New Superconducting Iron-oxypnictide
– First-principles Study of Parent Phase

By

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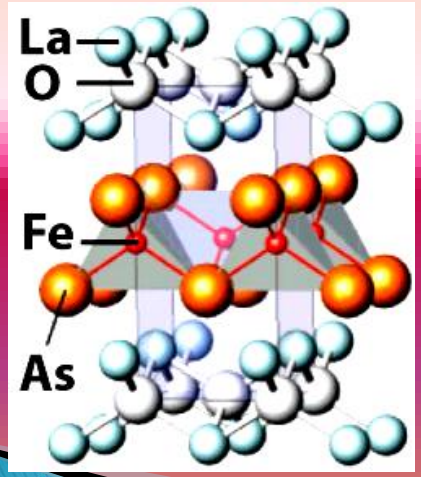


Superconductivity Research at CMP Lab, RU

- SCing materials research carried out at the CMP Lab at RU since 2001, the year of discovery of intermediate-T_c MgB_2:

  Materials: YBCO, $Ba_xK_{1-x}BiO_3$, Li, MgB_2, NbB_2, BeB_2, ZrB_2, TiB_2, TaB_2, AgB_2, AuB_2, SiH_4, SnH_4, GeH_4, BC_4, AlH_3, $LaO_{1-x}F_xFeAs$, $SmO_{1-x}F_xFeAs$ FeSe, $SrNi_2P_2$, Ta_4AlC_3 covering several interesting classes of SC.

Superconductor Classification

By their physical properties

- Type I superconductors: Just one T_c, changing abruptly from one state to the other.
- Type II superconductors: Two T_c --- T_{c1} and T_{c2}, being a perfect SC under T_{c1} & leaving completely the SCing state above T_{c2}, being in a mixed state when between both temperatures.

By the understanting we have about them

- Conventional SC: can be fully explained with the BCS or related theories.
- Unconventional SC: those that failed to be explained using such theories.

By their critical temperature

- LTS: with $T_c < 77K$.
- HTS: with $T_c > 77K$.

