The Puzzle of Superconductivity at $T_c \approx 22$ K in Ba(or Sr)Fe_2As_2 Exposed to *Reactive Gases*

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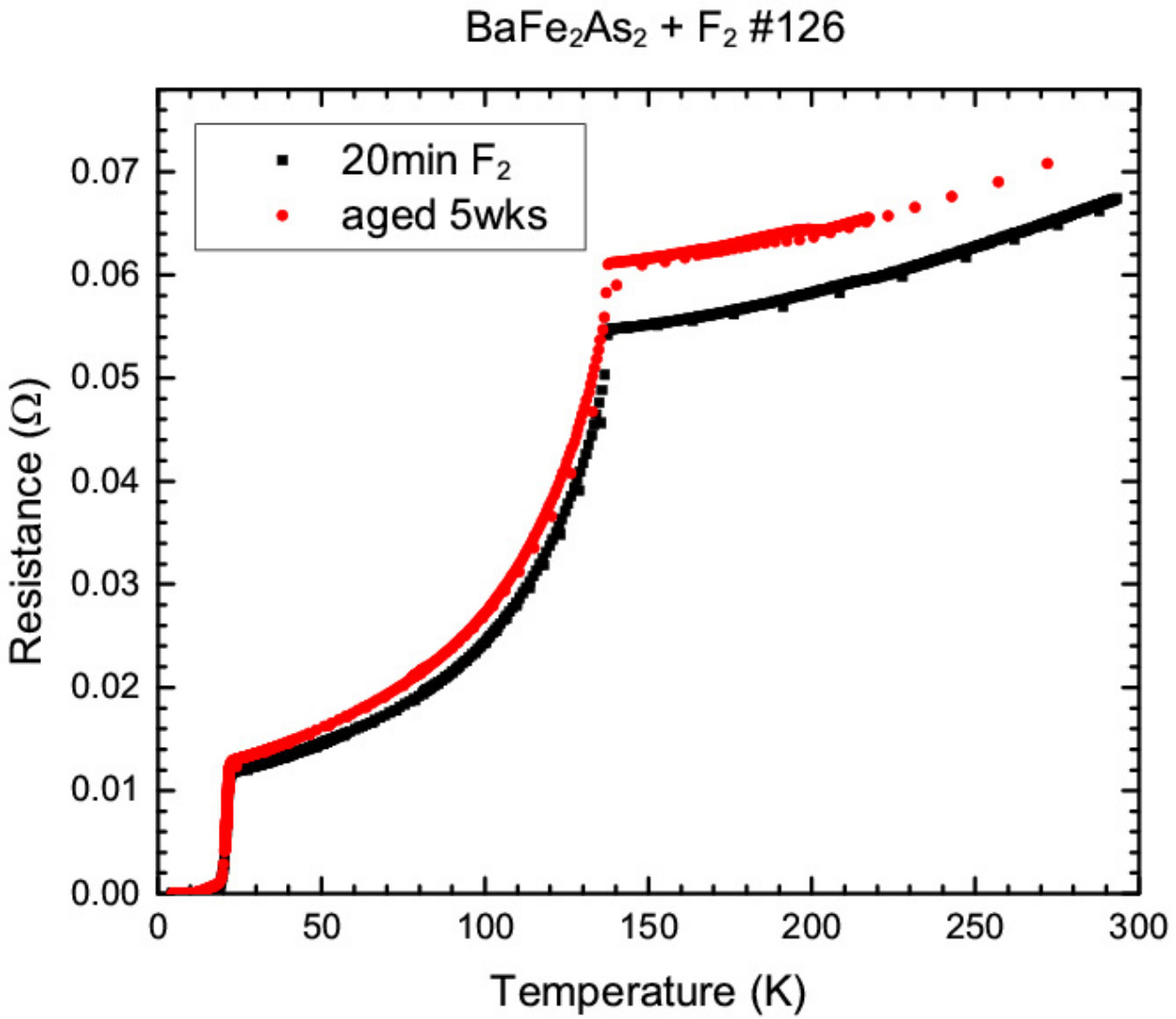
