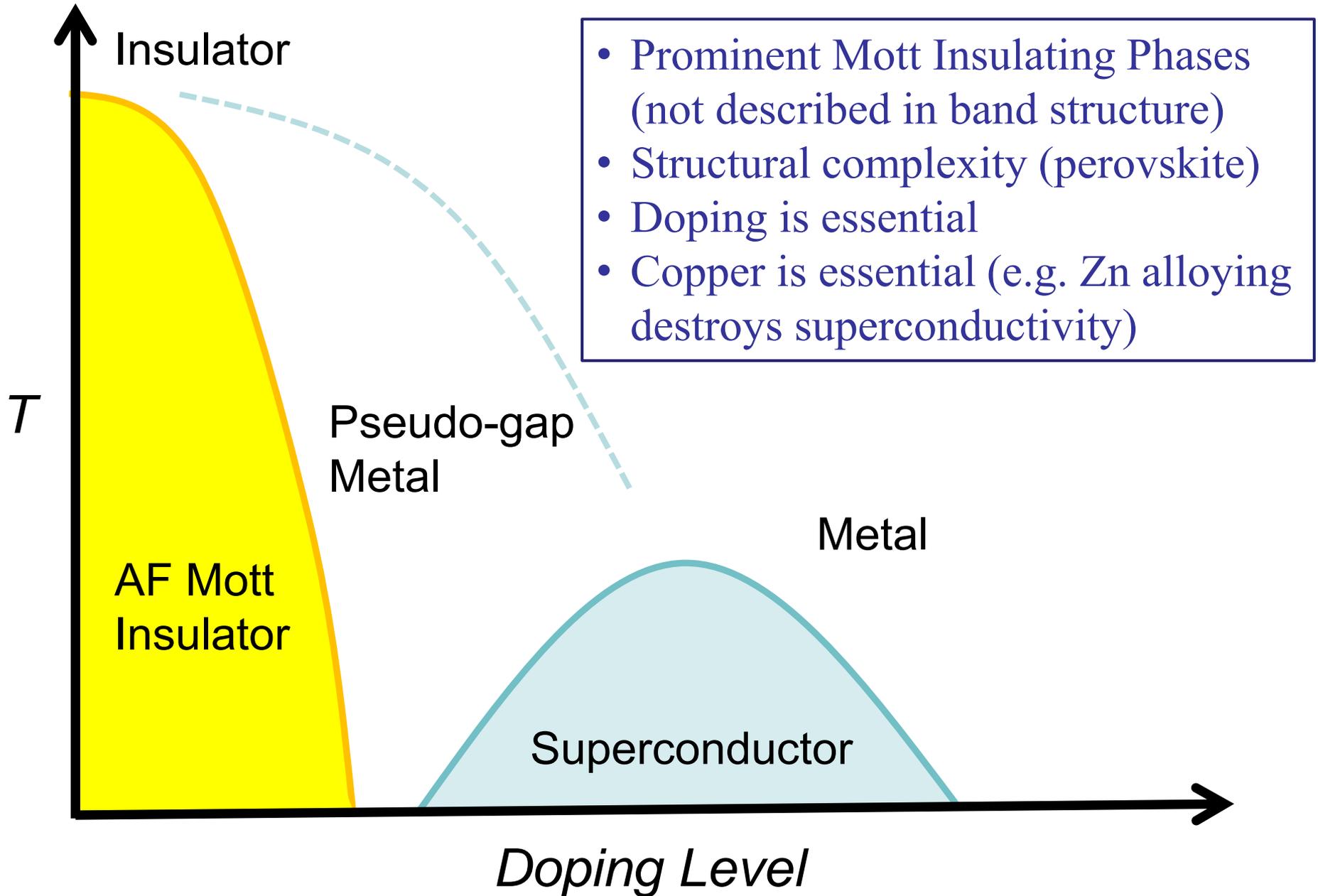
Discovery of Superconductivity in Fe-As Compounds

Kamihara *et al.*, JACS, 2006

LaFePO, $T_c \sim 4K$

Kamihara, Watanabe and Hosono, JACS, Feb. 2008

LaFeAsO$_{1-x}$F$_x$ T_c=26K
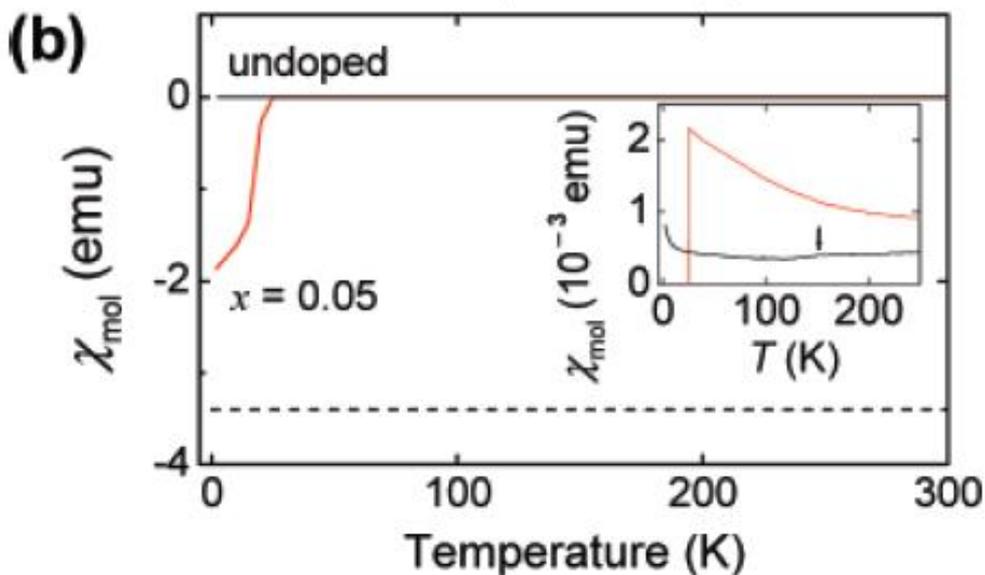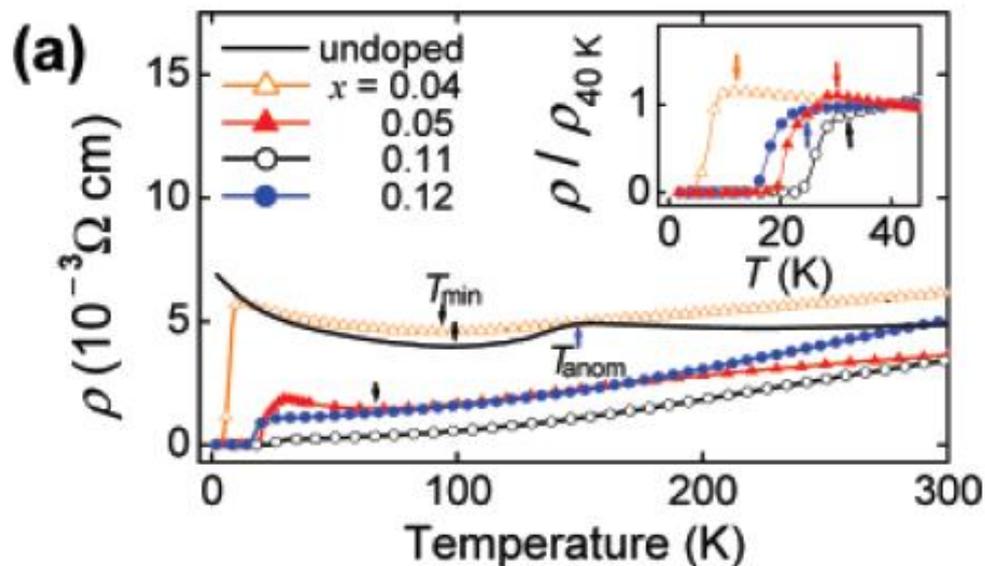
A Big Family of High T_c Superconductors

1111

122

Li or Fe

111, 11
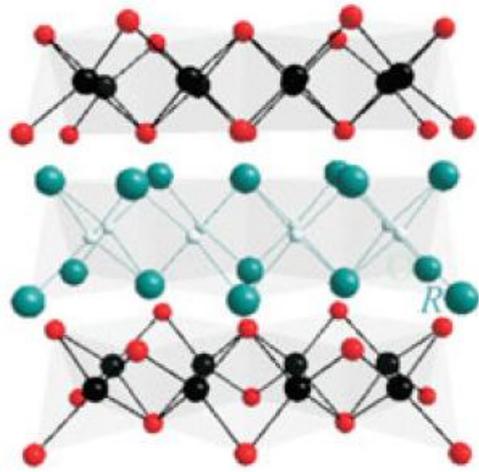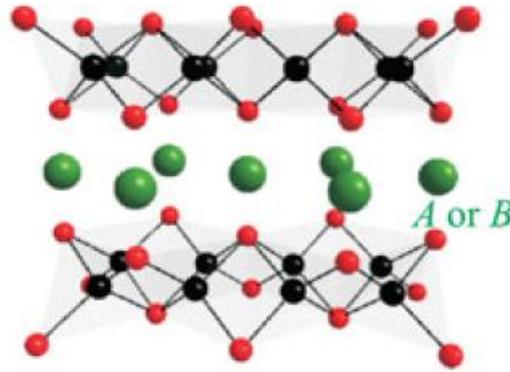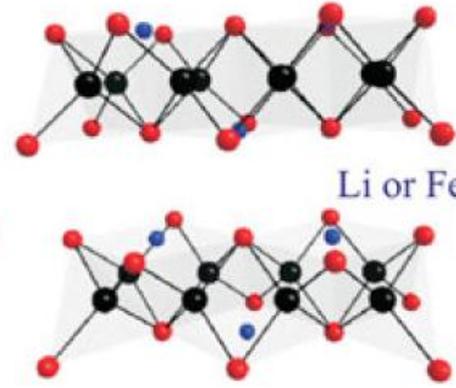
Sefat *et al.*, MRS
Bull. **36**, 216 2011
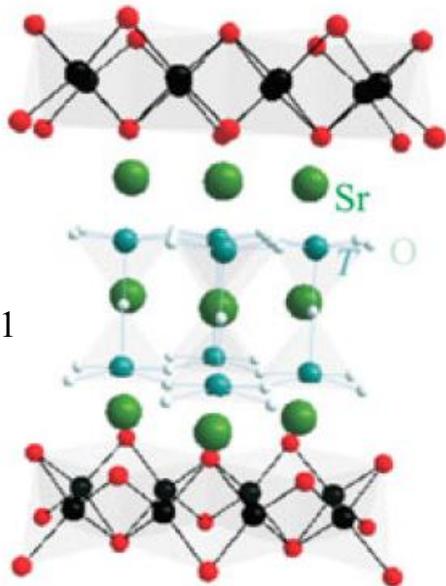
32522
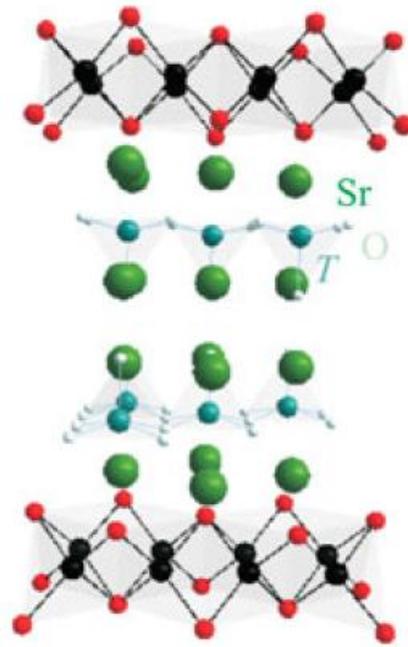
42622

Common Features:

- High T_c.

- Near magnetism.

- Fe square lattice.

- Near divalent Fe.

- Tetrahedral coordination.

A Word About Structure

- Large size of As^{3-}, Se^{2-} relative to Fe^{2+} leads to tetrahedral structures with anion contact (edge shared tetrahedra). Tendency to high symmetry, small unit cells without structural distortion.

- Cuprates, etc. are based on corner shared units, with resulting tendency to complex structure distortions. The interplay with properties greatly complicates the physics.

2b = 53.8 Å

2c = 61.2 Å

Bi-2212 – Zandbergen et al.

Experimental Proof of a Structural Origin for the Shadow Fermi Surface of $Bi_2Sr_2CaCu_2O_{8+\delta}$

A. Mans,[1] I. Santoso,[1] Y. Huang,[1] W. K. Siu,[1] S. Tavaddod,[1] V. Arpiainen,[2] M. Lindroos,[2] H. Berger,[3] V. N. Strocov,[4]
M. Shi,[4] L. Patthey,[4] and M. S. Golden[1]

[1]van der Waals-Zeeman Institute, University of Amsterdam, NL-1018XE Amsterdam, The Netherlands
[2]Department of Physics, Tampere University of Technology, PO Box 692, FIN-33101 Tampere, Finland
[3]Ecole Polytechnique Fédérale de Lausanne, Institut de Physique de la Matière Complexe EPFL Bt. PH CH-1015
[4]Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen, Switzerland
(Received 3 August 2005; published 16 March 2006)

In summary, by proving the microscopic structural origins of the shadow bands in the Bi2212 and Bi2201 families of cuprate superconductors, we have finally been able to close this chapter in the rich and complex tale of the high T_c superconductors.

FeSe - The "Simplest" Fe-Superconductor

- Simple tetragonal structure, four atoms per unit cell (Hagg and Kindstrom, Z. Phys. Chem. (1933).
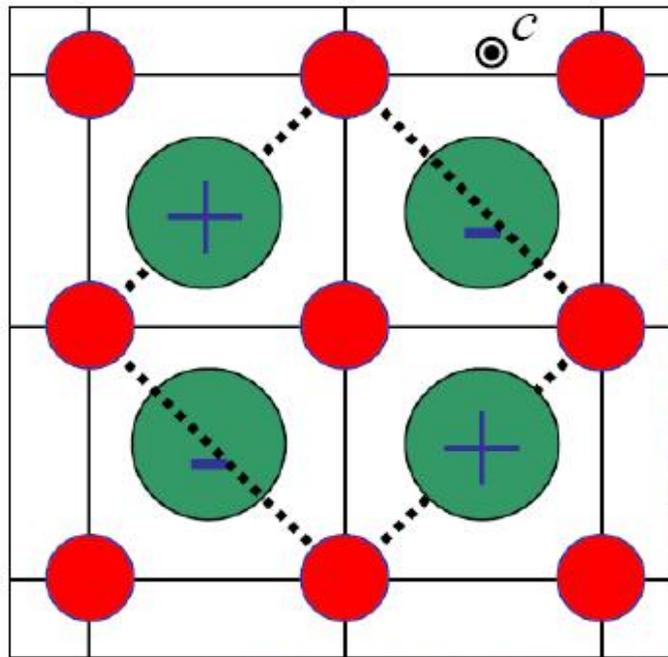
- Actual material is $Fe_{1+x}Se$, with extra Fe in holes of Se lattice.

- LiFeAs is similar, but extra sites are filled with Li.
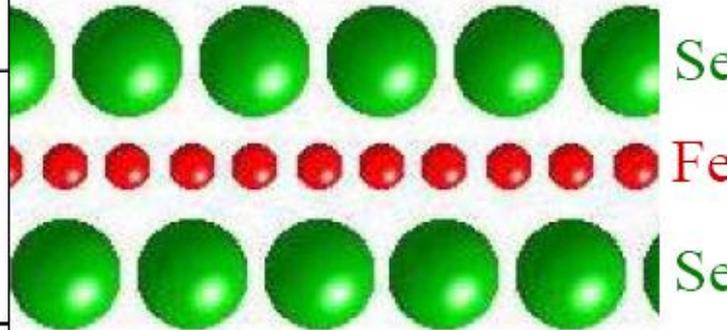
$d_{Fe-Fe} = 2.66$ Å
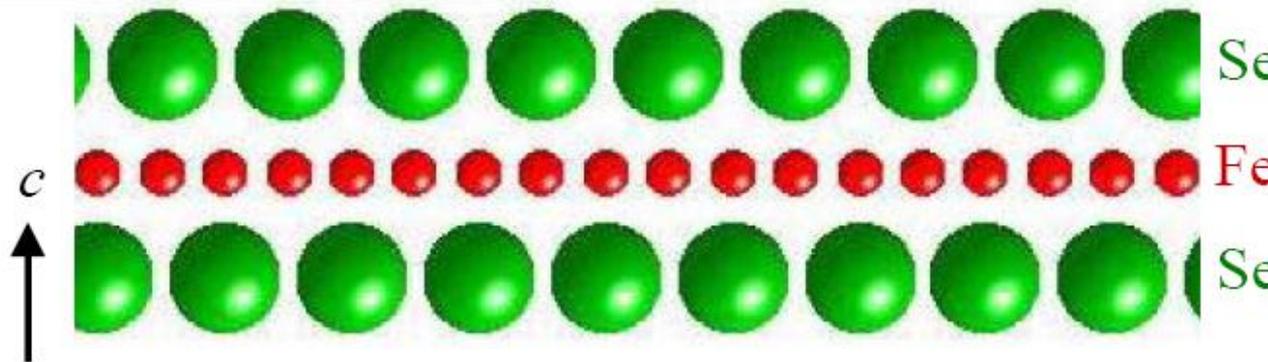
Some Phase Diagrams
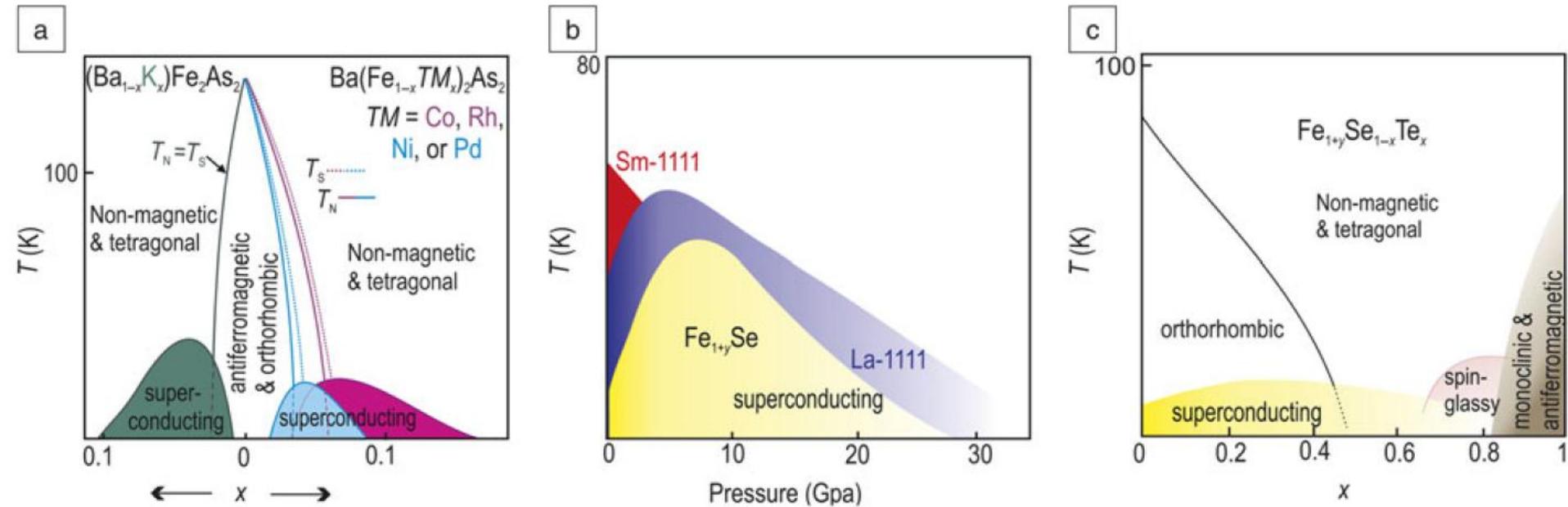
Sefat *et al.*, MRS Bull. **36**, 216 (2011)

Not List:

- Doping is not essential.