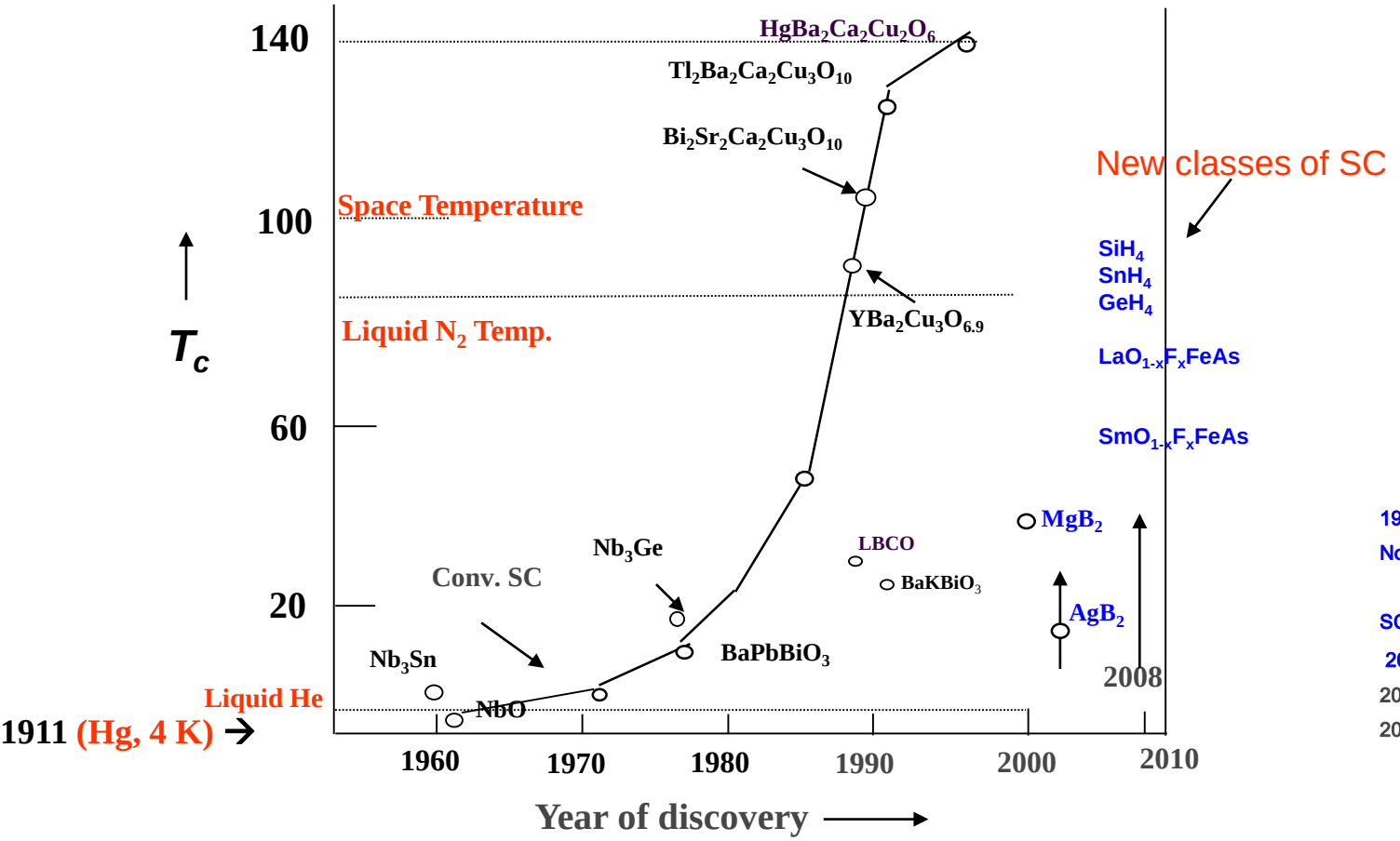
By material

- **Some pure elements,** such as Pb or Hg.
- **Some allotropes C :** such as fullerines, nanotubes, diamond or intercalated graphite.
- **Alloys** -- NbTi etc.
- **Ceramics**

  YBCO family: Especially $YBa_2Cu_3O_7$ - the most famous HTS.
- **MgB_2:** T_c ~39K, being the conventional SC with the highest known T_c.

300 => Room Temp. SC Necessary : Why? => Cooling cost

160 => Hg-Comp under Pressure



1911 to 1986 (75 yrs) : T_c rise 18 K

Nobel Prize 1987 : LBCO (30K) - G. Bednorz, Alex Mueller

SCy in Hg : 1911 (K.Onnes in Holland)