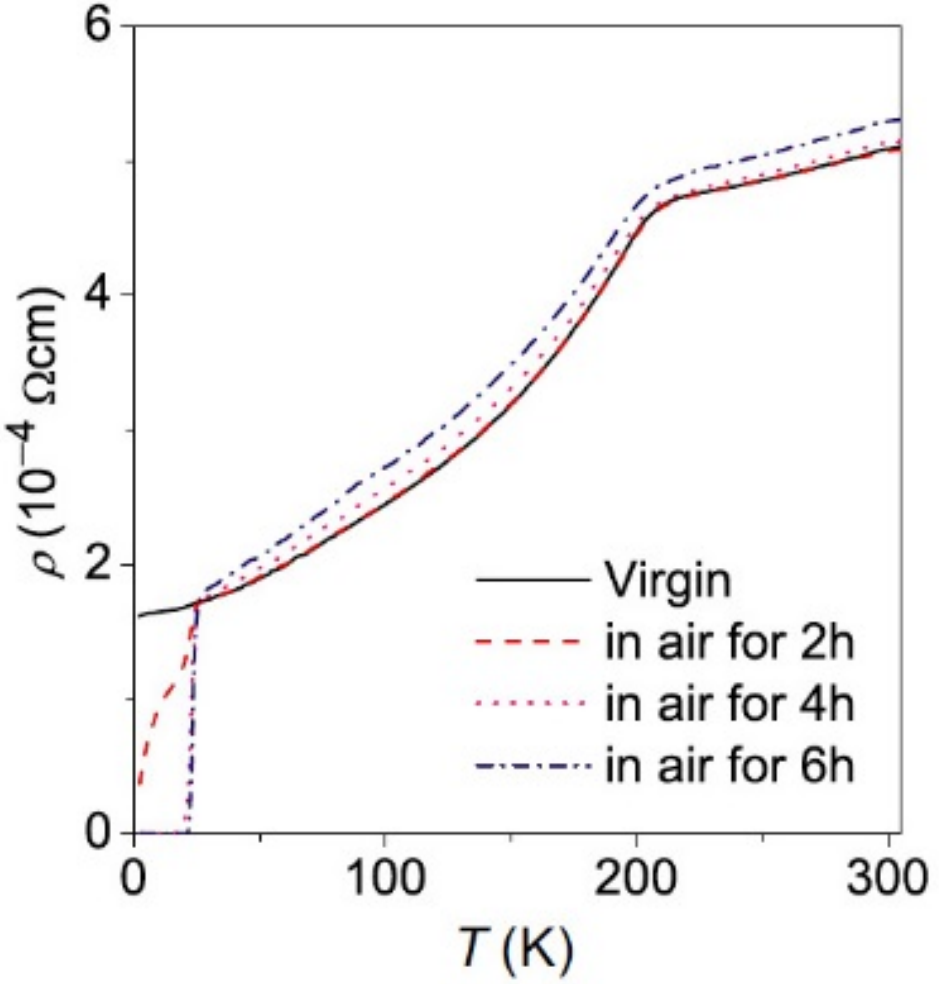
Just to set the stage, $BaFe_2As_2$ exposed to several reactive gases, including fluorine, shows a resistive transition to superconductivity at just over 20 K. This talk is about why?