- Not in proximity to Mott phases.

- Magnetic order & superconductivity not incompatible (compete).

- Orthorhombicity occurs without magnetic order, but not always, and highest T_c is tetragonal (but large orthorhombic regions).

- Maximum T_c in different families is not so different (factor of ~2).

Metallic Antiferromagnetic State

SrFe$_2$As$_2$ (Sebastian *et al.*)
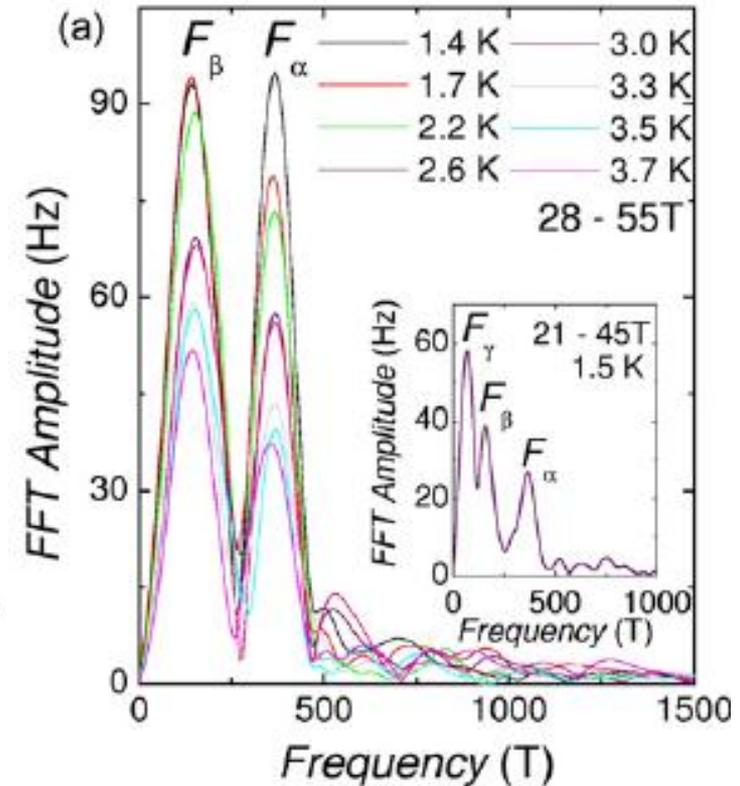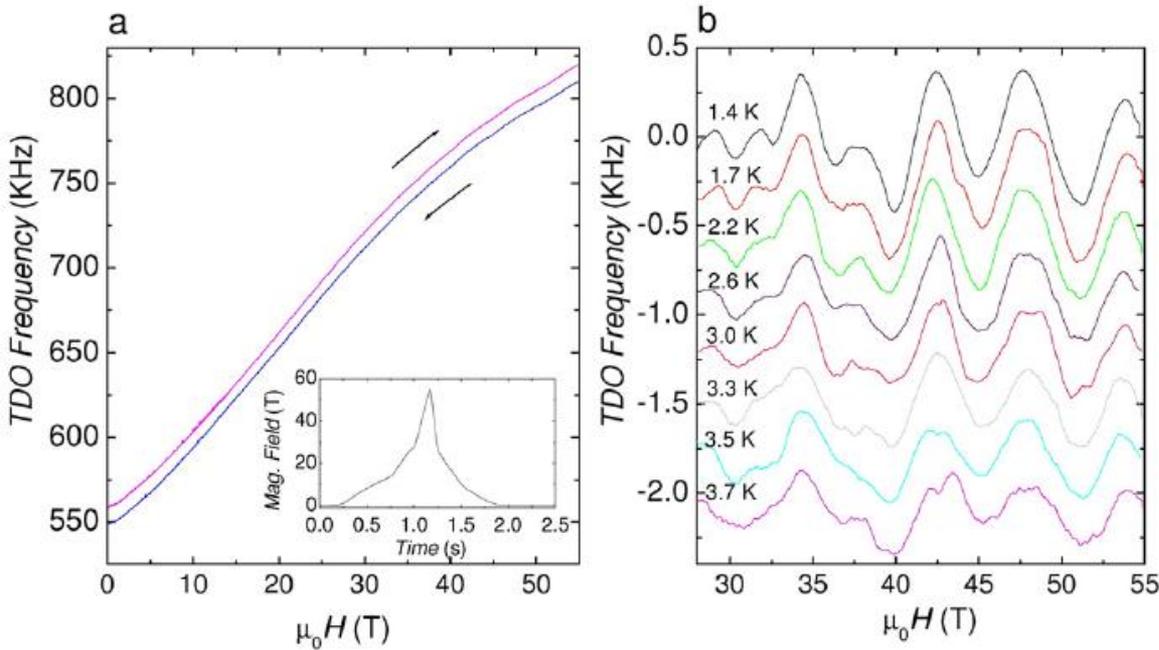
Shubnikov – de Hass measured by tunnel diode method.

SDW state has quantum oscillations reflecting a Fermi surface and is therefore a metal.

Phonons and Electron-Phonon Interaction

- First principles calculations allow direct calculation of pairing interaction, and almost first principles calculation of T_c.

- Calculations show weak coupling, no superconductivity ($\lambda_{ep} \sim 0.2$).
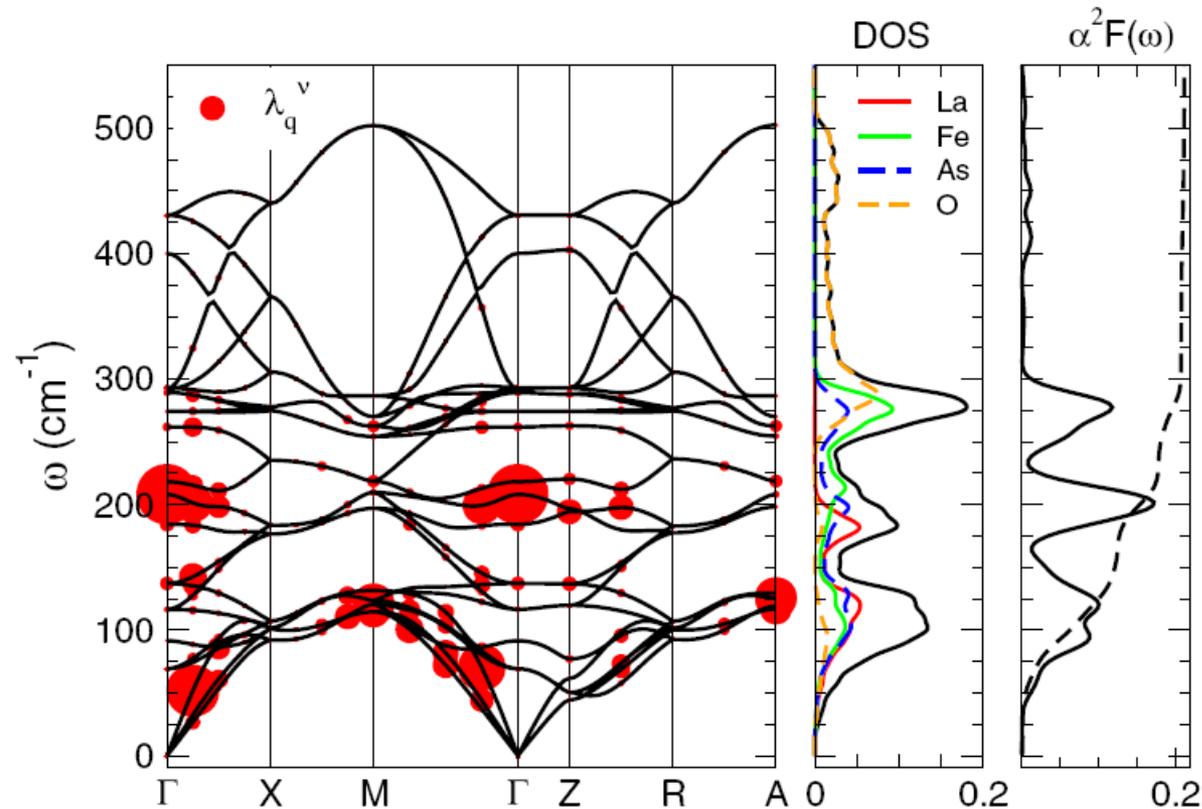
- Fe/As phonons are below 300 cm^{-1}.

- Corresponding Ni compounds, LaNiPO, LaNiAsO, BaNi$_2$As$_2$ ... are electron-phonon superconductors!

- Fe compounds are not electron-phonon superconductors.

Boeri, et al., PRL (2008); also Mazin, et al., PRL (2008).

Neutron Scattering – Magnetism & Structure

LaFeAsO:

Ordered m(Fe) = 0.36 μ_B
(other compounds so far are between 0.3 and 1 μ_B)

C. de la Cruz et al., Nature **453**, 899 (2008)
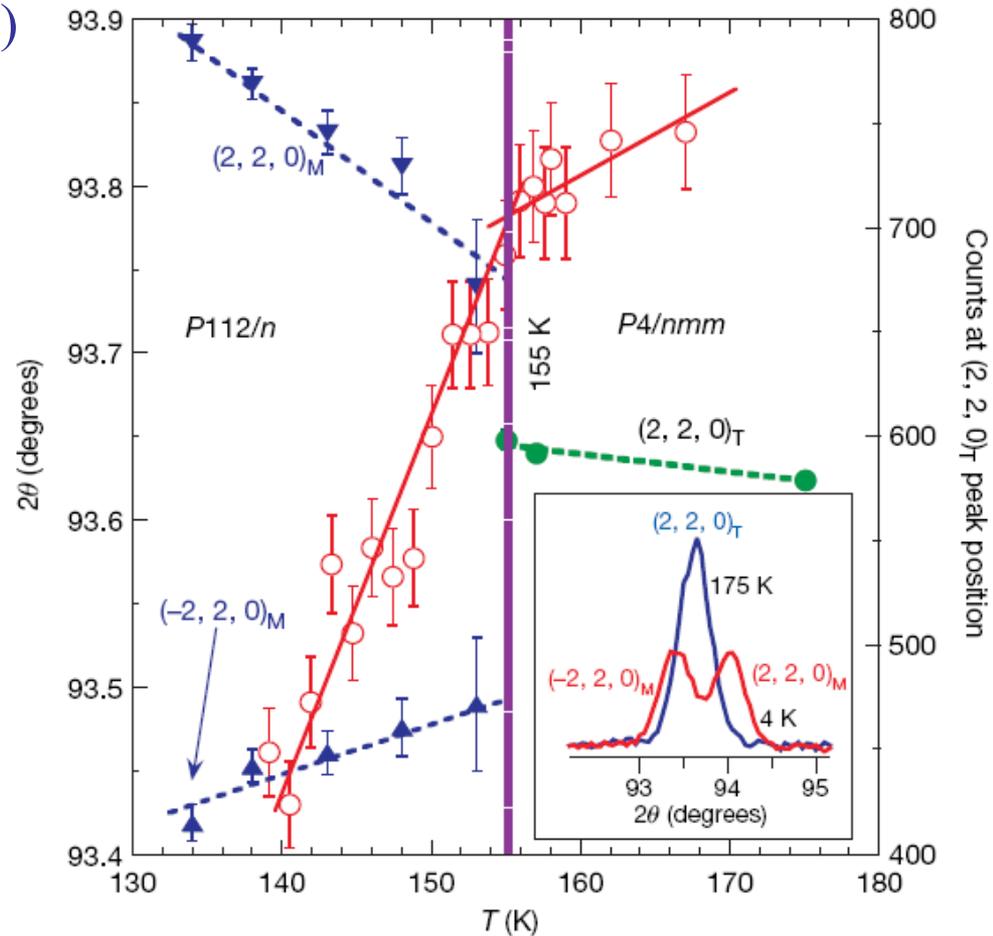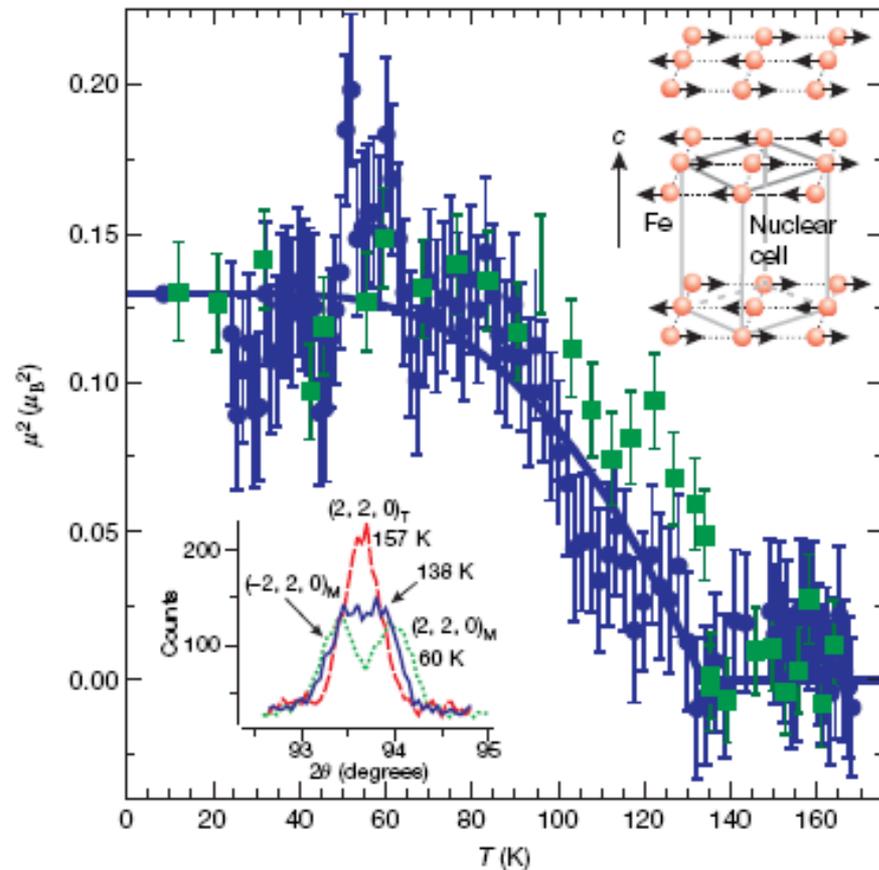
In-plane SDW structure
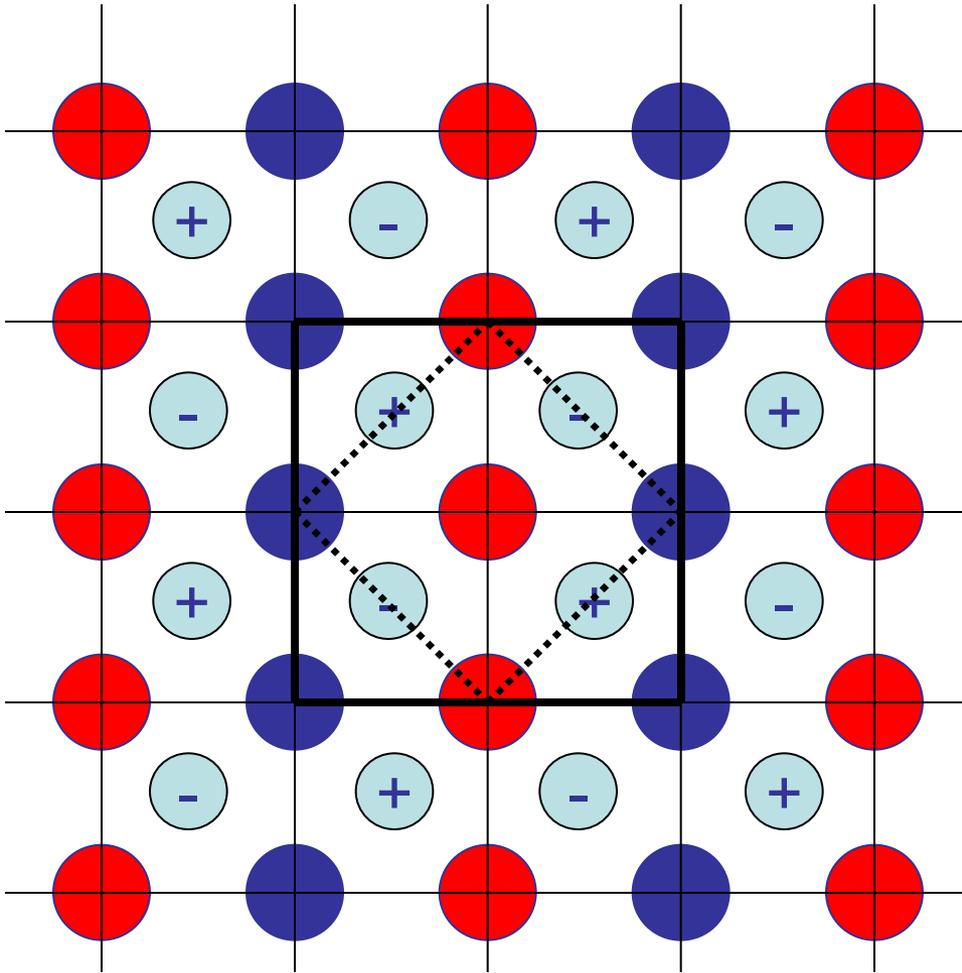
1 D Chains of parallel spin Fe atoms.

Hund's Coupling

- Hund's coupling in 3d ions is strong (Stoner $I \sim 0.8$ eV)

- Spin-fluctuations are then expected to couple to electronic states in the *d*-band going up to high energy (i.e. the *d*-band width) – may be observable in spectroscopy. Drude weight seems reduced in optics.