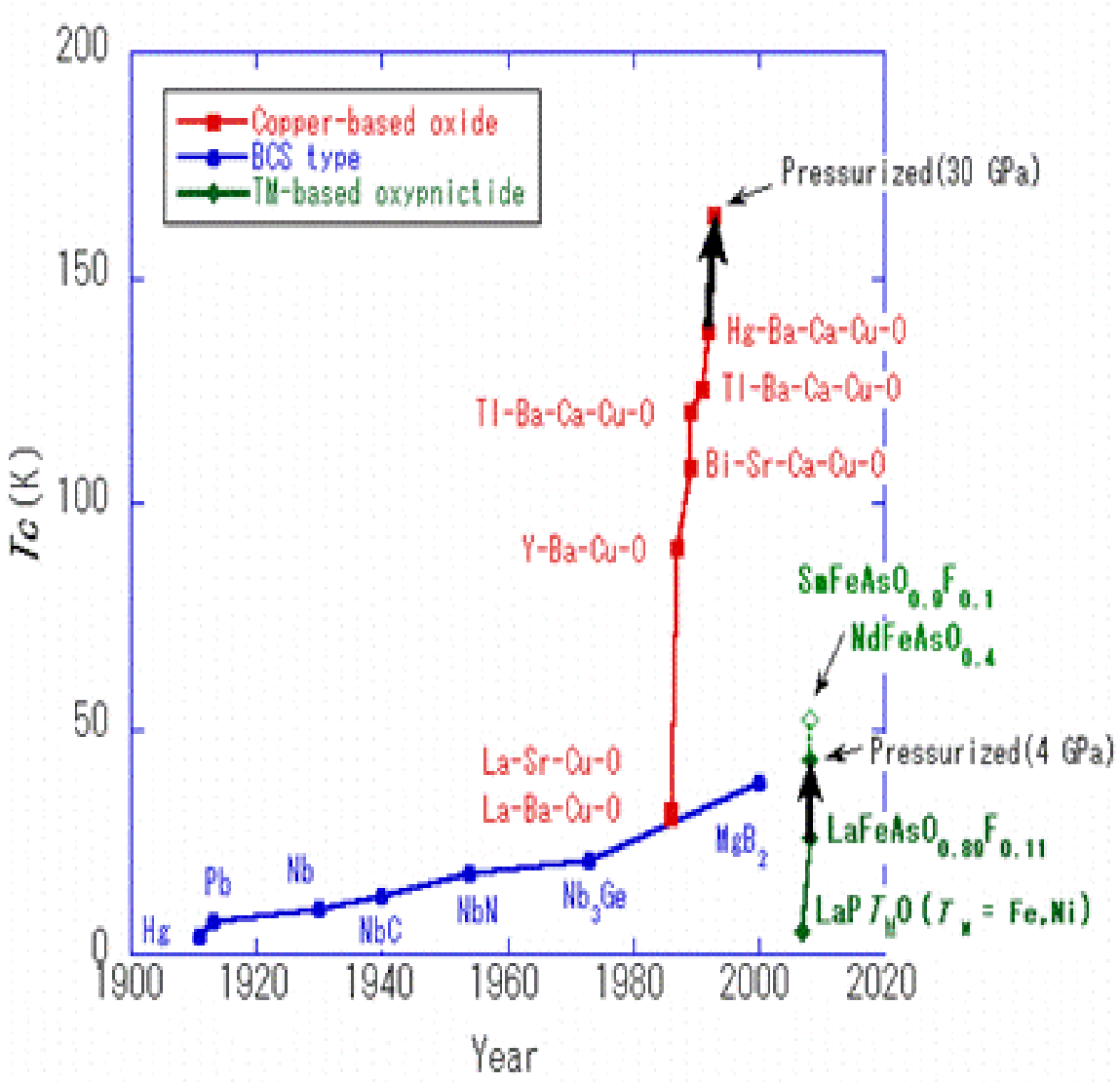
2001 : MgB_2 40 K (Japan)

2007 :

2008 :

Fig. Evolution of T_c vs Time

T_c vs Year


Copper-based oxide
BCS type
TM-based oxypnictide
Pressurized(30 GPa)
Hg-Ba-Ca-Cu-O
Tl-Ba-Ca-Cu-O
Tl-Ba-Ca-Cu-O
Bi-Sr-Ca-Cu-O
Y-Ba-Cu-O
SmFeAsO0.8F0.1
NdFeAsO0.4
Pressurized(4 GPa)
La-Sr-Cu-O
La-Ba-Cu-O
MgB2
LaFeAsO0.89F0.11
LaPTMO (TM = Fe,Ni)
Pb
Nb
Hg
NbC
NbN
Nb3Ge
Tc (K)
Year
200
150
100
50
0
1900
1920
1940
1960
1980
2000
2020

T_c	Materials	Class
138	$Hg_{12}Tl_3Ba_{30}Ca_{30}Cu_{45}O_{127}$	Copper-oxide superconductors 1986 →
110	$Bi_2Sr_2Ca_2Cu_3O_{10}$ (BSCCO)	
92	$YBa_2Cu_3O_7$ (YBCO)	
77	Boiling point of liq. N	
43	SmFeAs(O,F)	Iron-based superconductors 2008
41	CeFeAs(O,F)	
26	LaFeAs(O,F)	
40	MgB_2	Borides (2001)
18	Nb_3Sn	Metallic low-T_c superconductors 1911 →
10	NbTi	
4.2	Hg	