This Behavior ($T_c \approx 22$ K) Was First Observed[1] in Resistive Measurements of Thin Films of $SrFe_2As_2$ Exposed to *Water Vapor*



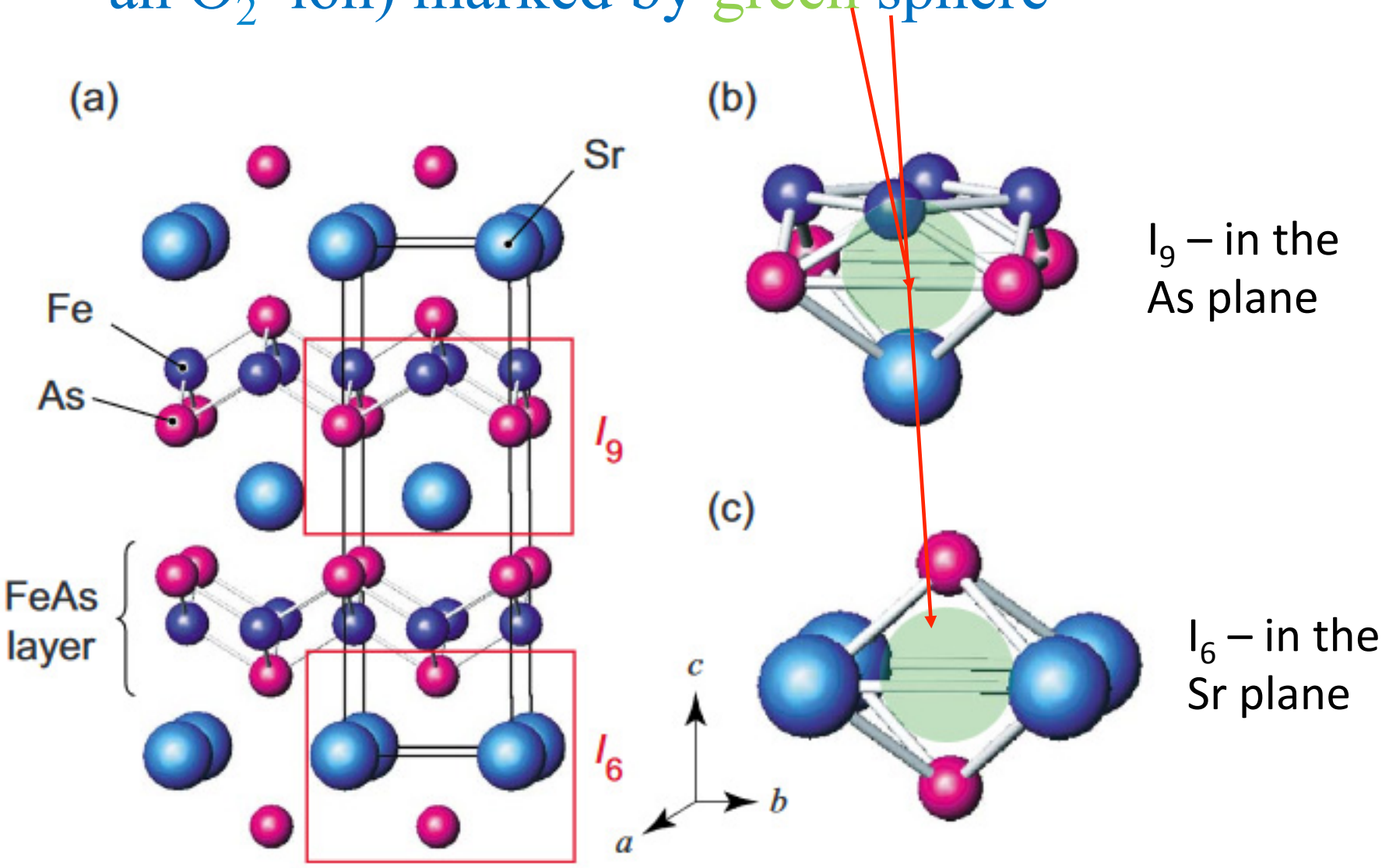
1. H. Hiramatsu, T. Katase, T. Kamiya, M. Hirano and H. Hosono, Phys. Rev. B 80, 052501 (2009). (47 citations to date)

This Behavior ($T_c \approx 22$ K) Was First Observed[1] in Resistive Measurements of Thin Films of $SrFe_2As_2$ Exposed to *Water Vapor*

- Upon exposure to water vapor they measured a decrease in the c-axis lattice parameter. They considered possible intercalation of O_2^- into interstitial sites.