Cr metal: Machida et al., JPSJ (1984).
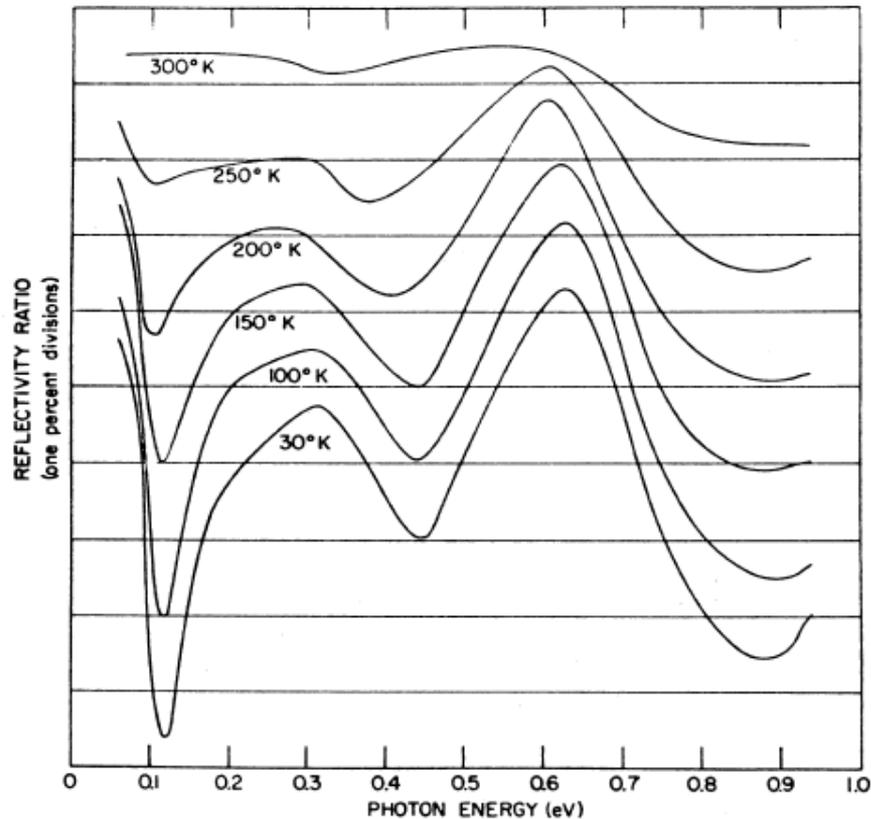
Fig. 3. The temperature dependent reflectivity of chromium normalized to $T = 400$ K.
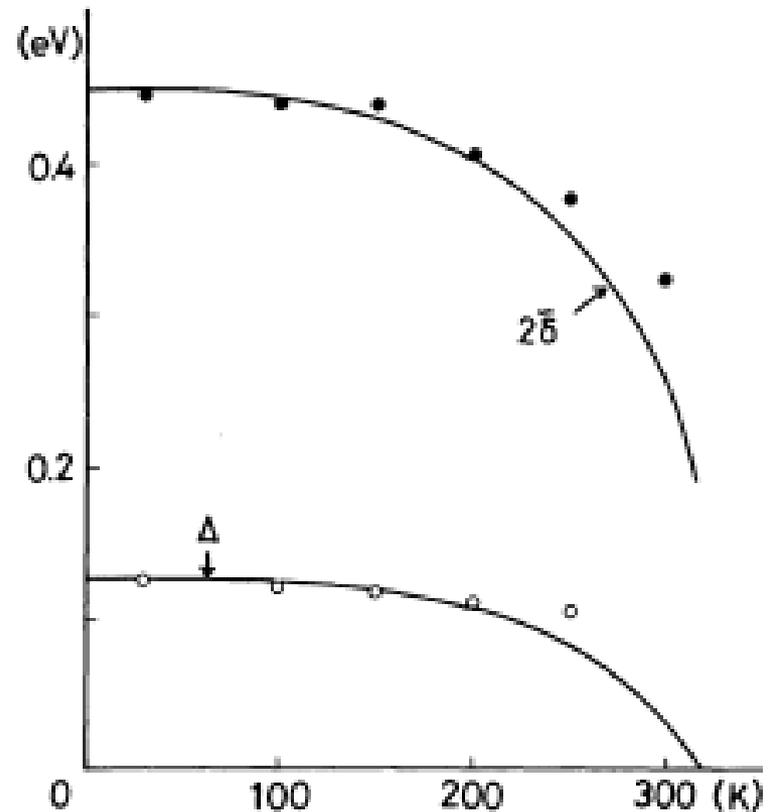
NMR: Connection of SDW and SC States

$1/T_1T$ shows strong spin fluctuations (constant for ordinary F.L.)
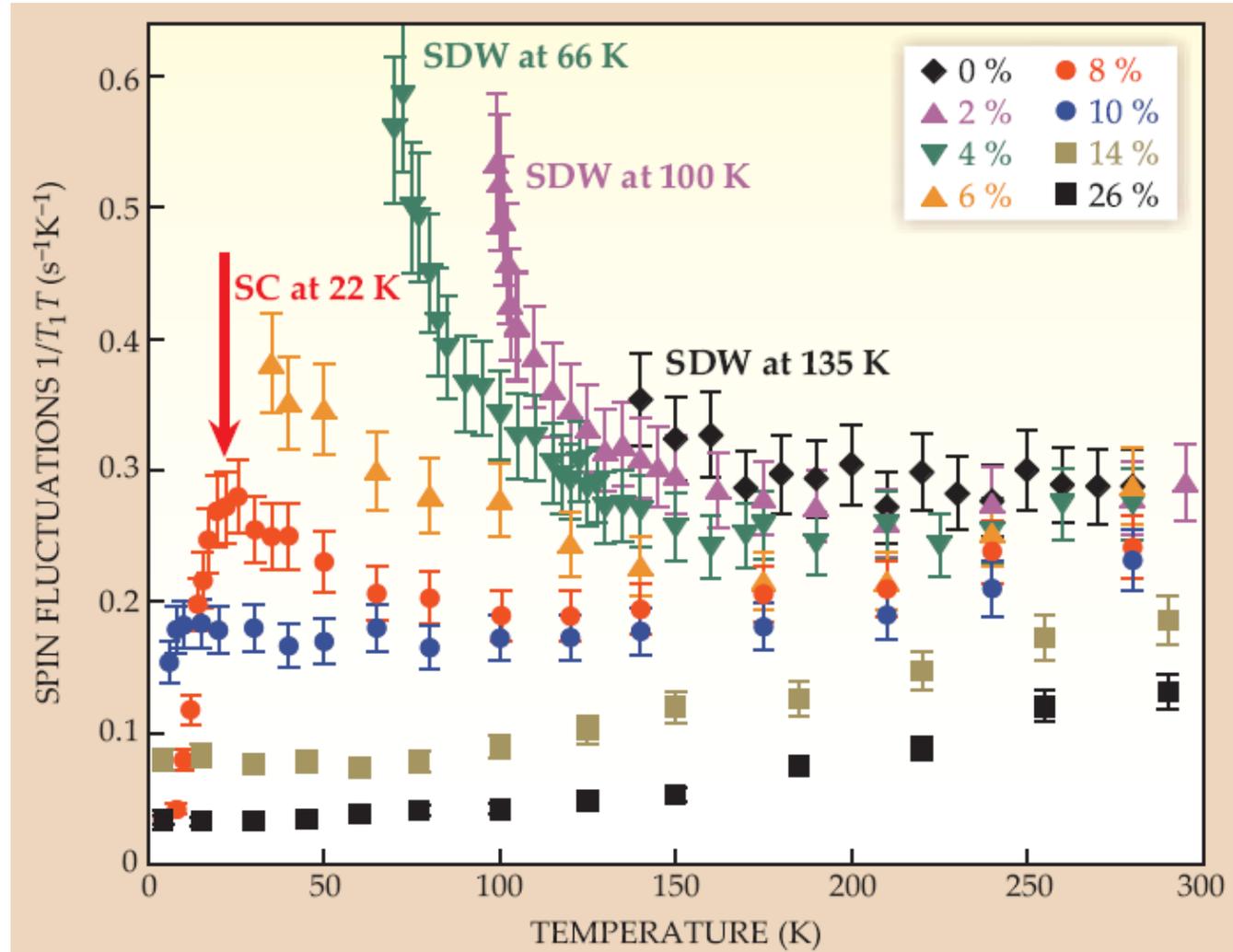
Ning, et al., JPSJ **78**, 013711 (2009).

LDA Electronic Structure of FeSe

- A rather ionic material – Fe^{2+} and Se^{2-} with some hybridization, as in an oxide ➜ metallic sheets of Fe^{2+} modified by interaction of anions.

- Pauling electronegativities: Fe = 1.83; Se = 2.55; As = 2.18.

Fe^{2+} ➜ d^6

$N(E_F)$ is at bottom of pseudogap.
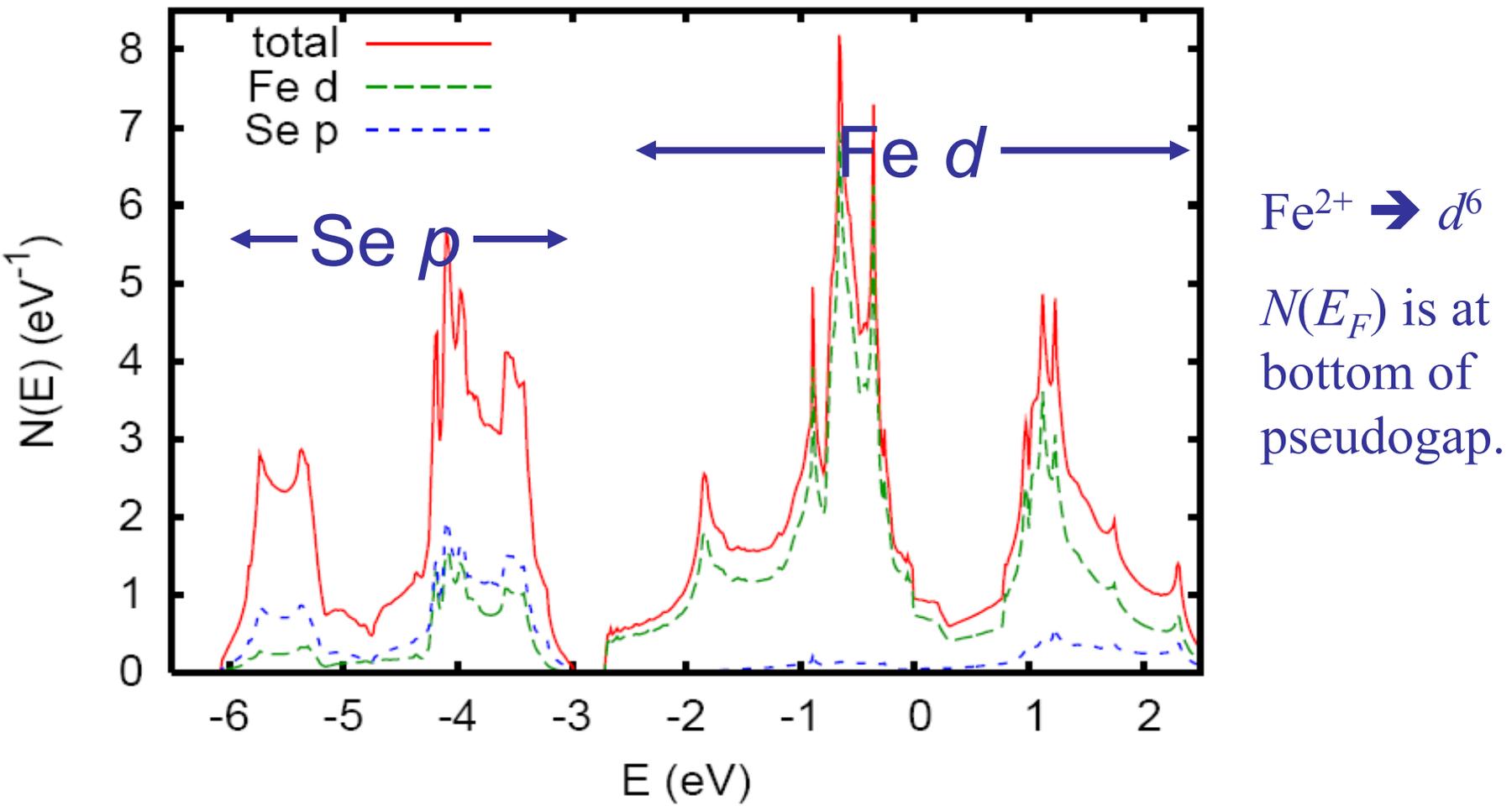
Formation of Band Structure

- Bands from -2 eV to +2 eV are derived from Fe^{2+} d-states.

- Fe^{2+} has 6 d-electrons.

Tetrahedral Crystal Field Scheme:

t_{2g} 6e

$3d$ 10e

e_g 4e
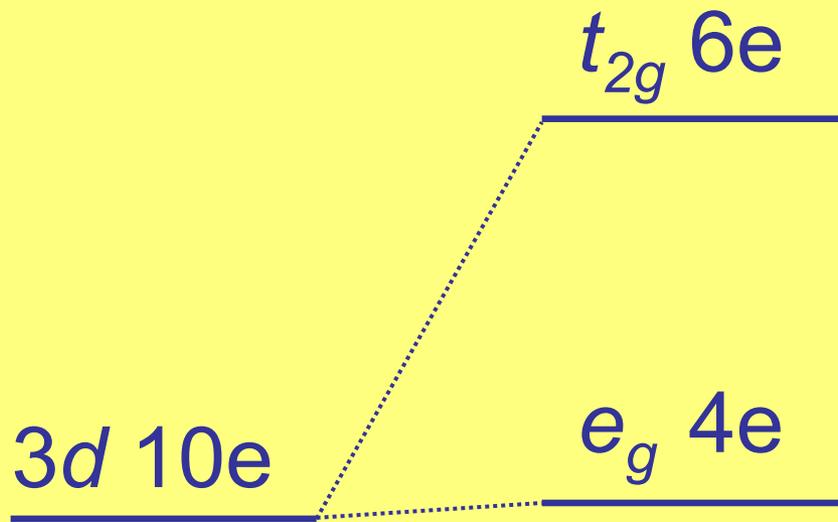
Does not correspond to the calculated electronic structure.

Key is the short Fe-Fe bond length →
direct Fe-Fe interactions.

Arsenide Electronic Structure: LaFeAsO

- LaFeAsO: Rather ionic electronic structure: O^{2-}, As^{3-}, La^{3+}
- Bands near E_F are derived from Fe with little As admixture
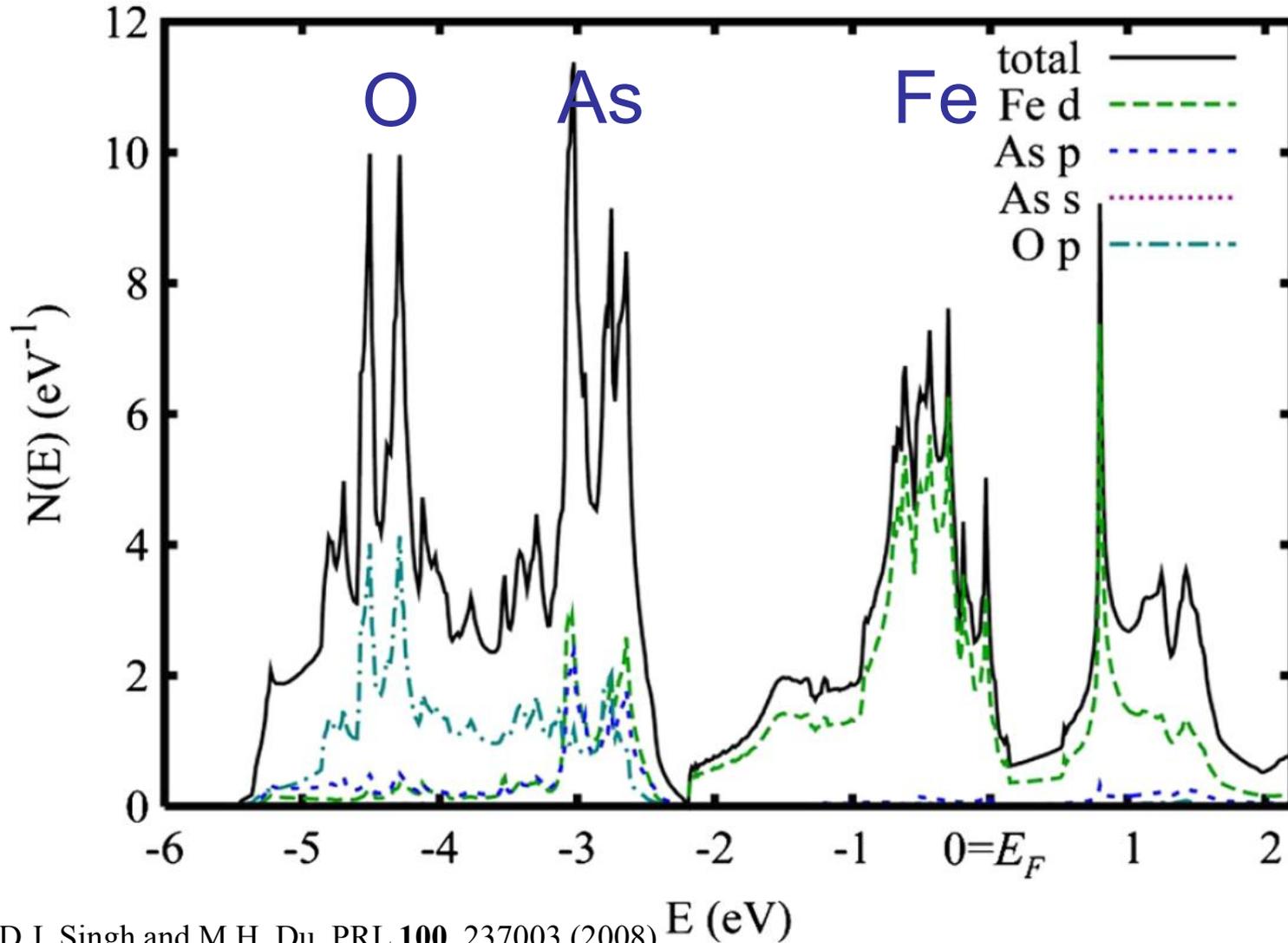
Metallic sheets of Fe^{2+}

E_F is at the bottom edge of a pseudogap

High $N(E_F)$ ➔ near magnetism

Metallic Character

Photoemission: LaFePO (D.H. Lu et al.)

O p ,As p

Fe d
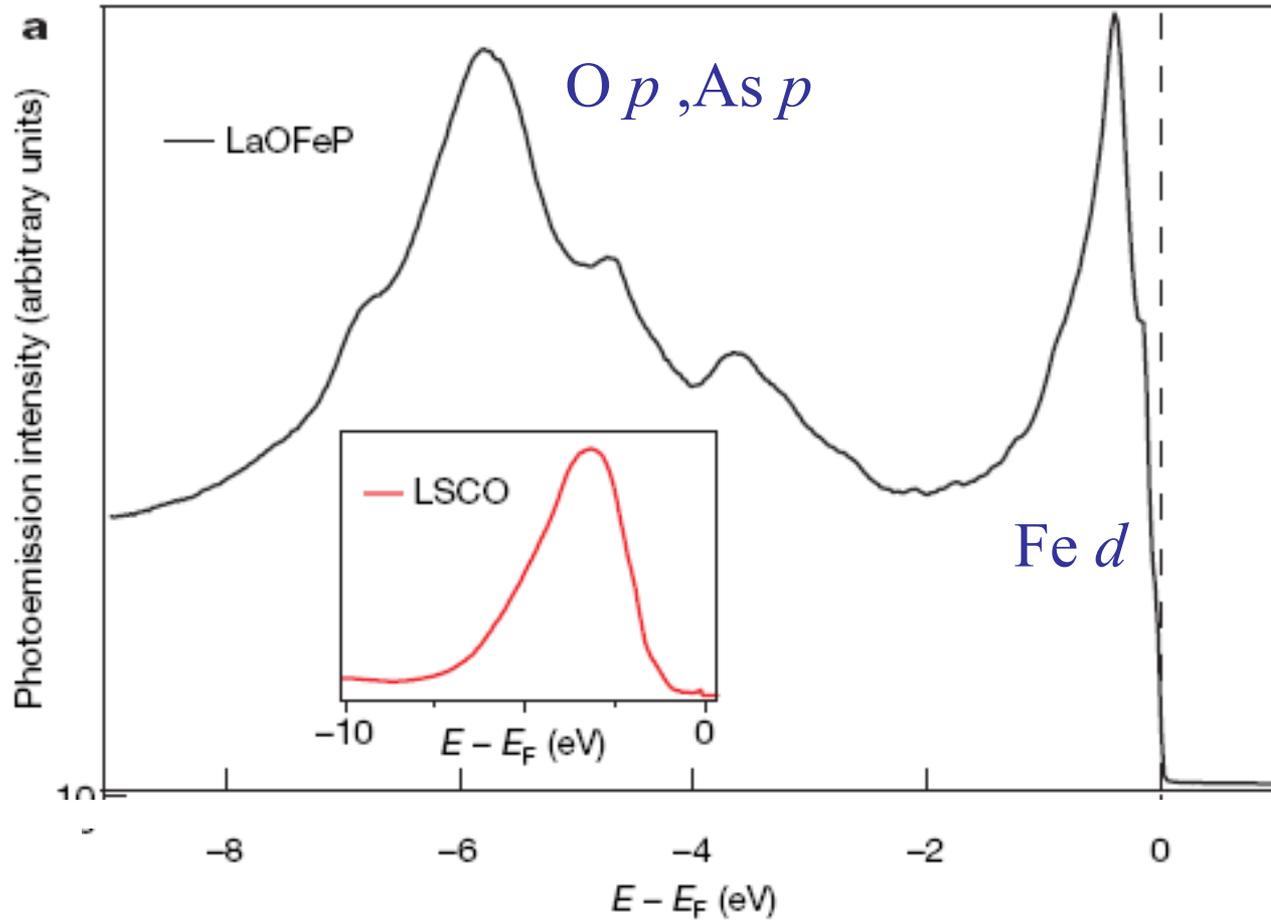
Very prominent Fermi edge (not like cuprates).