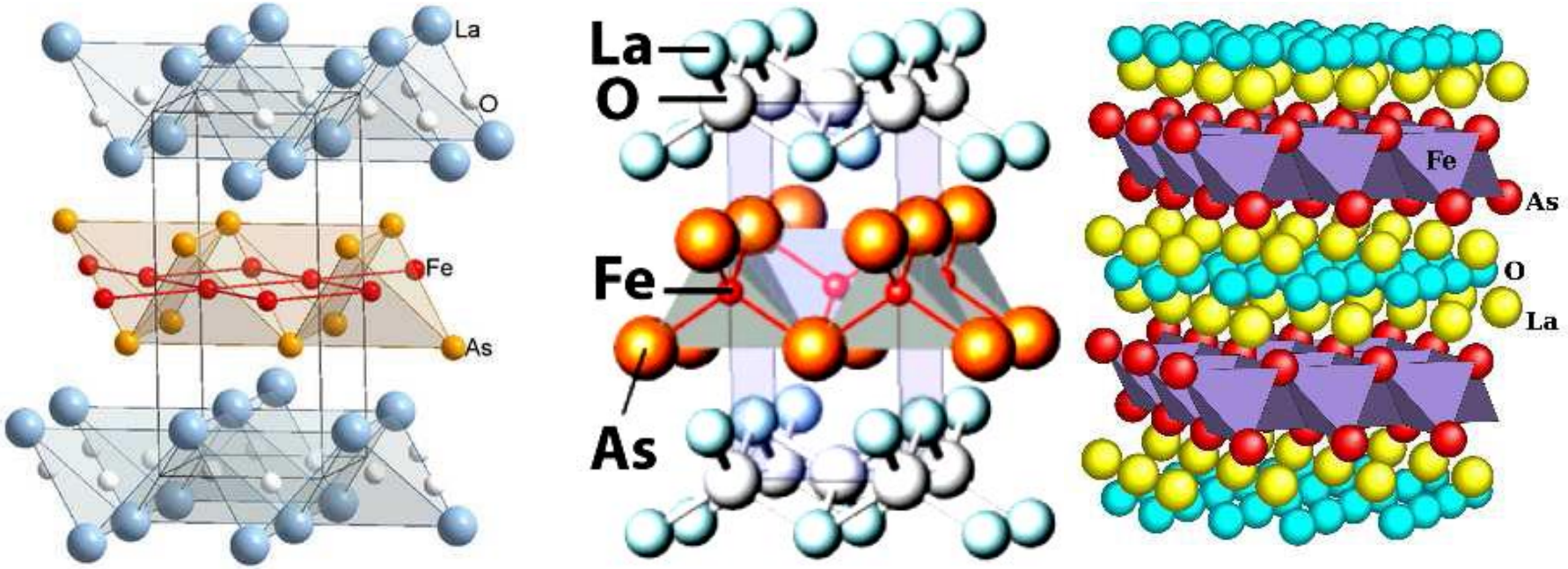
FeAs BASED SCs – NEW CLASS OF MATERIALS

- For the first time in years, a new class of HTS based on the parent compound LaOFeAs has been discovered in late Feb-08, prompting labs around the world to begin synthesizing variants with ever higher T_c.
- This newest family of HTS consists of layers of a F-doped RE-metal oxide sandwiched between layers of FeAs. These are:

  $LaO_{1-x}F_xFeAs$ (T_c= 26 K), $SmO_{1-x}F_xFeAs$ (55 K), $PrO_{1-x}F_xFeAs$ (52 K), $NdO_{1-x}F_xFeAs$ (51.9 K).

  Their structure is shown in Fig.

Crystal structure of LaOFeAs



- Fig. Two views of the tetragonal crystal structure of LaOFeAs compound. FeAs layers are formed by Fe ions tetrahedraly surrounded by As ions.
- Tetragonal Crystal Structure (a =4.035, c=8.741 A): Space group 129.

LaOFeAs

- The crystalline material LaOFeAs, stacks Fe & As layers (where the electrons flow) between planes of La and O.

  Ex: Nearly dried river & fountain from Hills

  [stack of alternating LaO and FeAs layers]

- La–O chemical bond in the (LaO) layer is ionic whereas Fe–As has a predominantly covalent nature. The conductive carriers are confined two dimensionally in the $(FeAs)^{-}$ layers, and their concentration can be increased by the substitution of the O^{2-} ions with F^{-} ions.

- Replacing up to 11% of O with F improved the compound — it became SCive at 26 K.

- New material has FeAs planes rather reminiscent of the CuO planes in the Cu-O SCs. It is quite unusual to have an iron-based SC, since ferromagnetic correlations are usually associated with destrying ordinary SCy. More exciting is the fact that this is not directly related to the cuprates & when doped with *e* (by replacing some of the O with F) it has a $T_c = 26$ K.