1. H. Hiramatsu, T. Katase, T. Kamiya, M. Hirano and H. Hosono, Phys. Rev. B 80, 052501 (2009). (47 citations to date)

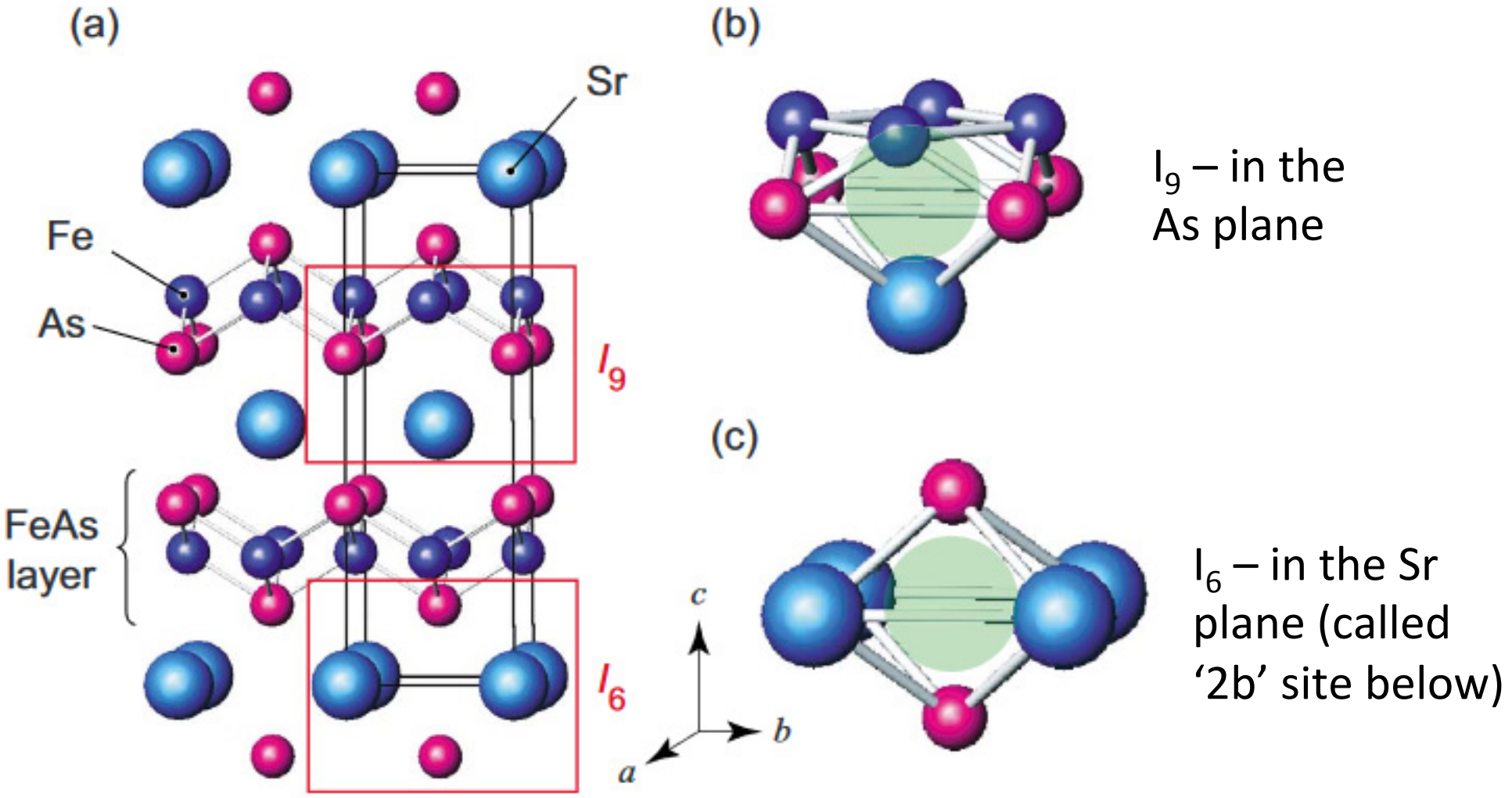
In $SrFe_2As_2$: 2 large interstitial sites (both large enough to hold an O_2^- ion) marked by green sphere



l_9 – in the As plane

l_6 – in the Sr plane

Rather than interstitial doping, Hiramatsu, et al. also considered the possibility of creation of Sr vacancies through a reaction with the H_2O molecule to form an alkaline earth hydroxide $Sr(OH)_2$. (Remember this for later)