Fe d bands are narrower (by ~2) compared to LDA.

Optics

LaFePO (M.M. Qazilbash et al.)
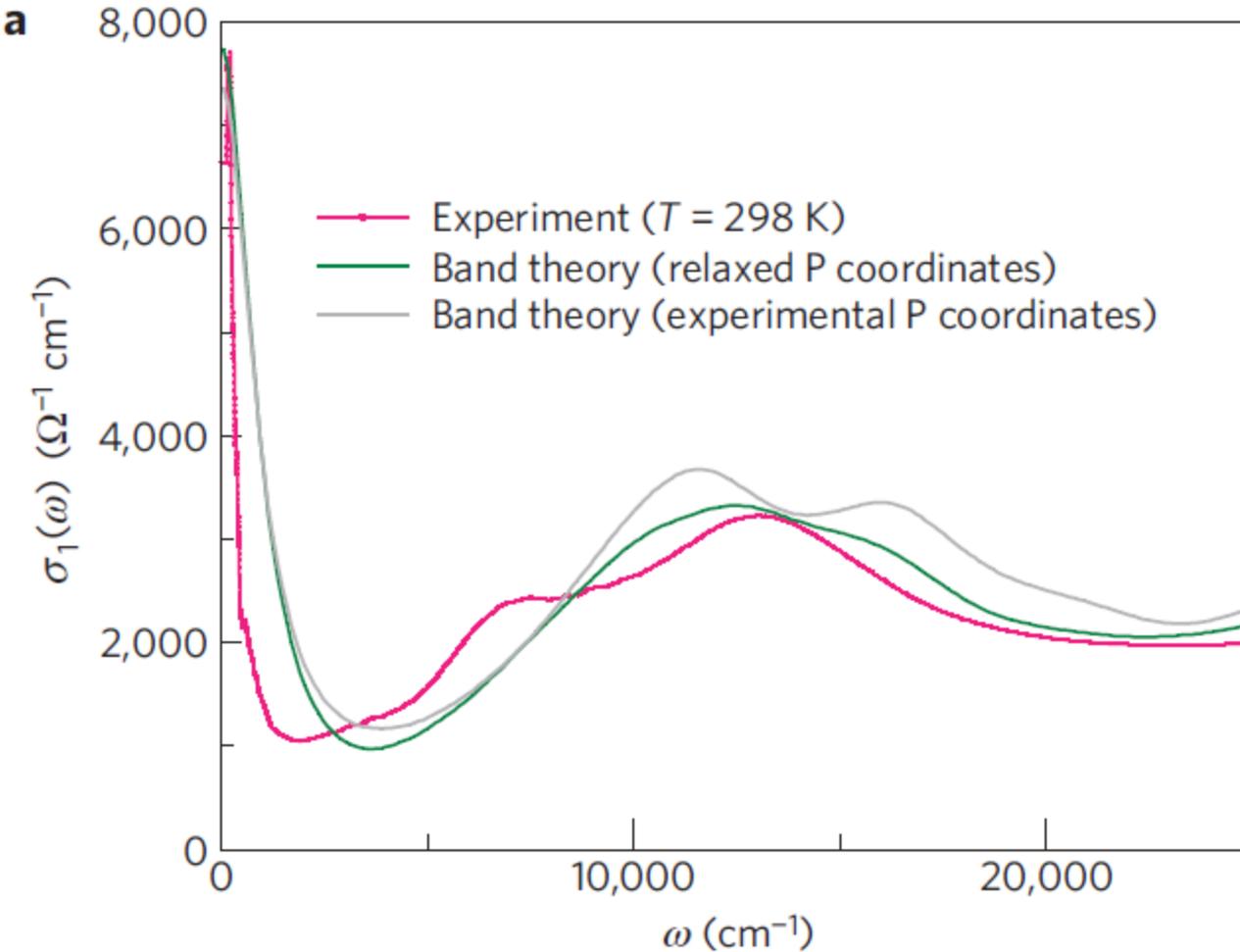
Drude has lower weight than in band calculation.

Re-distrubution of spectral weigh in d-bands.

No Hubbard bands.

Coulomb Correlations

- LDA and correlated approaches give different predictions.

- So far Hubbard bands are not seen; strong Fe d character is seen at Fermi edge.

- There is however a renormalization of ~2 in band width c.f. LDA.

X-ray spectra, Kurmaev, et al.

Fe 3d DOS

Fe L$_3$ RXES

DMFT

Fe (d)
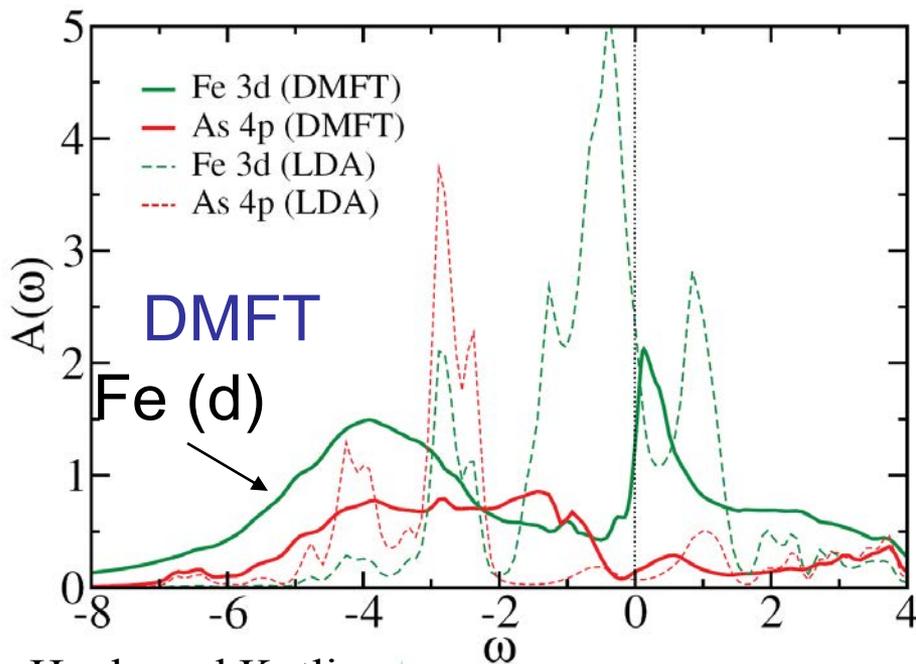
Haule and Kotliar
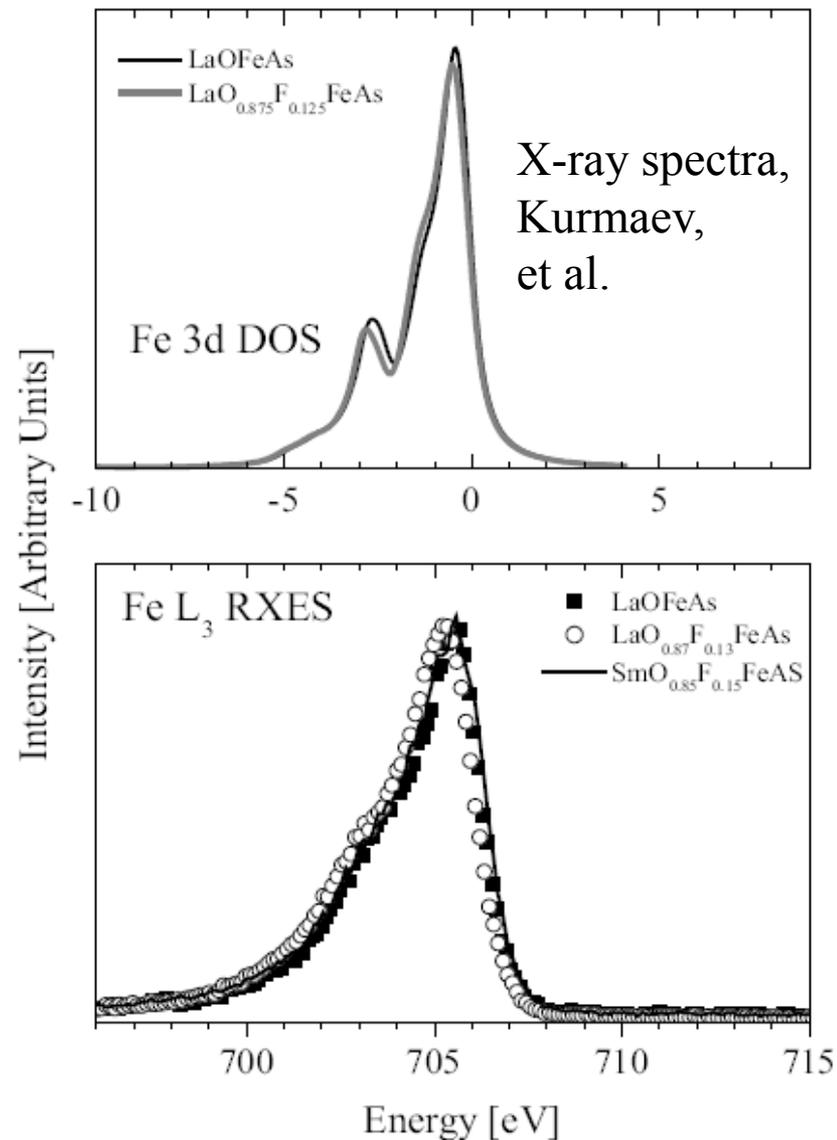
Density Functional Study of $LaFeAsO_{1-x}F_x$: A Low Carrier Density Superconductor Near Itinerant Magnetism

D. J. Singh and M.-H. Du

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114, USA
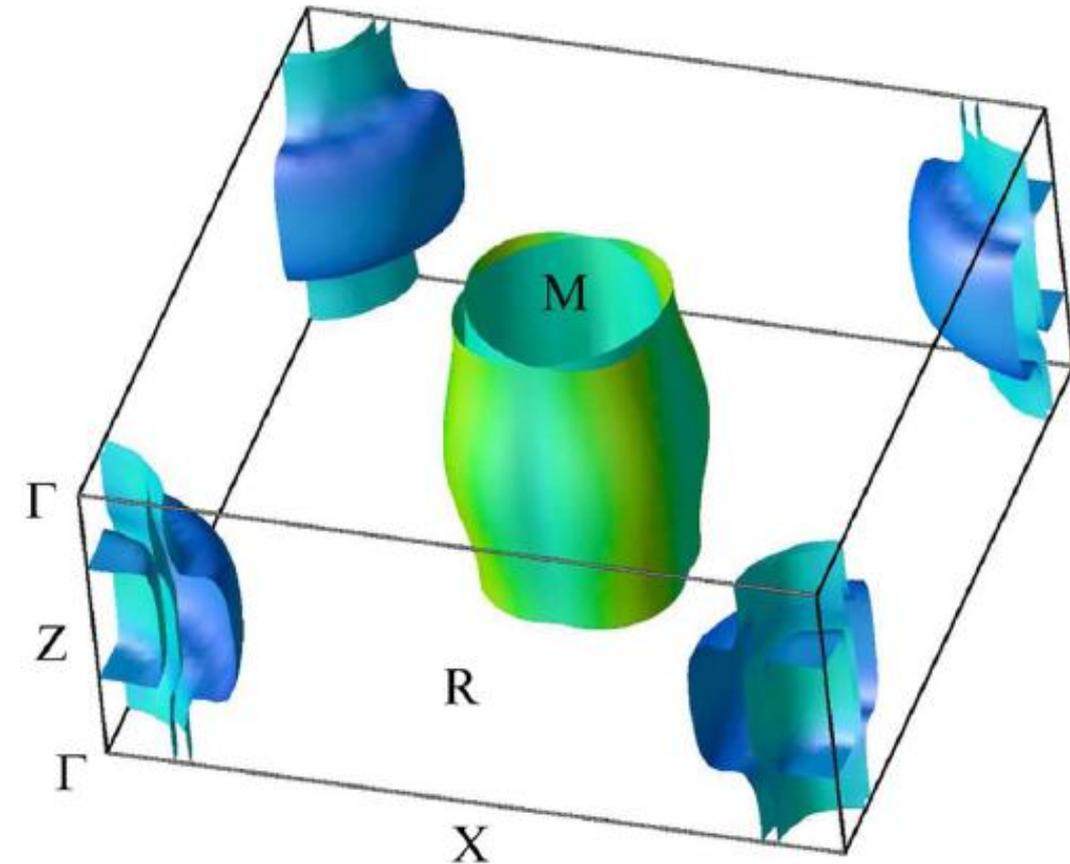
Fermi Surface of LaFeAsO

(not spin polarized)

Low carrier density:
$n_e=n_h=0.13$ / Fe

Band anisotropy: $\langle v_x^2\rangle / \langle v_z^2\rangle \sim 15$ ➔
a modest value that is favorable for applications.

Lindhard Function (Metal Physics)

- LaFeAs(O,F) neglecting matrix elements:

$\mathrm{Im}\ \chi_0/\omega$ $\mathrm{Re}\ \chi_0$

Scattering, Transport   Magnetism, Superconductivity
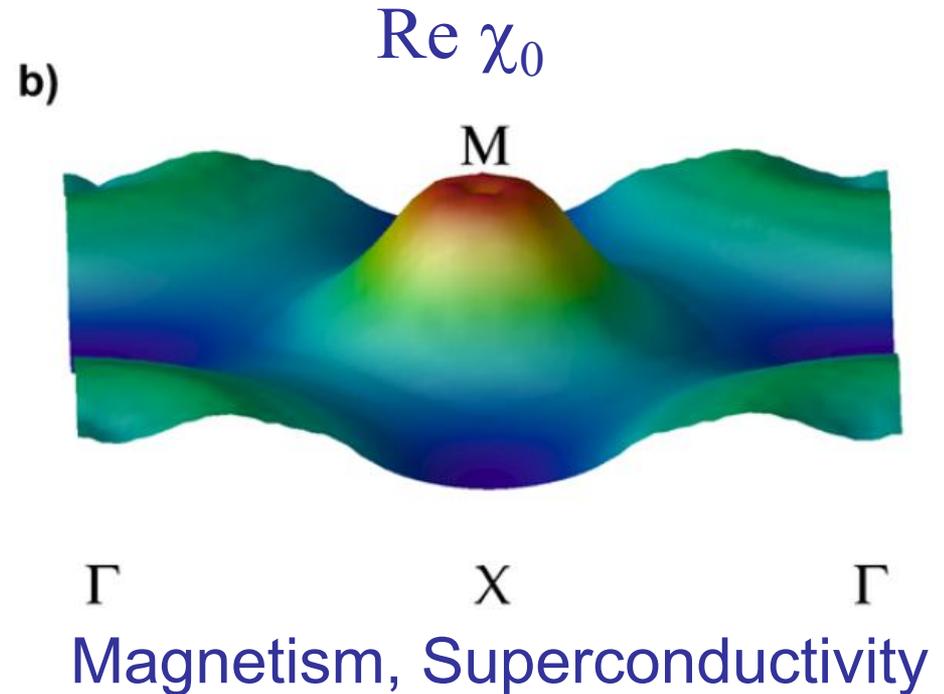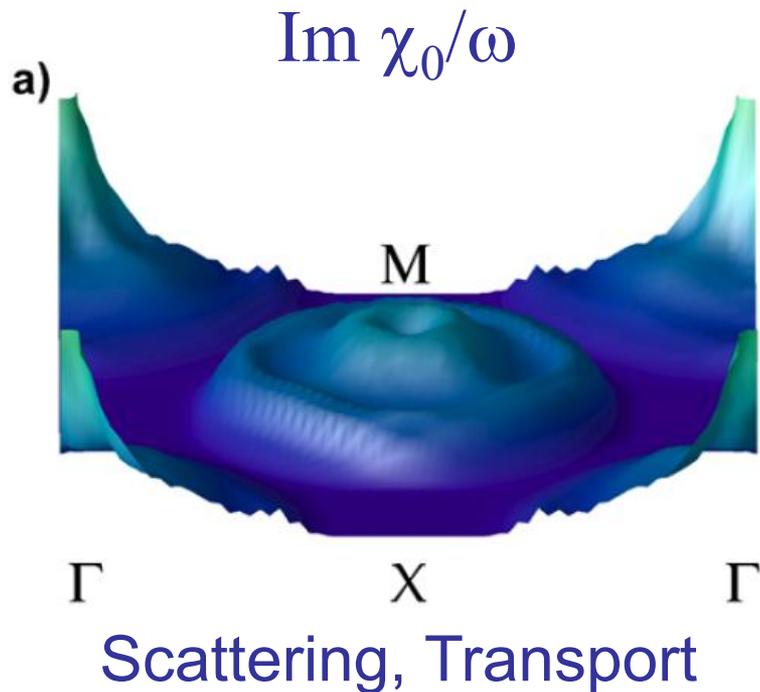
Note the pronounced peak at the zone corner.

I.I. Mazin, D.J. Singh, M.D. Johannes and M.H. Du, PRL **101**, 057003 (2008)

Spin Fluctuations and Superconductivity

One way to proceed (weak coupling):
- Calculate matrix elements $V_{k,k'}$ for a set of k,k' on the FS.
- Set-up gap equation -- diagonalize V.

Berk-Schrieffer-Fay-Appel weak coupling theory, 1966-1980:

Singlet:

$$V(\mathbf{q}) = - \frac{I^2(q)\chi_0(\mathbf{q})}{1 - I^2(\mathbf{q})\chi_0^2(\mathbf{q})}$$

Electron doped LaFeAsO
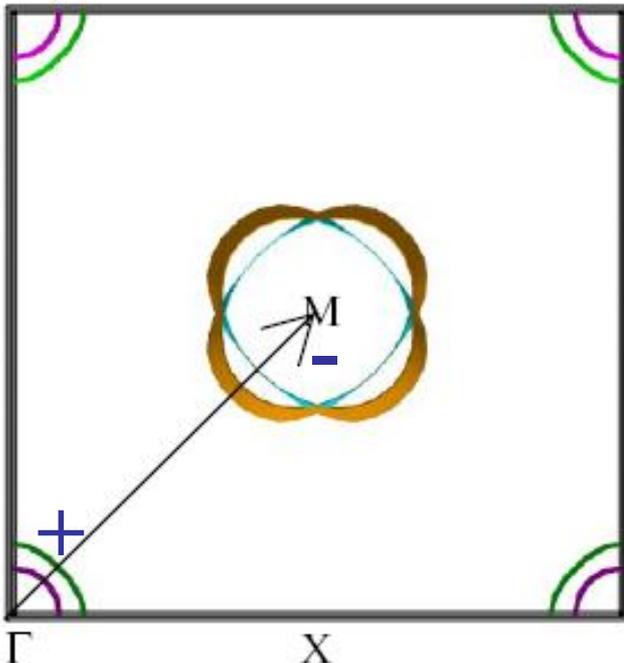
In a singlet channel there is a minus sign for spin fluctuations (repulsive), which then favors opposite order parameters on the electron and hole sheets ➔ s +/- state.

Note prior work, Aronov & Sonin (1972); Kuroki and Arita (2001)

Does not have an obvious strongly q-dependent interaction for nodes in a FS.