- Indications for higher T_c values of unconv. SC are on the way. 'It is believed that the layered structure of the cuprates, the ability of electrons to hop from Cu ion to Cu ion, & the shielding provided by Cu-free layers all contribute to the SCy. These materials also have a similar type of layered structure, are bad conductors before the transition, & exhibit antiferromagnetism.'

  Thus it is expected that they can offer new insights into a general mechanism(s) of HTS.

Importance of Studying Parent Compound

- Understanding of the ground state electronic & lattice dynamical properties of the parent compound is of paramount importance since the emergence of SCy on carrier doping (alternatively on suppression of SDW) must be related to the presence of various interactions in the undoped strongly correlated electronic material.

- Elastic constants, on the other hand, are related to the mechanical properties & are of considerable importance in view of future tech. applications.

- In this study we have performed first-principle DFT calc. of the electronic band structure, phonon dispersion, & the various independent elastic constants for the undoped LaOFeAs compound.

- We have analyzed the electronic band structure & the phonon spectrum & discussed the possible implications of these on the occurrence of SCy in the doped compounds.

COMPUTATIONAL METHODS

First-principles total *E* cals of the structural, elastic, electronic properties –

Based on GGA of DFT.

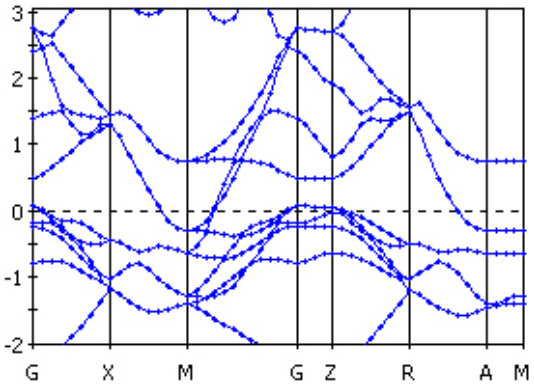
- Perdew-Burke-Ernzerhof (PBE) is used as exchange-correlation functional.
- Non-local ultra-soft pseudopotentials generated by the method of Vanderbilt are used to describe e-ion interactions.
- The valence electron wavefunctions are expanded in a plane wave basis set with e_{cut} ~ 300 eV. This converges E~ 1 meV/atom.
- BZ zone integrations are performed on a Monkhorst-Pack grid (taken large enough to reach a similar level of convergence in *E* as the wavefunction cut-off).

- The KE-cutoff controls no. of plane waves at given k.

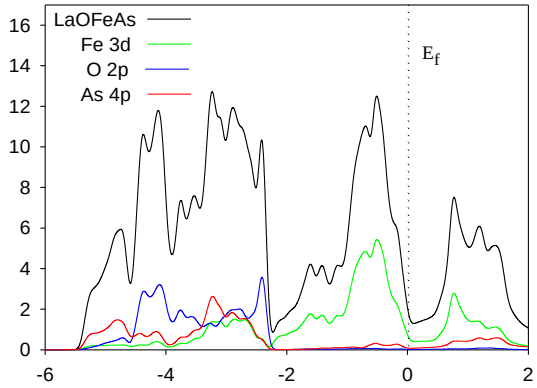
This is the single parameter which can have an enormous effect on the quality of the calc., basically the large ecut is, the better converged the calc is.

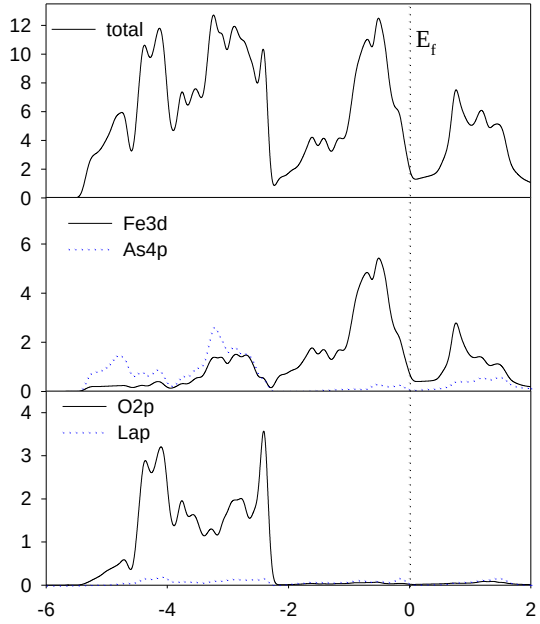
- Ultrasoft pseudopotentials attain much smoother (softer) pseudo-wave functions => so use considerably fewer plane-waves for calc of the same accuracy. **This is achieved by relaxing the norm-conservation constraint, which offers greater flexibility in the construction of the pseudo-wavefunctions.**