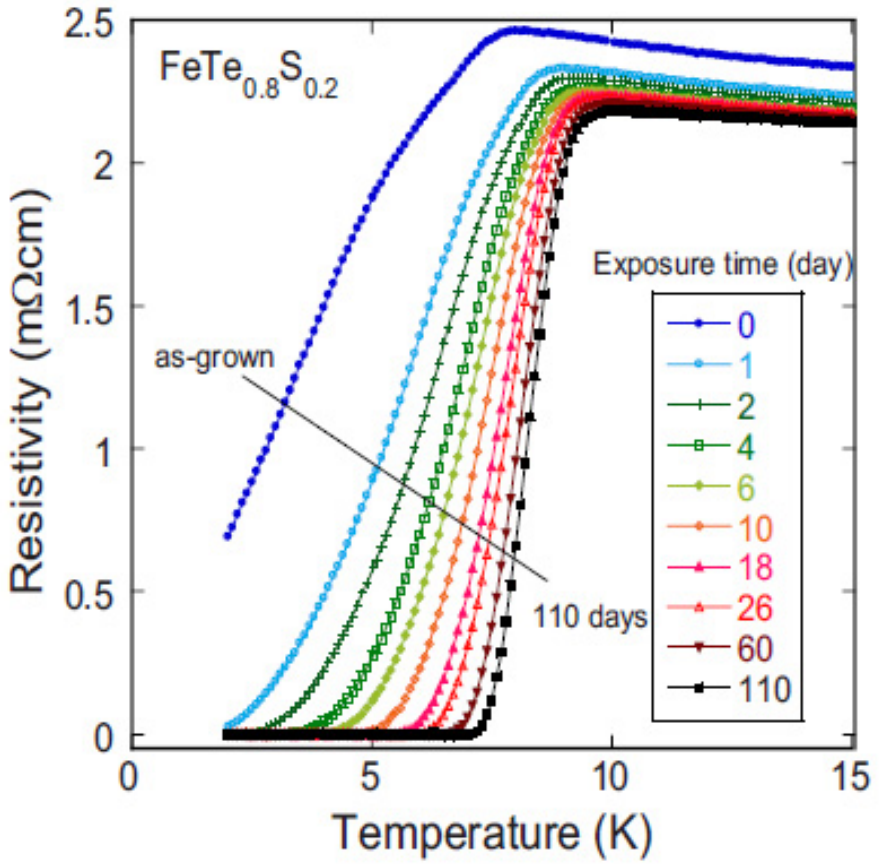
I_9 – in the As plane

I_6 – in the Sr plane (called '2b' site below)

Works Related to the Hiramatsu et al. $SrFe_2As_2$ + Water Vapor Work:

- Y. Mizuguchi, K. Deguchi, S. Tsuda, T. Yamaguchi, and Y. Takano, Phys. Rev. B 81, 214510 (2010)

- induced superconductivity in $Fe_{0.8}Te_{0.2}S_{0.2}$ (just like $SrFe_2As_2$ also normally not superconducting) by exposure to air containing water vapor. Speed of evolution of T_c with time "strongly enhanced" by immersion in 70 °C water. Up to 48% diamagnetic shielding.