I.I. Mazin, D.J. Singh, M.D. Johannes and M.H. Du, PRL **101**, 057003 (2008)

LETTERS

Unconventional superconductivity in $Ba_{0.6}K_{0.4}Fe_2As_2$ from inelastic neutron scattering

A. D. Christianson[1], E. A. Goremychkin[2,3], R. Osborn[2], S. Rosenkranz[2], M. D. Lumsden[1], C. D. Malliakas[2,4], I. S. Todorov[2], H. Claus[2], D. Y. Chung[2], M. G. Kanatzidis[2,4], R. I. Bewley[3] & T. Guidi[3]

T=7K

T=50K
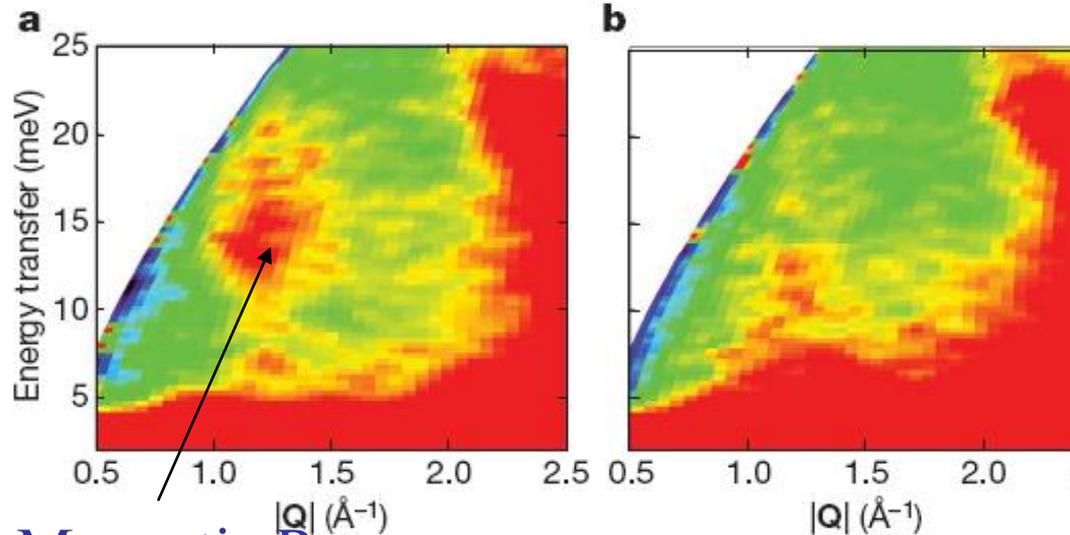
Magnetic Resonance
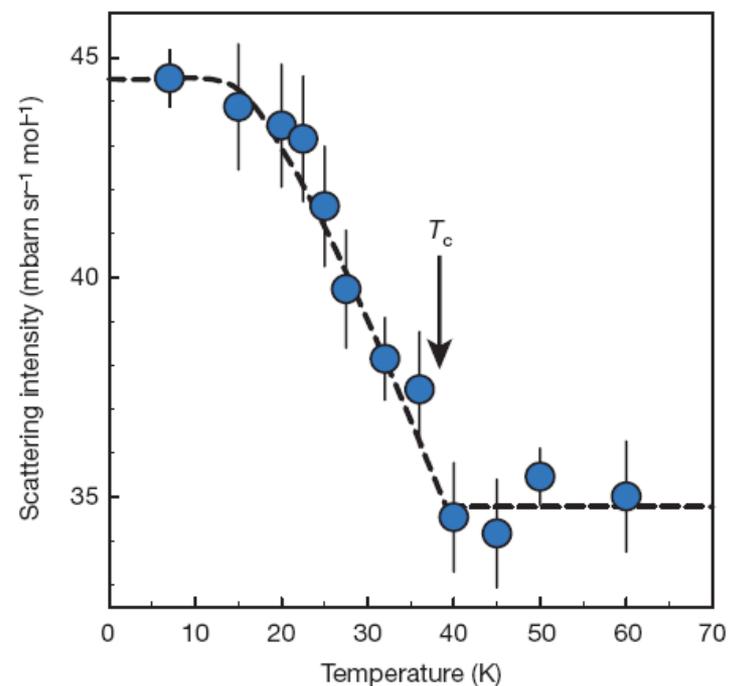
Sign changing gap with q corresponding to (π,π)

Small Fermi Surfaces in General

- Does superconductivity arise in general if one has small Fermi surfaces with nesting driven spin fluctuations? – Answer seems to be no.
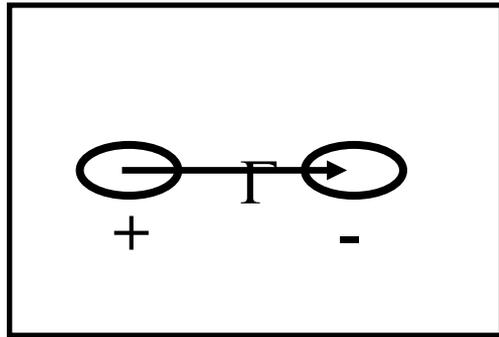
p-wave state (triplet): spin-fluctuation pairing interaction has + sign ➤ Pair breaking for the state shown.
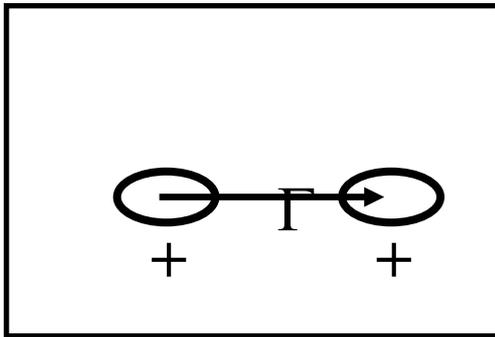
s-wave state (singlet): spin-fluctuation pairing interaction has – sign ➤ Pair breaking for the state shown.

e.g. small pockets on Na_xCoO_2 (Johannes et al., 2004).

In such cases, look for chemistry with strong electron phonon and low Stoner parameter, to obtain Kohn anomaly and e-p superconductivity or maybe strange states, e.g. odd frequency.

Normal Metallic State

- Low carrier density semi-metal (dis-connected small Fermi surfaces).

- Less anisotropic than cuprates, even $YBa_2Cu_3O_7$.

- High $N(E_F)$.

  - Near itinerant magnetism in general.

  - Expect short coherence length relative to T_c.

  - Expect high superfluid density.

- Electron-Phonon interaction is weak ($\lambda \sim 0.2$, $T_c = 0$)

Nesting, Doping and the Lindhard Function
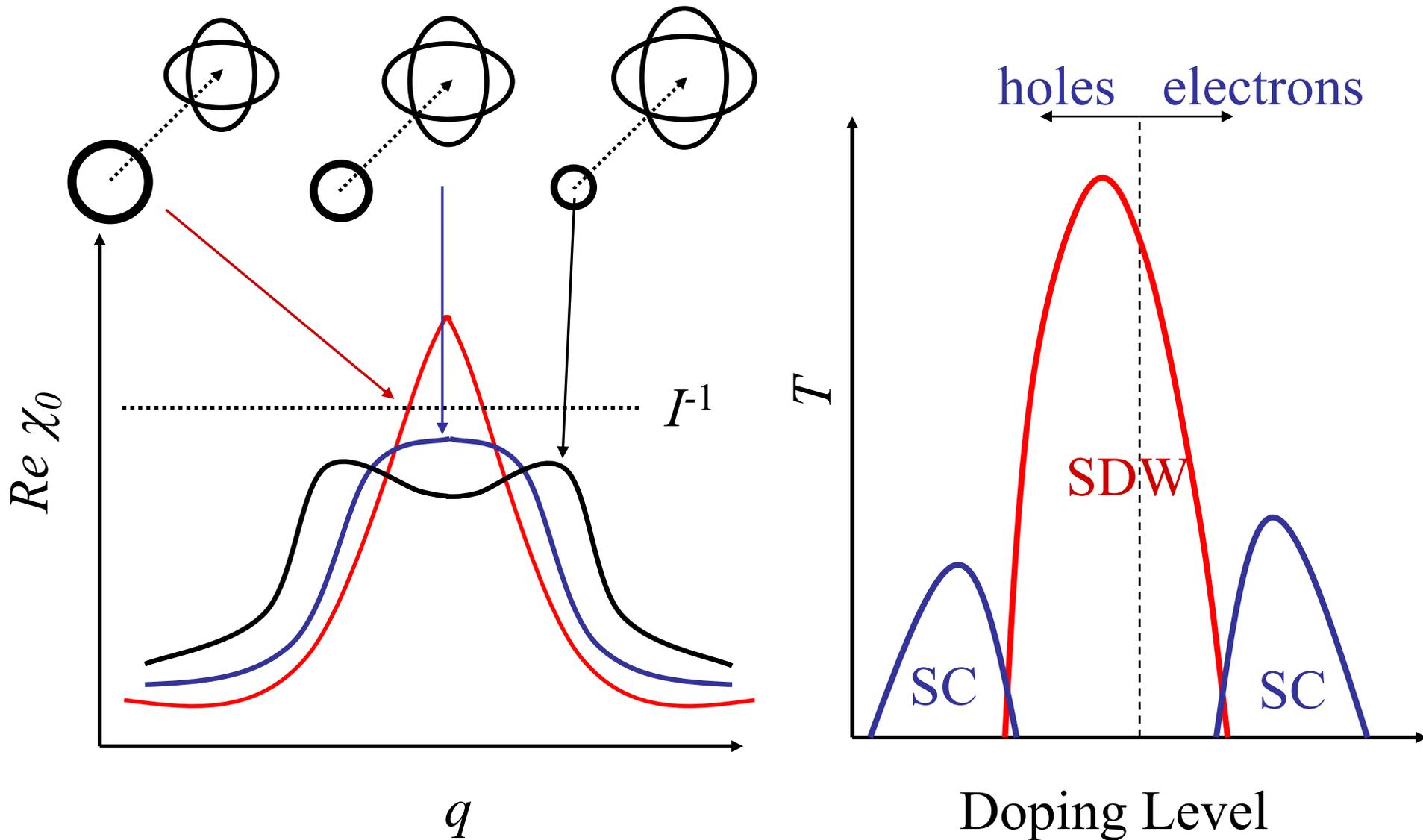
Disorder affects both magnetism and superconductivity

Neutron Scattering – Structure Details

LaFeAsO (Tetragonal → Orth/Mono):

Table 2 | Properties of LaOFeAs at 4 K

a, Refined structure parameters

Atom	Site	x	y	z	B (Å²)
La	2e	¼	¼	0.1426(3)	0.54(6)
Fe	2f	¾	¼	0.5006(12)	0.16(4)
As	2e	¼	¼	0.6499(4)	0.23(7)
O	2f	¾	¼	−0.0057(17)	0.69(7)

z_{As}(4K) = 1.308 Å

z_{As}(175K)=1.317 Å

LaFeAsO$_{0.92}$F$_{0.08}$ (Tetragonal):

Table 3 | Properties of LaO$_{0.92}$F$_{0.08}$FeAs at 10 K (first line), 35 K (second line) and 175 K (third line)

a, Refined structure parameters

Atom	Site	x	y	z	B (Å²)
La	2c	¼	¼	0.1448(3)	0.40(5)
		¼	¼	0.1458(3)	0.50(5)
		¼	¼	0.1446(3)	0.73(5)
Fe	2b	¾	¼	½	0.32(4)
		¾	¼	½	0.41(4)
		¾	¼	½	0.65(4)
As	2c	¼	¼	0.6521(4)	0.41(7)
		¼	¼	0.6515(4)	0.40(6)
		¼	¼	0.6527(4)	0.69(7)
O/F	2a	¾	¼	0	0.53(6)
		¾	¼	0	0.62(6)
		¾	¼	0	0.71(6)

z_{As}(10K) = 1.323 Å

z_{As}(175K)=1.331 Å

Non-magnetic LDA calc.
(LaFeAsO – Tetragonal)
z_{As}(LDA) = 1.159 Å

A huge difference!

C. de la Cruz et al., Nature **453**, 899 (2008)

Structure and Magnetism

- As height is too low by >0.1 Å in non-magnetic LSDA calculations.

- SDW is too robust in DFT.

- Using GGA and including magnetism one can obtain much better As height. In that case magnetism is extremely robust ($m \sim 2\mu_B$) contrary to experiment.

- Discrepancy in As height persists in the paramagnetic (superconducting) doped phases.

Metals Where the LSDA Overestimates Ferromagnetism

Class 1: Ferromagnets where the LDA overestimates the magnetization.

	m (LDA, μ_B/f.u.)	m (expt., μ_B/f.u.)
$ZrZn_2$	0.72	0.17
Ni_3Al	0.71	0.23
Sc_3In	1.05	0.20

Class 2: Paramagnets where the LDA predicts ferromagnetism

	m (LDA, μ_B/f.u.)	m (expt., μ_B/f.u.)
FeAl	0.80	0.0
Ni_3Ga	0.79	0.0
$Sr_3Ru_2O_7$	1.1	0.0
$Na_{0.7}CoO_2$	0.30	0.0

c.f. "Normal" Materials

	m (DFT, μ_B/f.u.)	m (expt., μ_B/f.u.)
bcc Fe	2.17	2.12
$SrRuO_3$	1.59	1.6

Renormalization and The Fluctuation Dissipation Theorem

Relates fluctuation amplitude to dissipation term, i.e. spin fluctuation spectrum:

$$\xi^2 = \frac{4\hbar}{\Omega} \int d^3q \int \frac{d\omega}{2\pi} \frac{1}{2} \operatorname{Im} \chi(\mathbf{q}, \omega)$$

Landau functional approach (after Moriya, Shimizu, others) is based on the magnetic moment dependence of the total energy *without* fluctuations

$$\Delta E(M) = aM^2 + bM^4 + cM^6 \quad a^{-1}/2 = \chi, \text{ susceptibility}$$

Spin fluctuations renormalize this dependence, i.e. $a \Rightarrow \alpha$, etc. via integration of the Landau functional with Gaussian of rms width ξ.

1. **Large renormalization ➜ large fluctuation amplitude.**
2. **Large amplitude requires large integral ➜ Im χ large over wide range of q and ω.**

Example: ZrZn$_2$ (Weak Itinerant Ferromagnet)

Bare LDA moment of ~0.7 μ_B to ~0.2 μ_B by fluctuations ξ ~ 0.4 μ_B
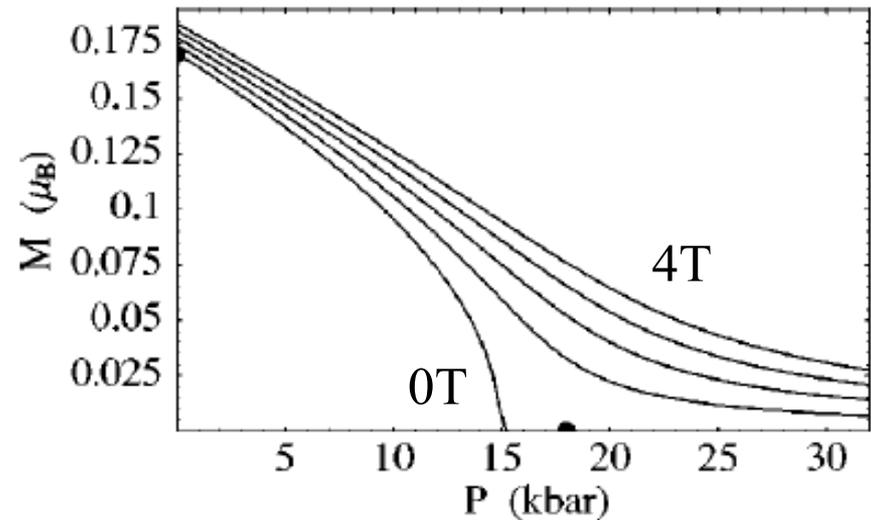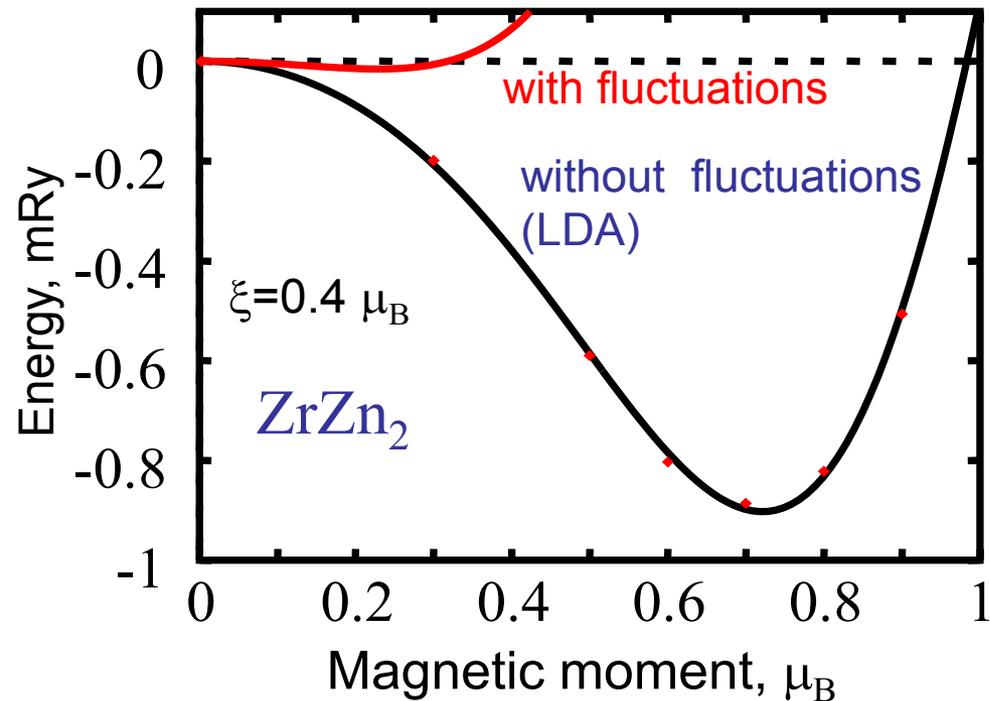
I.I. Mazin and D.J. Singh, Phys. Rev. B **69**, 020402 (2004).

Resistivity in LaFeAsO

McGuire *et al.* (cond-mat):

Hall:

Resistivity:
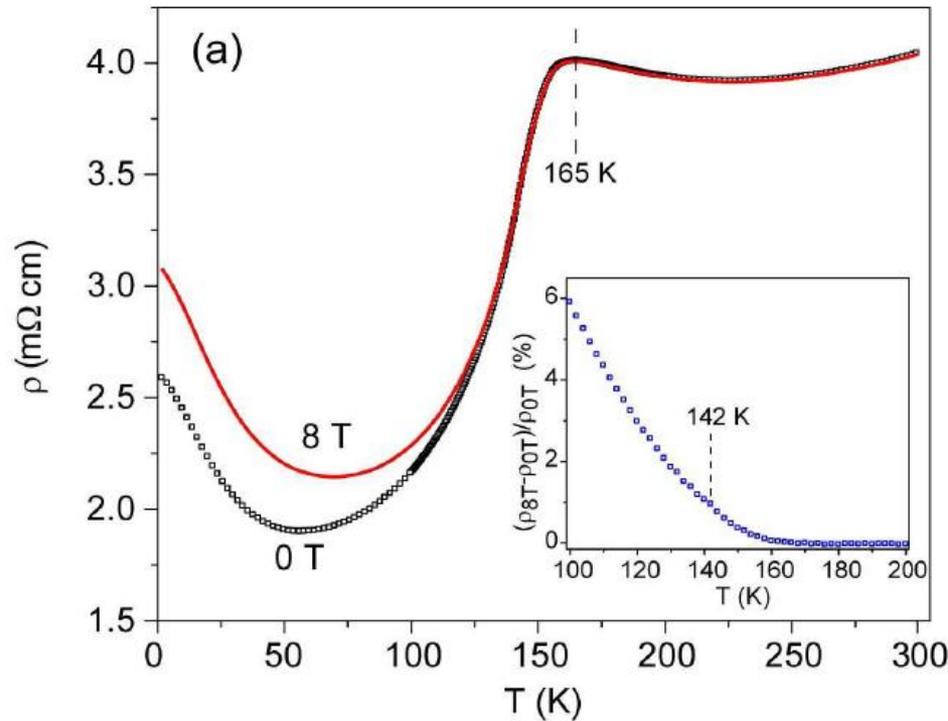
Evidence of strong interplay of magnetic ordering and Fermi surface.