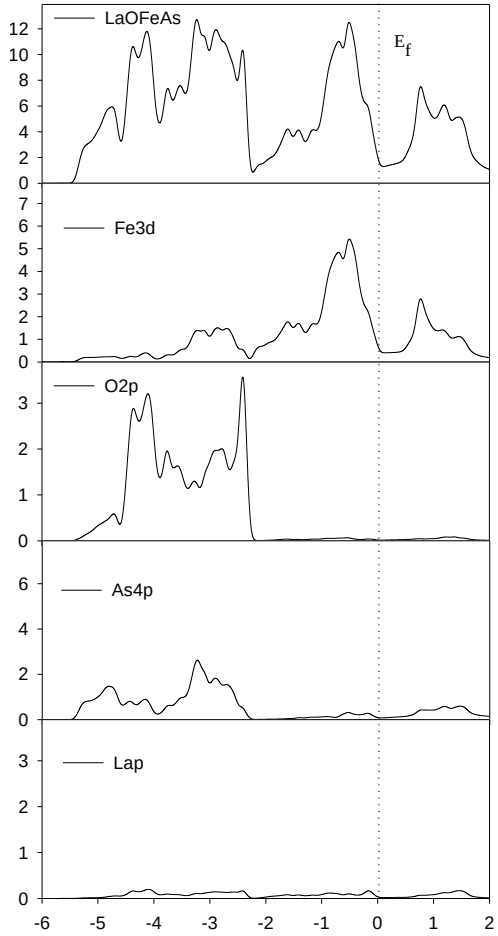
Band structure & DOS

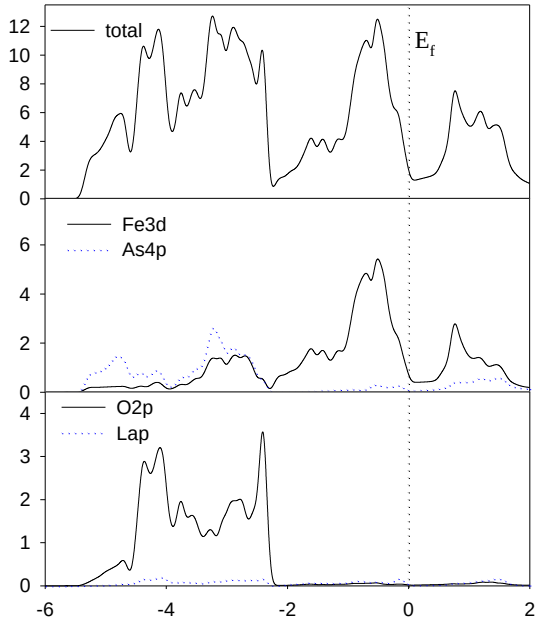


Band






LaOFeAs
E_f
Fe3d
O2p
As4p
Lap


total
E_f
Fe3d
As4p
O2p
Lap

Gross Features of the Band Structure

- Measuring energies from the Fermi level, O p and As p states form a group of 12 bands extending from −6 to −2 eV. La-f states are found at higher energies, at 2 eV.
- Apart from a weak hybridization of the t_{2g} states with As p states, at −3 eV, the ten Fe−d states are localized in an energy window extending ±2 eV around the Fermi level, where they give the dominant contribution to the DOS. The derived bands do not split simply into a lower eg (d_{x2-y2} and d_{3z2-1}) and higher t_{2g} manifold.
- Due to the presence of Fe-Fe directed bonds, $d_{x2\ -y2}$ orbitals, which lie along the bonds, create a pair of bonding-antibonding bands located at −2 and +1 eV. $d_{3z2\ -1}$ bands states split into two sub-bands. Due to the distortion of the Fe-As tetrahedra, d_{xy} states are inequivalent to d_{xz}, d_{yz} states, and the resulting the t_{2g} bands form a complicated structure centered at −0.5 eV.
- The Fermi level cuts the band structure in a region where the DOS is high (2.1 states/eV spin) and rapidly decreasing; a pseudo-gap opens in the electronic spectrum around 0.2 eV.