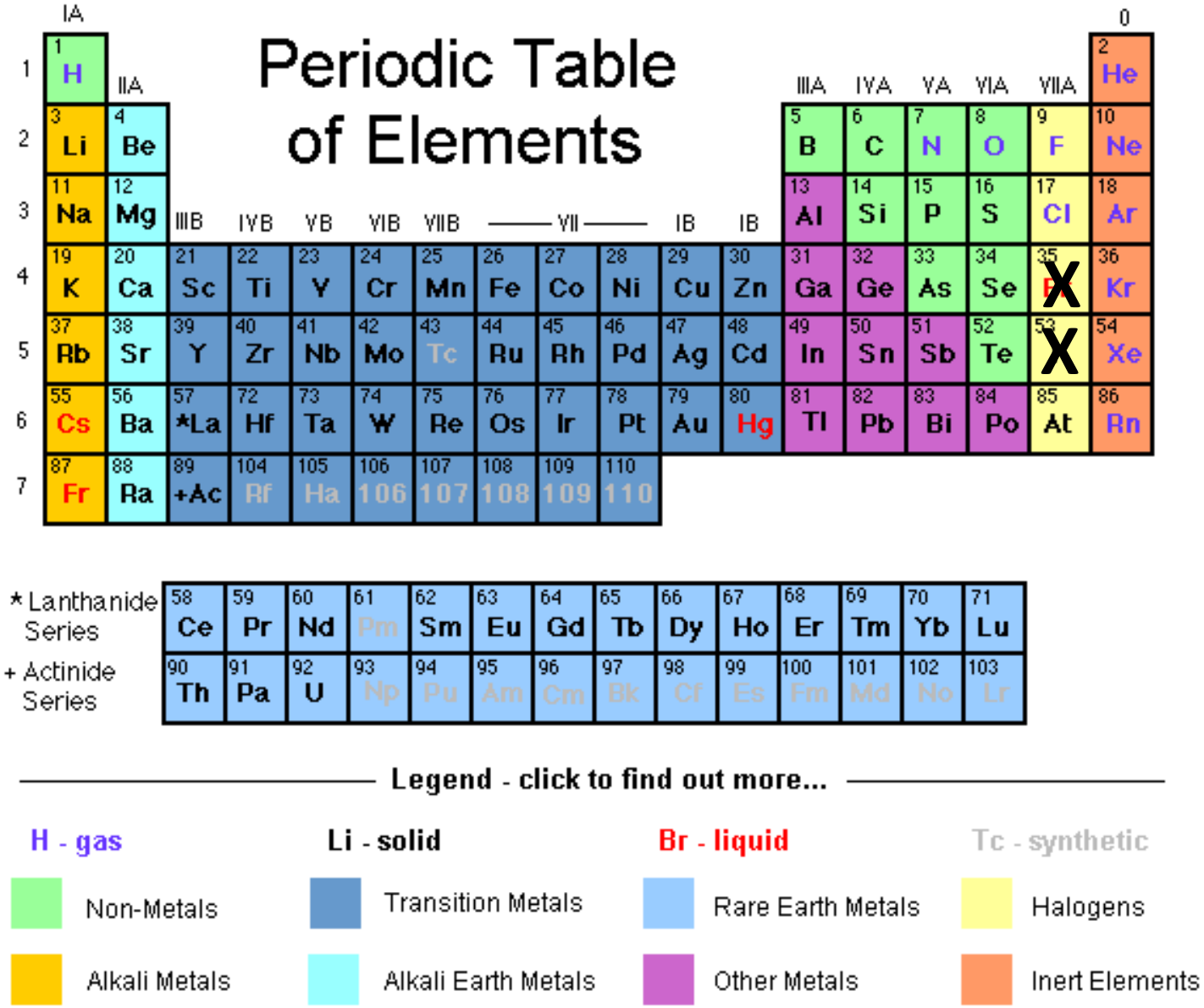


- cause of superconductivity: since the lattice shrinks, they consider H^+, OH^- and O_2^- as possible electron dopants. No microscopic data (e. g. XAFS) to corroborate.