Evidence of spin fluctuations.
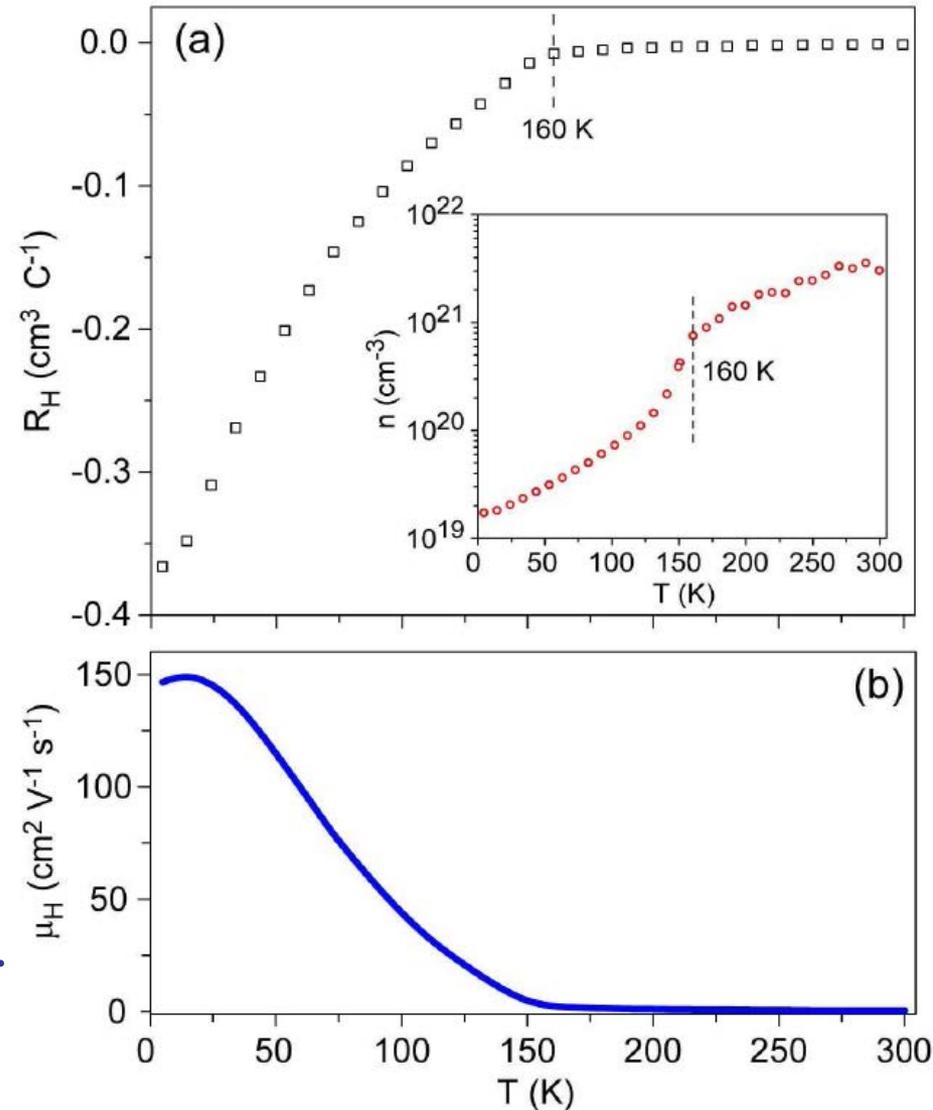
Strong Spin Fluctuations in Normal State

- Transport data.
- Susceptibility - $\chi(T)$.
- Spectroscopy.
- Scattering.
- Overly magnetic in LDA.
- Precursor structural transition.

Bondino et al. (2008); c.f. $NbFe_2$
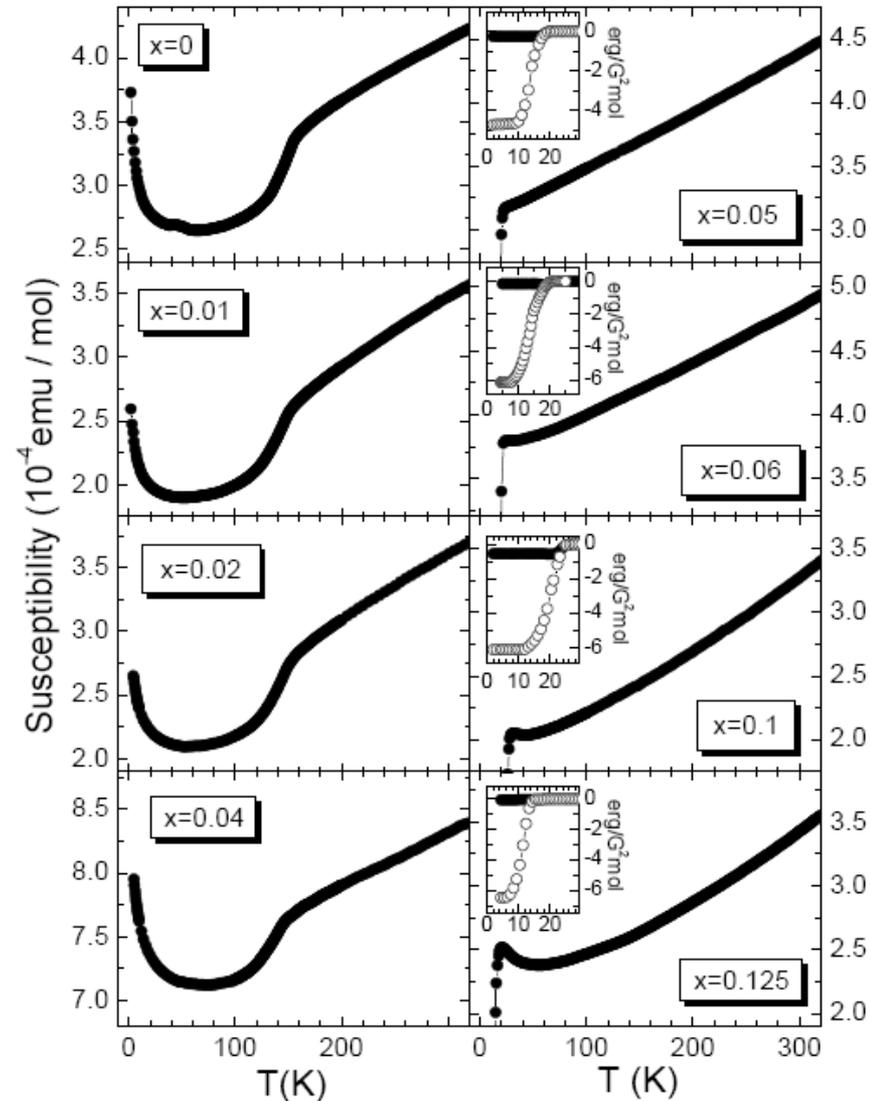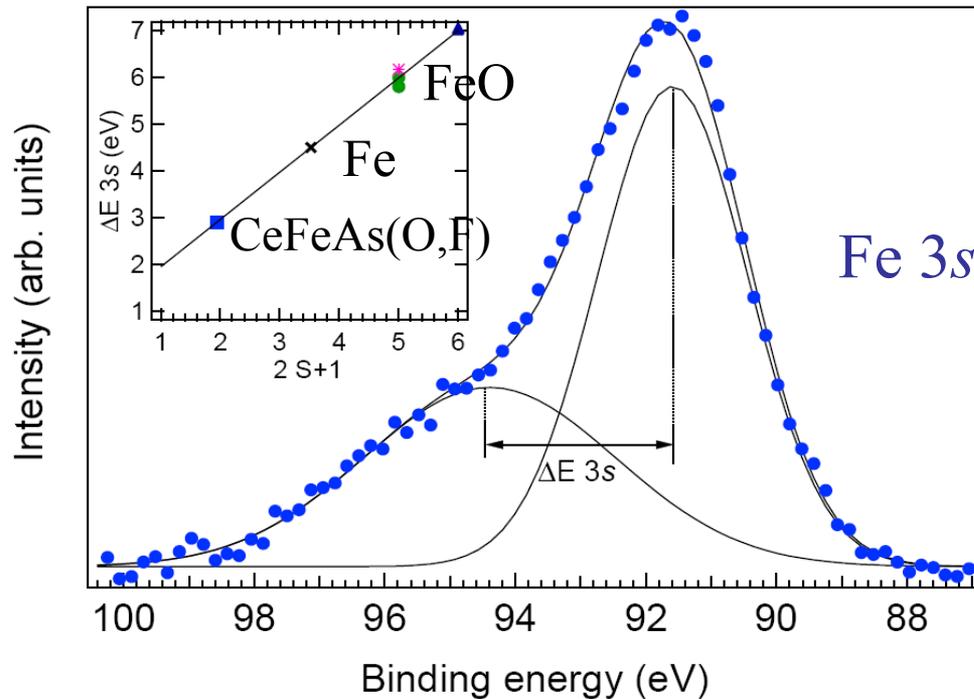
R. Klingeler et al., cond-mat
$LaFeAsO_{1-x}F_x$

Superconductivity in Metal Doped Materials

- Superconductivity requires destruction of SDW by doping.
- Remarkably, doping with Co or Ni works (*c.f.* cuprates).
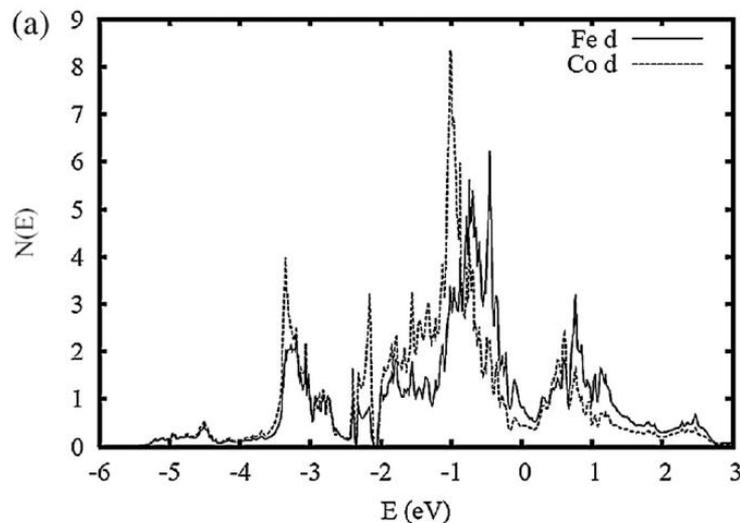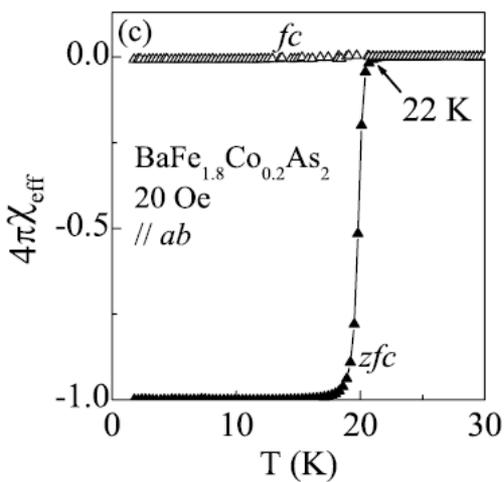
Calculations show that alloy behaves very much in a rigid band sense.

Fe-Co-Ni behave very similarly apart from electron count.

Mn and Cr show strong spin dependent hybridization (different).
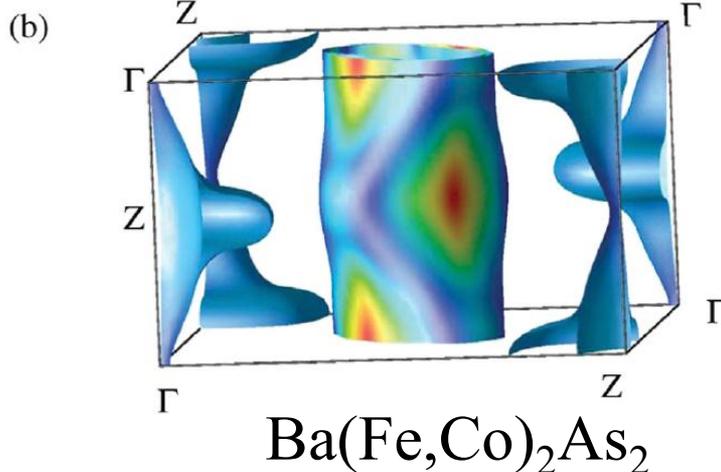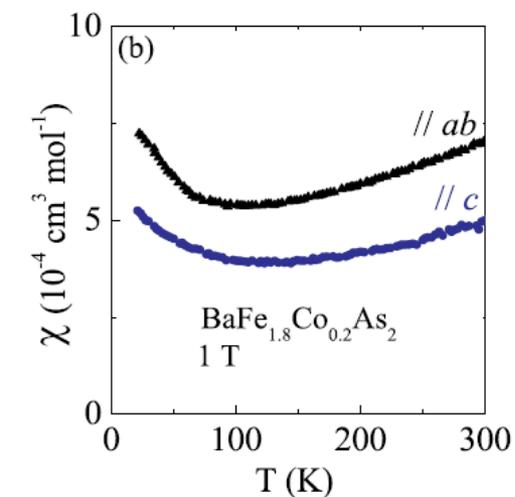
$Ba(Fe,Co)_2As_2$

Is iron essential?

A.S. Sefat, et al., PRL (2008).

ThCr$_2$Si$_2$ Structure

The Most Populous of All Crystal Structure Types—the Tetragonal BaAl$_4$ Structure

W. B. PEARSON

Departments of Physics and of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

The BaAl$_4$ (ThCr$_2$Si$_2$) *tI*10 structure, MN_2X_2, is not only the most populous of all known structure types, being adopted by some 400 phases, but is representative of a new group of metallurgically

Pearson data-base now has 2,000+ ThCr$_2$Si$_2$ entries

Can be stabilized with different bonding patterns
➔ *extremely wide variety of properties.*

Examples: BaZn$_2$P$_2$, BaFe$_2$As$_2$, BiN$_2$Th$_2$, CaAl$_2$Ga$_2$, SrCd$_2$Ga$_2$ …
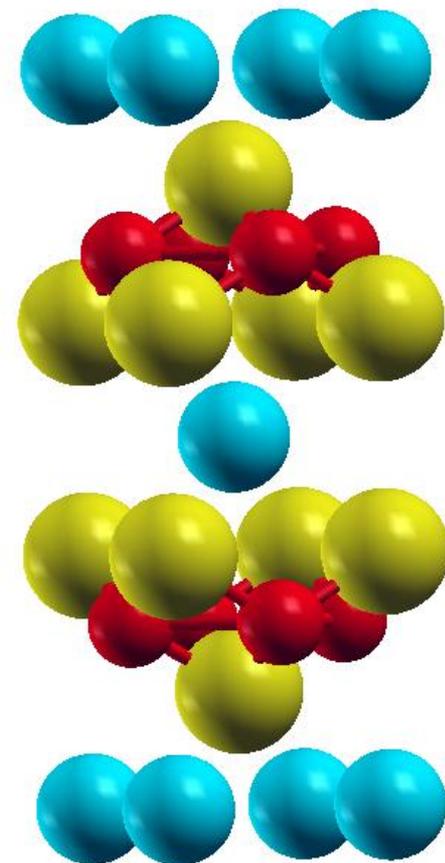
ThCr₂Si₂ Structure DT_2As_2

V	Cr	Mn	Fe	Co	Ni	Cu
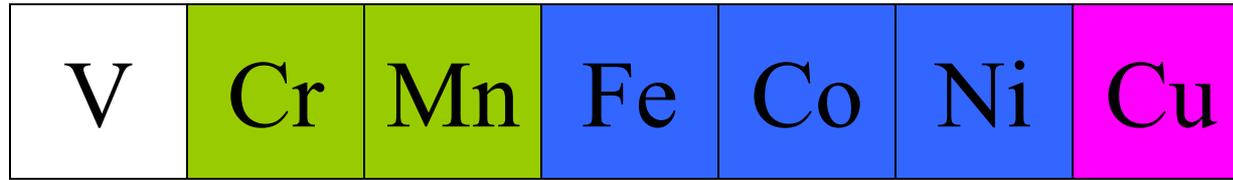
Strong spin dependent T-As hybridization, G-type AF with high T_N.
$BaCr_2As_2$ is itinerant metal. $BaMn_2As_2$ is a semiconductor.

Metallic M^{2+} sheets. As is anionic. M can be alloyed.
Fe: SDW and superconductivity.
Co: Near FM
Ni: electron-phonon superconductor.

$BaCu_2As_2$ has Cu d^{10} with As-As and Cu-As sp bonding.

Chemistry of chalcogenides may be expected to differ.

Properties of the Over-Doped Side: $TlFe_2Se_2$

Haggstrom, 1986
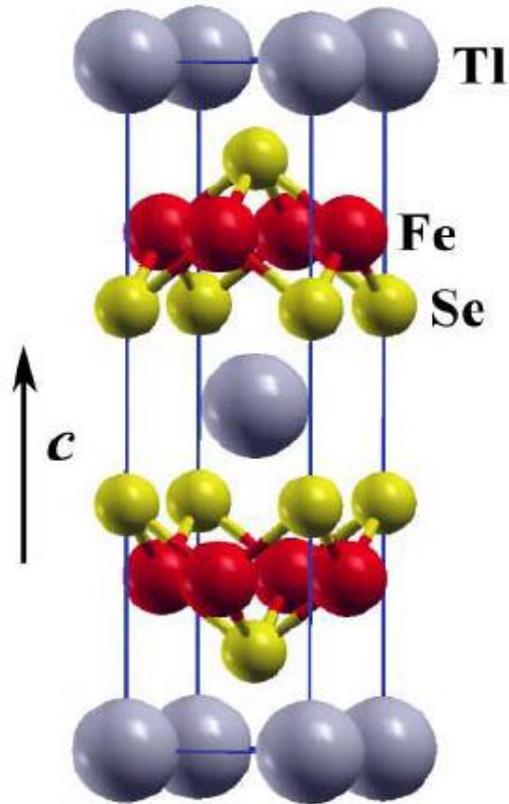
Antiferromagnetic with $T_N \sim 450$ K. Unknown order.

First Principles Results (GGA):

- Electronic structure is very similar to FeSC, but with higher electron count (0.5 e/Fe).

- Strong instability against nearest neighbor AFM (78 meV/Fe) and weaker instability against FM (44 meV/Fe). No instability for SDW type chain order → itinerant n.n. AFM
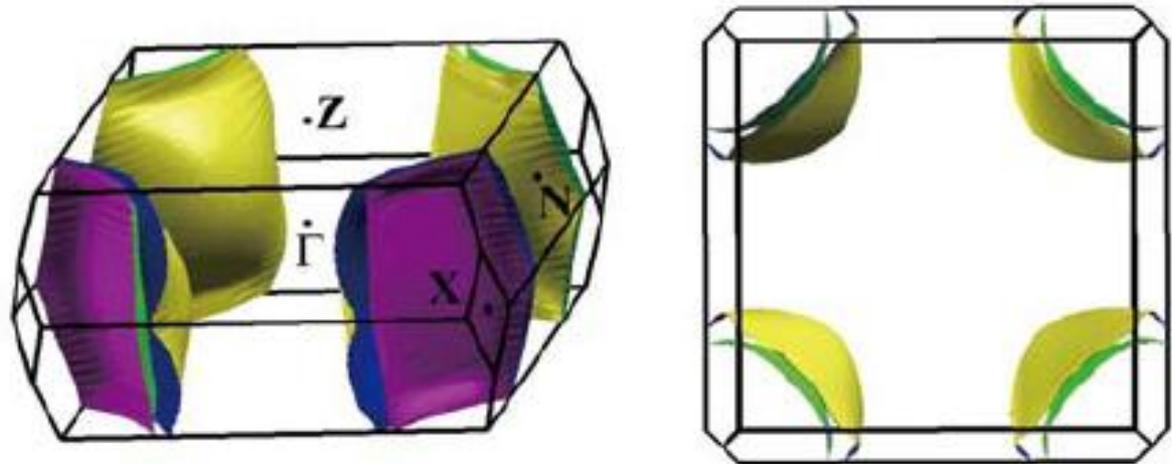
Non spin polarized Fermi surface

Competing Magnetic States

Competition between different magnetic states provides phase space for fluctuations and works against ordering.