Total & Partial DOS:

- **The valence band (VB) includes two main subbands, where the high-energy subband (ranges from -5.5 to -2.2 eV below the Fermi level, E_F) comprises the contributions of Fe 3d, As 4p states (from [FeAs] layers) & O 2p and La p states (from [LaO] layers).**
- **The topmost region of the VB (ranges from -2.2 eV to E_F) is derived basically from Fe 3d states.**
- **We can conclude that in LaFeAsO**
- **(a) the electronic bands around the Fermi level are formed mainly by Fe 3d states of [Fe-As] layers, and these delocalized states are responsible for metallic-like Fe-Fe bonds;**
- **(b) the general bonding mechanism does not correspond to the "pure" ionic picture, rather it includes covalent interactions inside [LaO] & [FeAs] layers, as well as inter-layer [LaO]-[FeAs] interactions due to hybridization of As 4p - La p orbitals.**

Elastic Properties

==========
Elastic constants
(GPA)
==========

C_{11} = 218.5
C_{33} = 151.0
C_{44} = 63.8
C_{66} = 68.0
C_{12} = 75.5
C_{13} = 87.8

Bulk modulus = 118.35 ± 0.76 (GPa)

Compressibility = 0.00845 (1/GPa)

Axis	Young Modulus (GPa)	Poisson Ratios
X	163.94	E_{xy}= 0.1460 E_{xz}= 0.4963
Y	163.94	E_{yx}= 0.1460 E_{yz}= 0.4963
Z	98.60	E_{zx}= 0.2985 E_{zy}= 0.2985

Mechanical Stability

C_{ij} for polycrystalline material (GPa)

==========

		Voigt	Reuss	Hill
Bulk modulus	:	121.11	118.35	119.73
Shear modulus (Lame Mu)	:	61.59	58.75	60.17
Lame lambda	:	80.05	79.18	79.62

Magnetic Fluctuations Play Important Role in Mechanism for SCy in Iron-Pnictides

- Two materials, the cuprates (discovered in 1980), & the iron-based pnictides (2008), have been classified as unconv. SCs. In these materials, the mechanism for SCy is believed to be different to that of conv. SCs, such as Al in which lattice vibrations bind electrons into the so-called Cooper pairs that carry the supercurrent.
- Rather, in unconventional SCs, many theorists believe that magnetic fluctuations are needed to pair electrons into Cooper pairs.

- Muon team's measurements (UK & elsewhere) show that slow, magnetic fluctuations in $SmFeAsO_{1-x}F_x$ increase at or just above T_c. The main sources of these magnetic fluctuations are the spins on the Fe ion sites.
- Moreover, these fluctuations are largest near the SCing transtion.

- The results support the idea that Fe spin fluctuations play an active role in the pairing mechanism for SCy. It is already known, for example, that the T_c is lower in pnictide compounds where spin fluctuations are weaker.

Mechanism *contd.*

- High-T SCy in these layered iron compounds completely surprised investigators, who thought that the magnetic nature of iron would disrupt the pairing of electrons.
- Perhaps, as seems to be the case for cuprates, the electrons get paired with the aid of spin fluctuations—disturbances in the magnetic fields of atoms making up the superconductor.
- These Fe-based SCs could give us new hints on how to understand cuprates.

μSR measurement

- In a μSR measurement, a beam of muons–charged particles, such as protons, that carry a net spin impinges on the sample.
- The muon beam is prepared so that all of the muon spins are pointing in the same direction, but when the muons experience the field associated with any magnetism in the sample, their spins begin to depolarize.
- Specialized detectors can tell the final spin direction of the muon and from that, determine the local magnetic properties of the sample and how these properties evolve with time.

Thank you


YAMANASHI
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