SDW - c(2x2)   N.N (1x1)   (2x1)
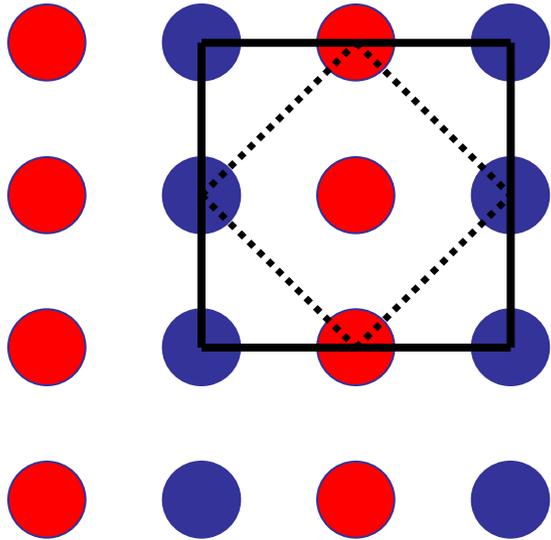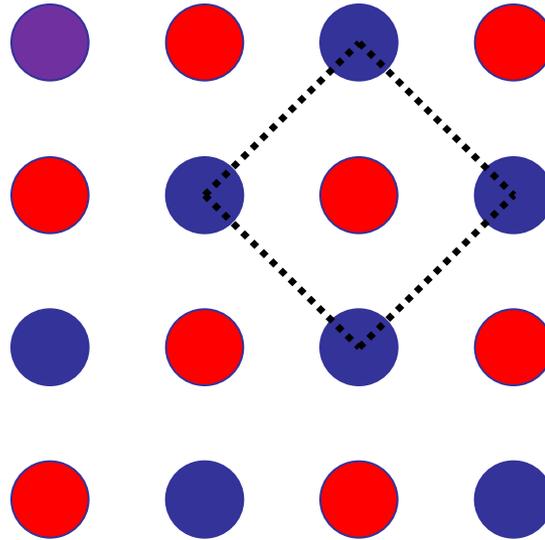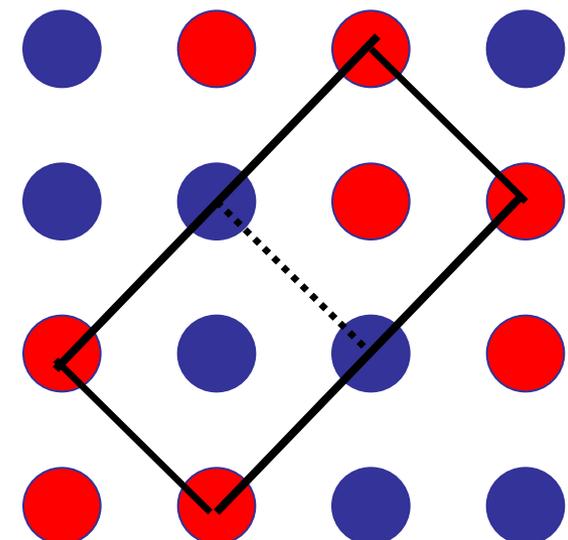
LaFeAsO $TlFe_2Se_2$ $Fe_{1+x}Te$

Possible Electron Doped Phase Diagram

T

Metal with strong spin fluctuations – competing magnetic orders.

Itinerant AFM Metal (n.n. ordering)

No competition from SDW

Suppressed SDW

Superconductor

0

Loss of nesting

0.5

Doping
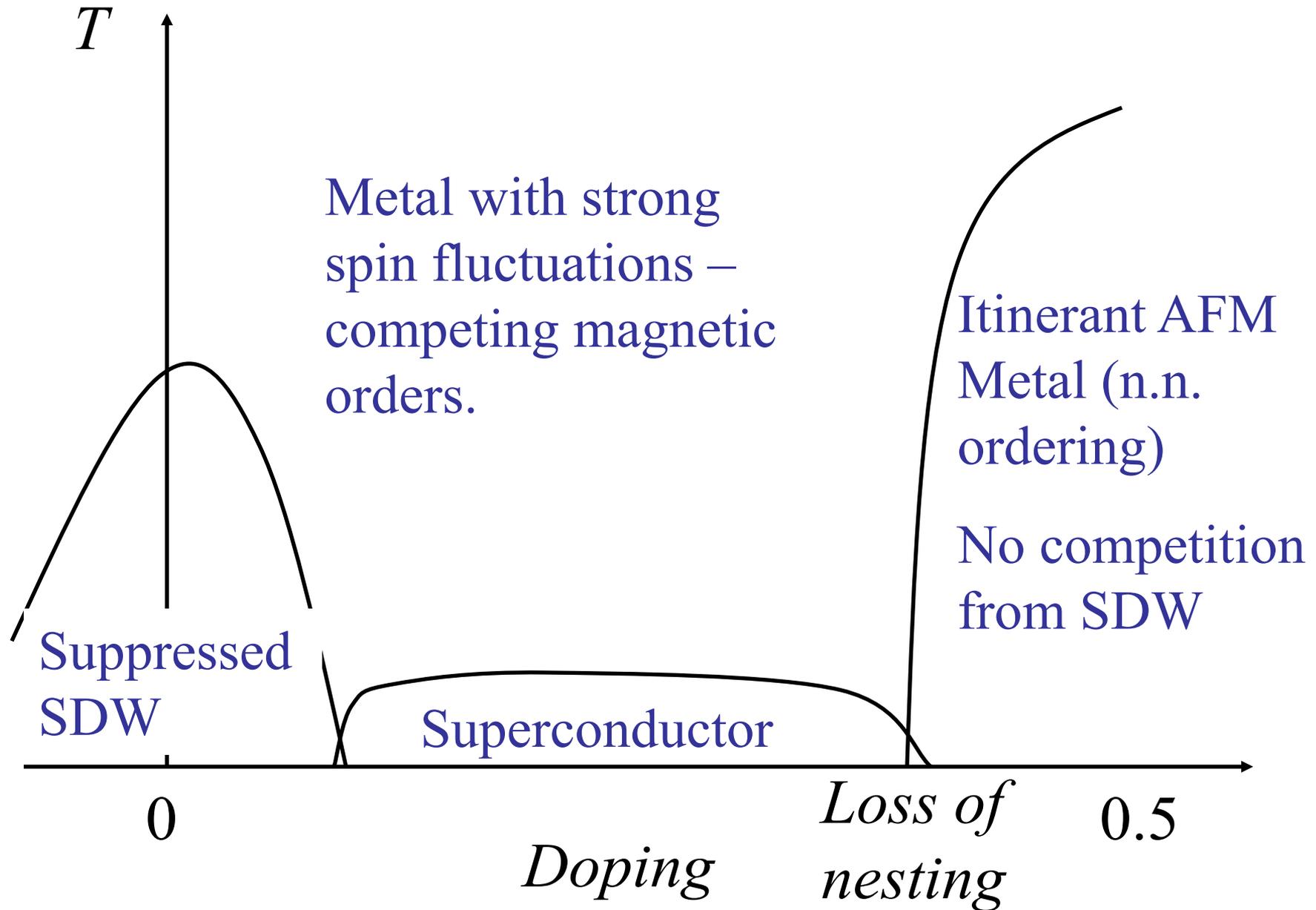
Conclusions

- Iron superconductors behave very differently from cuprates – perhaps a rather different mechanism or perhaps we need to look deeper for the connections.

- Strong renormalization of magnetic properties due to strong spin fluctuations – almost certainly necessary for understanding of the normal state and the superconductivity.

- Extended s-wave (+/-) state.

- Interesting interplay between magnetism and structure.

- *Competition between different magnetic states helps set up superconductivity as opposed to order magnetism in Fe-based superconductors and Ruthenates.*

Questions

- Can we identify materials with "strong" spin fluctuations and quantify "strong"?

- Can we identify competing magnetic states, even those with relatively weak q-dependence?

- Could we connect inelastic scattering with magnetic renormalization (fluctuation-dissipation)?

- Can we connect with transport experiments?

- Can we identify trends in magnetic behavior that would allow us to predict new superconductors, or ways to vary composition to improve superconductivity?

- …
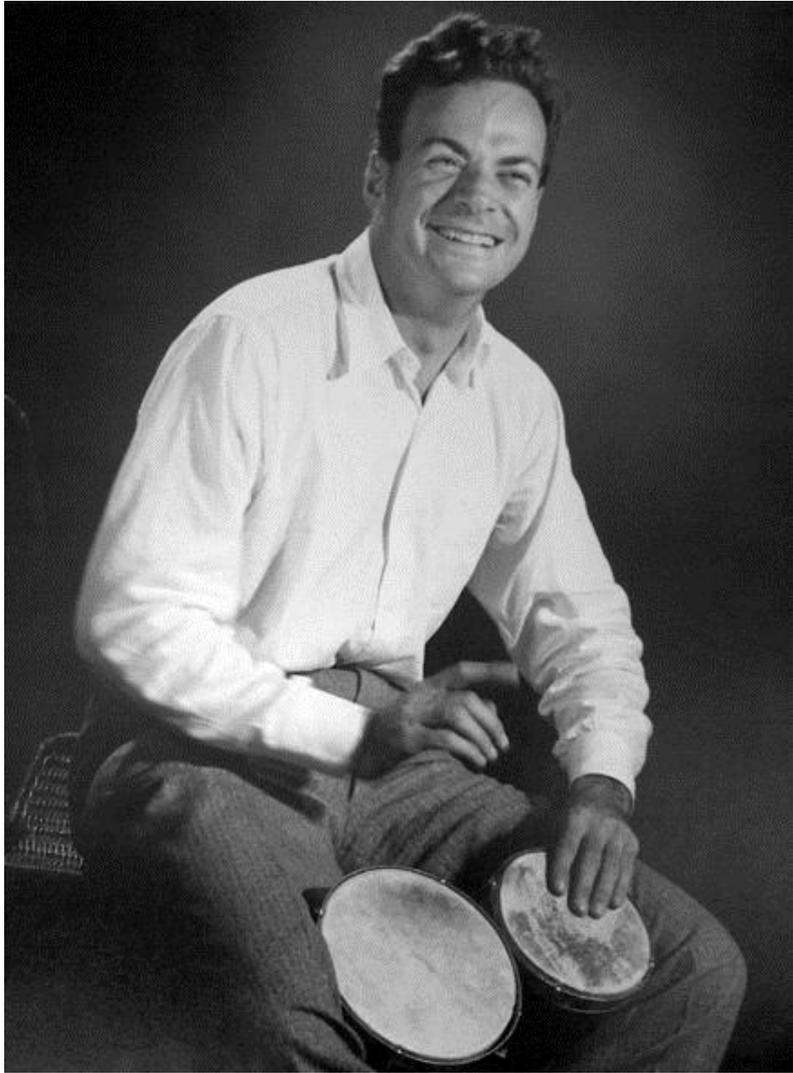
Hands On Science

SOME NUMBERS

Binding energy of Fe: 2541.025 Ry
bcc-fcc energy difference in Fe: 0.013 Ry (austenite-ferrite in steels)

Binding of PZT (Piezoelectrics): 46730.476 Ry
Ferroelectric instability in PZT: 0.006 Ry

Binding of Mn-ferrite (oxide mag.): 15987.192 Ry
Magnetic coupling of Mn-ferrite: 0.070 Ry

Small differences between very large energies are the keys to materials properties

➔ We rely on careful choice of numerical methods and error cancellation in the differences.

The Linearized Augmented Planewave (LAPW) Method

$$E_T[\rho] = T_s[\rho] + E_{ei}[\rho] + E_H[\rho] + E_{xc}[\rho] + E_{ii}$$

$$\{T_s + V_{ks}[\rho, r]\} \varphi_I(r) = \varepsilon_i \varphi_i(r)$$

Need tools that are reliable and predictive.

DFT ALGORITHMS

- Find φ_I and ρ to solve:

$$\{ T_s + V_{ks}[\rho, r] \} \varphi_I(r) = \varepsilon_i \varphi_i(r)$$

ρ^{in}

Compute V

↓

Find Eigenvectors

↓

Determine E_F

↓

Calculate ρ^{out}

↓

Converged? — No → Mix ρ^{out} ρ^{in}

Yes → Done
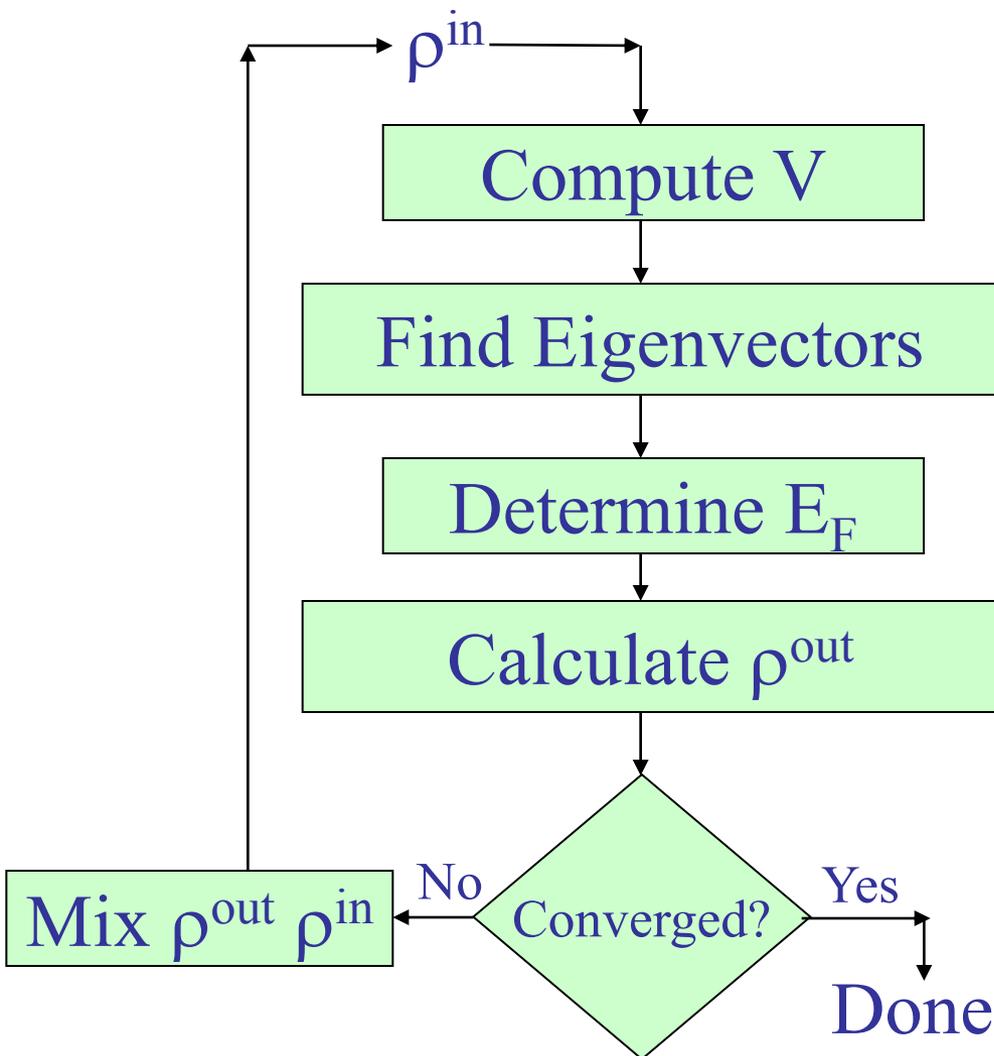
Standard Solution:

- Expand φ_I in a basis $\{\phi_j\}$.
- Many methods, PW, FE, LAPW, LMTO, LCAO ...
- For fixed V_{KS} get a linear algebra problem. (eigenvalue).

$$<\phi|H|\phi> x_i = \varepsilon_i <\phi|\phi> x_i$$

- Iterate to find self-consistent ρ.

Some Numbers:

- # φ_I ~ 10 / atom.
- # ϕ_j ~ 10's - 1000's / atom.
- # atoms (State of the Art): 100 – 1000's.

Motivation for Augmentation

Schrödinger Equation:

$$(T+V-\varepsilon)\varphi = 0$$

For valence states: ε is small ➜

Tφ is also small except where V is strong, i.e. near the nucleus.
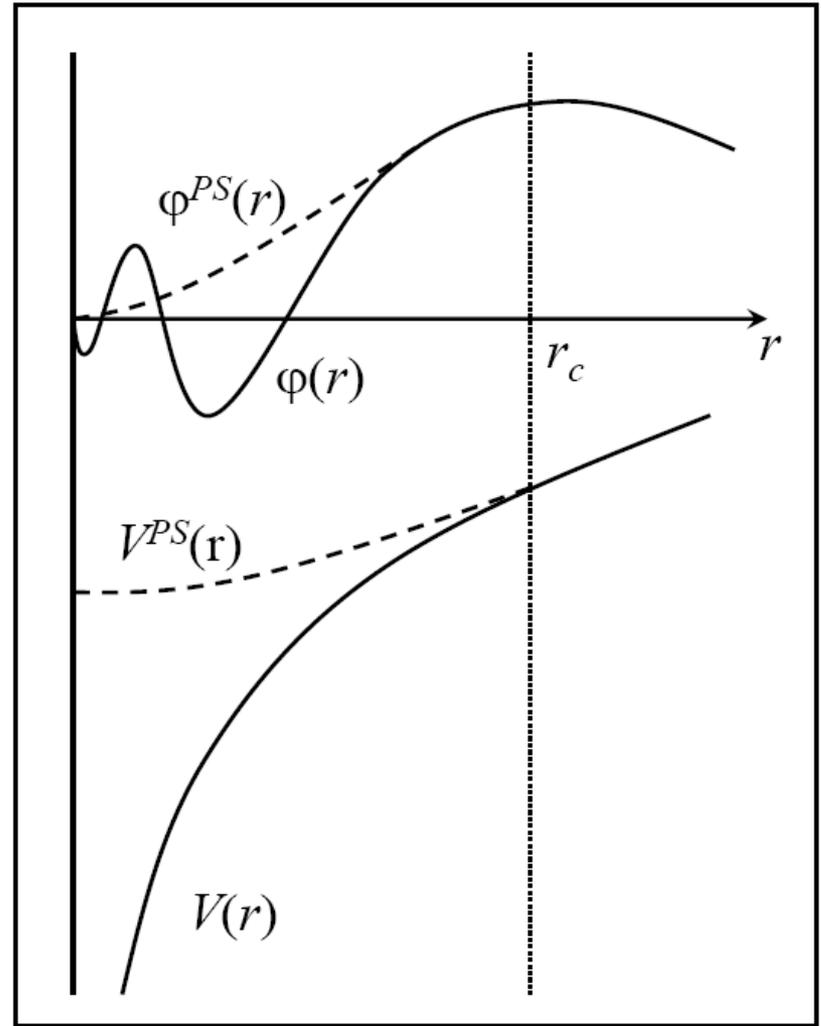
Augmented Planewave (APW) Method

- J.C. Slater, *Phys. Rev.* **51**, 846 (1937); *Phys. Rev.* **81**, 385 (1951).
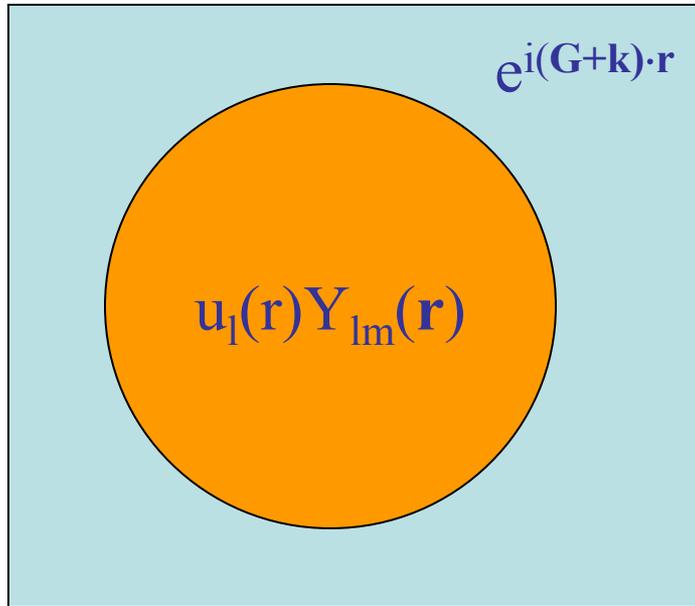
$e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$

$u_l(r)Y_{lm}(\mathbf{r})$

Divide Space Into 2 Regions:

- Atom Centered Spheres
- Interstitial

"Basis" Consists of Planewaves in the Interstitial and Radial Functions in the Spheres.

$$\varphi(\mathbf{r}) = \begin{cases} \Omega^{-1/2} \sum_{\mathbf{G}} c_{\mathbf{G}}\, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} & r \in \text{Interstitial (I)} \\ \sum_{lm} A_{lm}\, u_l(r)\, Y_{lm}(\mathbf{r}) & r \in \text{Sphere (S)} \end{cases}$$

- $u_l(r)$ are the radial solutions of Schrodinger's equation at the energy of interest (i.e. the band energy).

Augmented Planewave (APW) Method

$$\varphi(\mathbf{r}) = \begin{cases} \Omega^{-1/2} \sum_{\mathbf{G}} c_{\mathbf{G}} \, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} & r \in \text{Interstitial (I)} \\ \sum_{lm} A_{lm} \, u_l(r) \, Y_{lm}(\mathbf{r}) & r \in \text{Sphere (S)} \end{cases}$$

Key points:

1. The A_{lm} are not variational parameters. They are determined by a matching condition. That is the value of the basis functions, $\phi_{\mathbf{k}+\mathbf{G}}$ is fixed to be continuous at the sphere boundary.

2. The full crystal potential can be used because one may show that the u_l are orthogonal to "core" states.

$$[-d^2/dr^2 + l(l+1)/r^2 + V(r) - E_l] \, r u_l(r) = 0$$

So:

$$(E_2 - E_1) \, r \, u_1 u_2 = u_2 \, (d^2 r u_1/dr^2) - u_1 \, (d^2 r u_2/dr^2)$$

Integrate by parts to get overlap of u_1 *and* u_2. They are orthogonal if one of them is 0 on the sphere boundary.

Problems with the APW Method

1) Must solve secular equation for each energy band: prohibitive for many bands. No clear way to make full-potential.

2) Asymptote problem: cannot match at energies where $u(\mathrm{r})$ is zero on the sphere boundary. This will in general happen at some energy – particular problem for d and f band materials.

The Linearized Augmented Planewave (LAPW) Method

O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).

Key Ideas:

- The problem with the APW method is the energy dependence of the secular equation which is a result of the energy dependence of the augmenting function.

- Solution: Add variational freedom: particularly $\mathring{u}(r) = \partial u(r)/\partial E$.

$$\varphi(\mathbf{r}) = \begin{cases} \Omega^{-1/2} \sum_{\mathbf{G}} c_{\mathbf{G}}\, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} & r \in I \\[2ex] \sum_{lm} (A_{lm}\, u_l(r) + B_{lm}\, \mathring{u}_l(r))\, Y_{lm}(\mathbf{r}) & r \in S \end{cases}$$

- Where A_{lm} *and* B_{lm} are determined by matching the value and derivative of the basis functions at the sphere boundary.

THE LAPW METHOD

Results of adding $\mathring{u}_l$ to the basis:

1. Basis is flexible enough to use a single diagonalization (energy errors are now $O(\delta^4)$).

2. Must have additional matching conditions to connect both u and $\mathring{u}$ to the planewaves. This means that for a given level of convergence, more planewaves are needed.

3. The transferability also extends to variations in the potential: this enables full-potential methods.

The full potential, all electron, nature combined with the flexible basis (fully flexible in the interstitial) made the (F)LAPW method the state of the art for calculating electronic structures, especially for transition elements and their compounds – Many groups developed codes 1980 – present.

References

1. D.J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials and the LAPW Method* (Springer, 2005). **Details about the LAPW method, connection with pseudopotentials and inner workings of codes.**

2. O.K. Andersen, Phys. Rev. B **12**, 3060 (1975). **Formalism for the LAPW method.**

3. D. Singh, Phys. Rev. B **43**, 6388 (1991). **Local orbitals.**

4. E. Sjostedt, L. Nordstrom and D.J. Singh, Solid State Commun. **114**, 15 (2000). **APW+LO method.**

5. J.C. Slater, Phys. Rev. **51**, 846 (1937). **APW method.**

6. T.L. Loukes, *The Augmented Planewave Method* (Benjamin, 1967). **Details about APW implementation.**

The Elk FP-LAPW Code

An all-electron full-potential linearised augmented-plane wave (FP-LAPW) code with many advanced features. Written originally at Karl-Franzens-Universität Graz as a milestone of the EXCITING EU Research and Training Network, the code is designed to be as simple as possible so that new developments in the field of density functional theory (DFT) can be added quickly and reliably. The code is freely available under the GNU General Public License.

Latest version: 1.3.31

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http://elk.sourceforge.net/
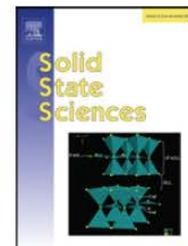
Superconducting-like behaviour of the layered Chalcogenides CuS and CuSe below 40 K

B. Raveau[*], Tapati Sarkar

Laboratoire CRISMAT, UMR 6509 CNRS ENSICAEN, 6 bd Maréchal Juin, 14050 CAEN, France

ARTICLE INFO

ABSTRACT

The investigation of strongly sintered "quasi molten" CuS and CuSe chalcogenides shows that they exhibit a sharp diamagnetic transition and a resistivity drop around 40 K. The reminiscence of such high temperature superconductivity features, never observed to date for these phases, is strongly supported by two chemical characteristics: bidimensionality of the structure and mixed valency of copper. The absence of zero resistance suggests that the internal chemical pressure in the samples has a key role in the existence of superconductivity: the S–S or Se–Se interlayer distances are very sensitive to the pressure, so that the critical distance for the percolation can be reached in the core of the samples, but not at the vicinity of the surface, where relaxation may appear.
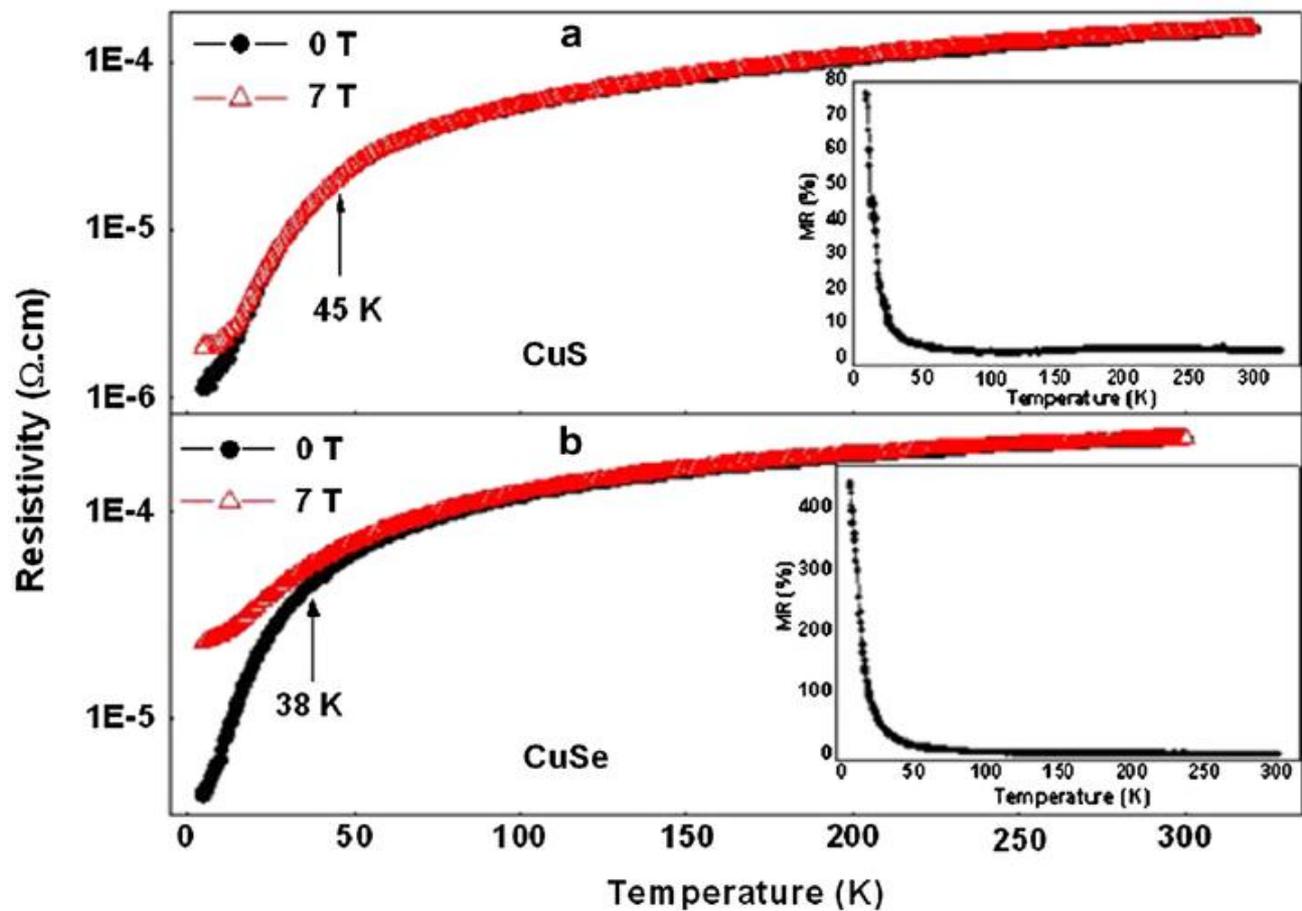
Fig. 3. Temperature dependence of resistivity of (a) CuS (sample 1) and (b) CuSe (sample 2) in the presence and absence of external magnetic field. The insets show the variation of the % MR as a function of temperature for the two samples.
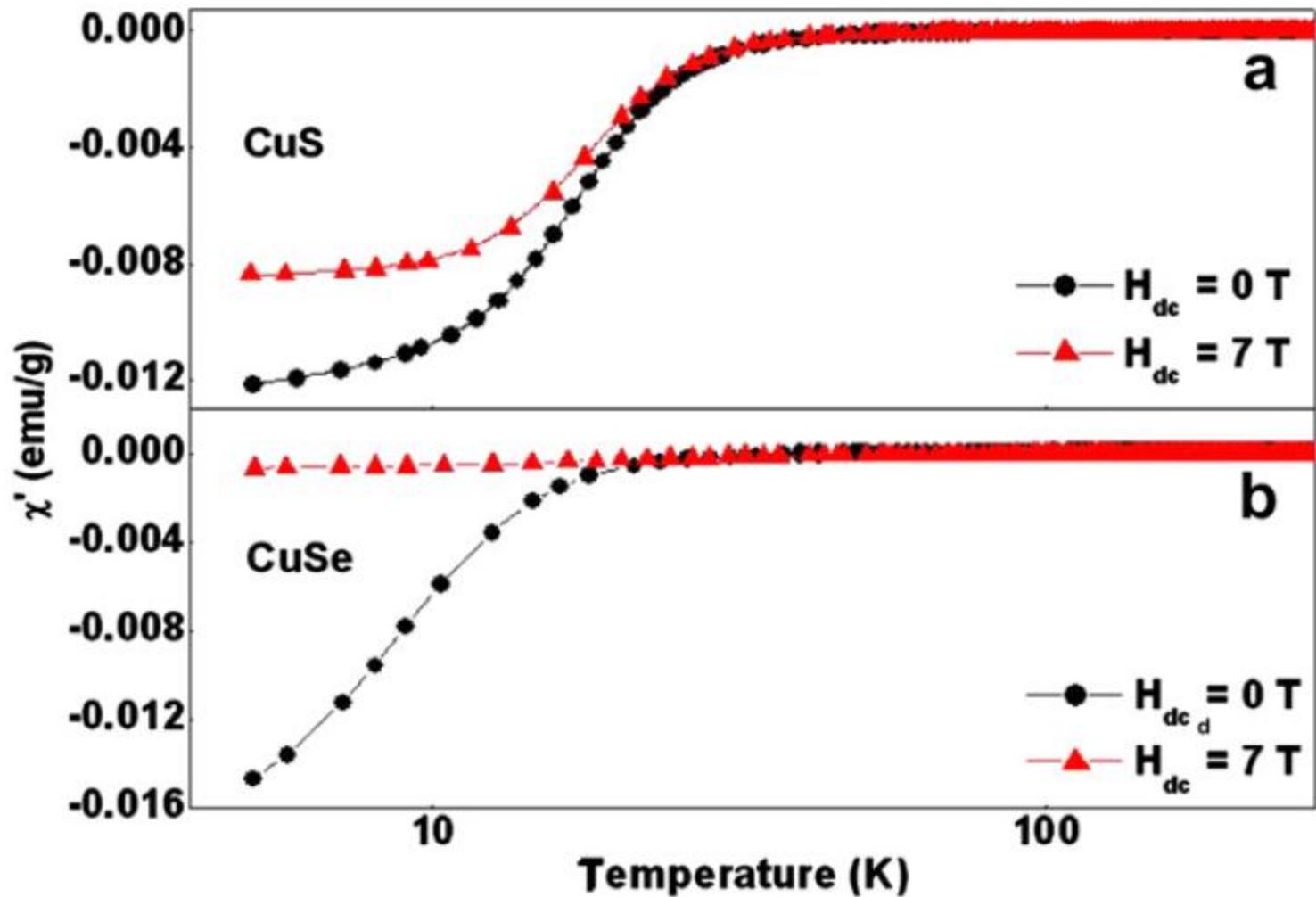
Fig. 2. Temperature dependence of a.c. magnetic susceptibility of (a) CuS (sample 1) and (b) CuSe (sample 2) measured in the presence of two different d.c. magnetic fields.

Structure of CuS
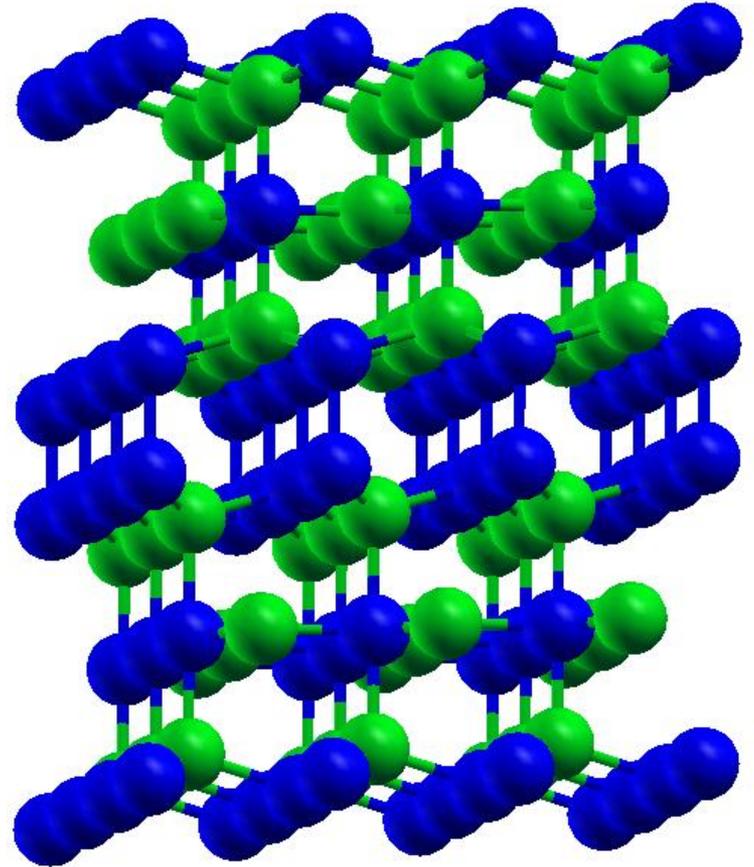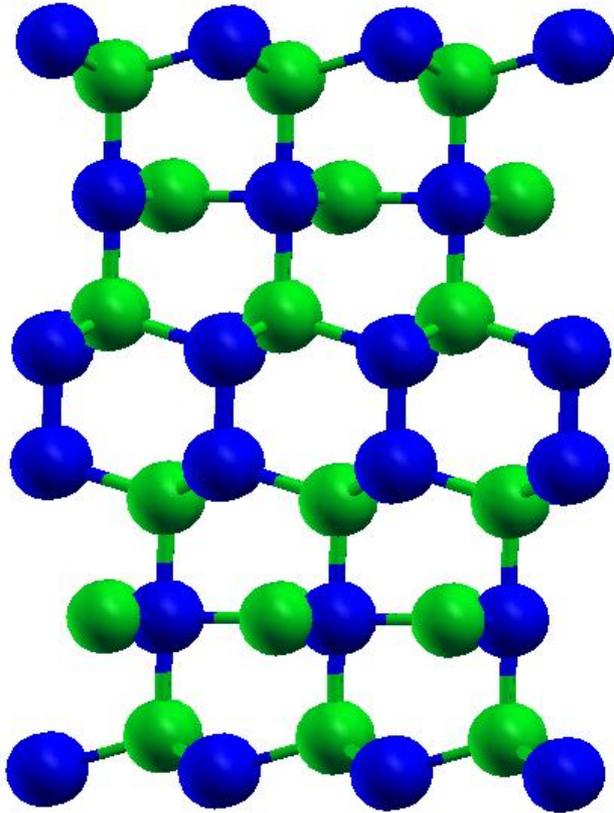
Experimental and theoretical investigation of the crystal structure of CuS

H J Gotsis†, A C Barnes‡§ and P Strange†

† Physics Department, Keele University, Keele, Staffs ST5 5BG, UK
‡ Neutron Division, Rutherford–Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

Abstract. The crystal structure of CuS has been confirmed experimentally using the powder diffraction method on the high-resolution powder diffractometer at the Rutherford–Appleton Laboratory. The observed crystal structure is $P6_3/mmc$. Standard density functional calculations on CuS on a variety of crystal structures are also reported. The calculations also predict $P6_3/mmc$ as the stable crystal structure. On the basis of the agreement between theory and experiment we are able to discuss the details of the bonding in this material.

Klockmannite, CuSe: structure, properties and phase stability from *ab initio* modeling

Victor Milman

Accelrys, The Quorum, Barnwell Road, Cambridge CB5 8RE, England

Correspondence e-mail: vmilman@accelrys.com

The details of the electronic and crystal structure, the nature of the interatomic bonding and the phase stability of three modifications of klockmannite, CuSe, are analysed using first principles modeling. The hexagonal modification of CuSe is predicted to be less stable than the orthorhombic phase under pressure. The stabilizing force for the orthorhombic phase is identified as the Cu—Cu bond formation between the Cu atoms in the flat hexagonal CuSe layer and in the buckled Cu_2Se_2 layer. Furthermore, klockmannite is shown to be unstable under compression with respect to the decomposition into umangite, Cu_3Se_2, and krutaite, $CuSe_2$ II.