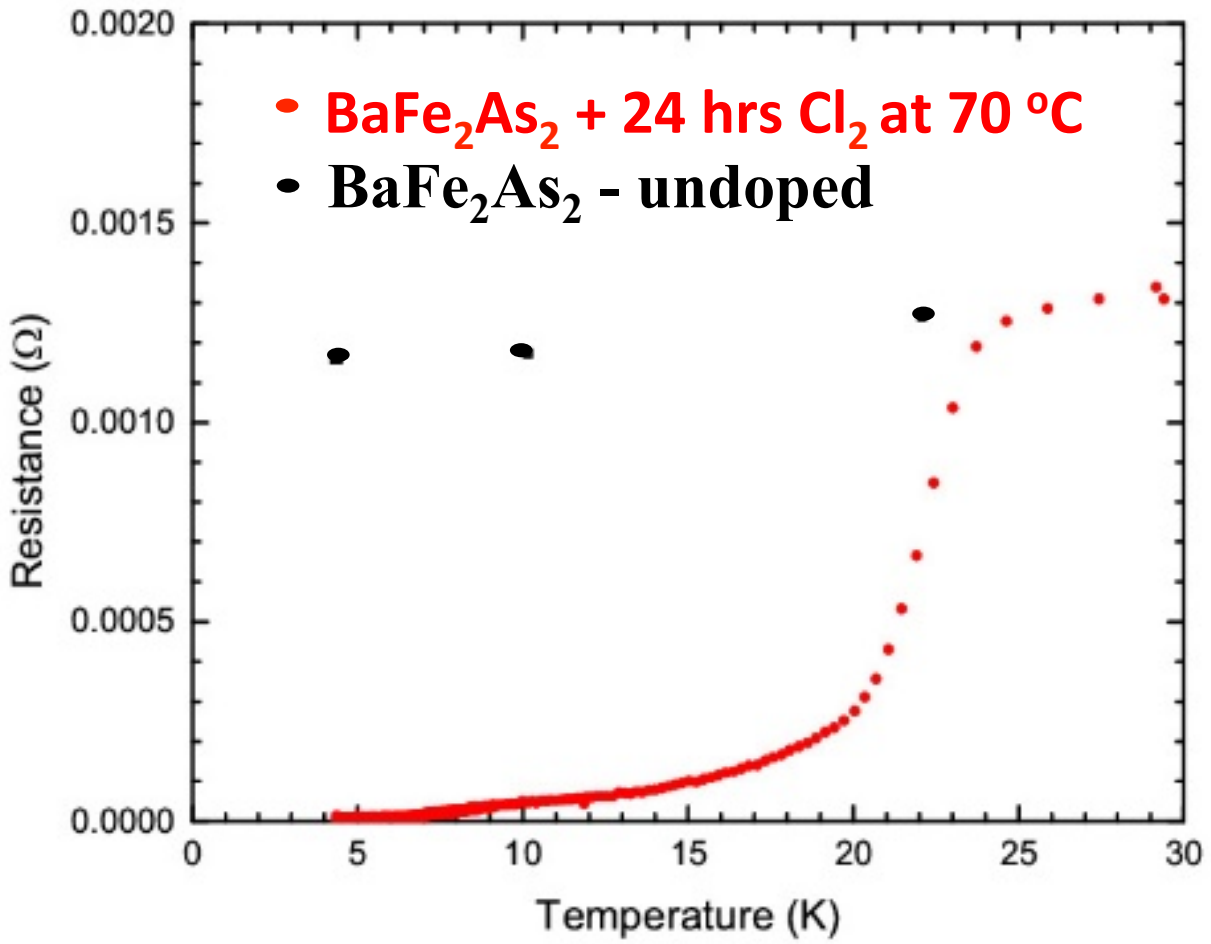
Works Related to the Hiramatsu et al. $SrFe_2As_2$ + Water Vapor Work:

- In a follow up paper (Deguchi et al., Supercond. Sci. Technol. 25, 084025 (2012)) correlated the presence of various acids in the liquids with superconductivity and suggested that – rather than electron doping – perhaps the cause of the superconductivity was removal of excess Fe from interlayer sites (not really germane to work on $(Sr,Ba)Fe_2As_2$.)

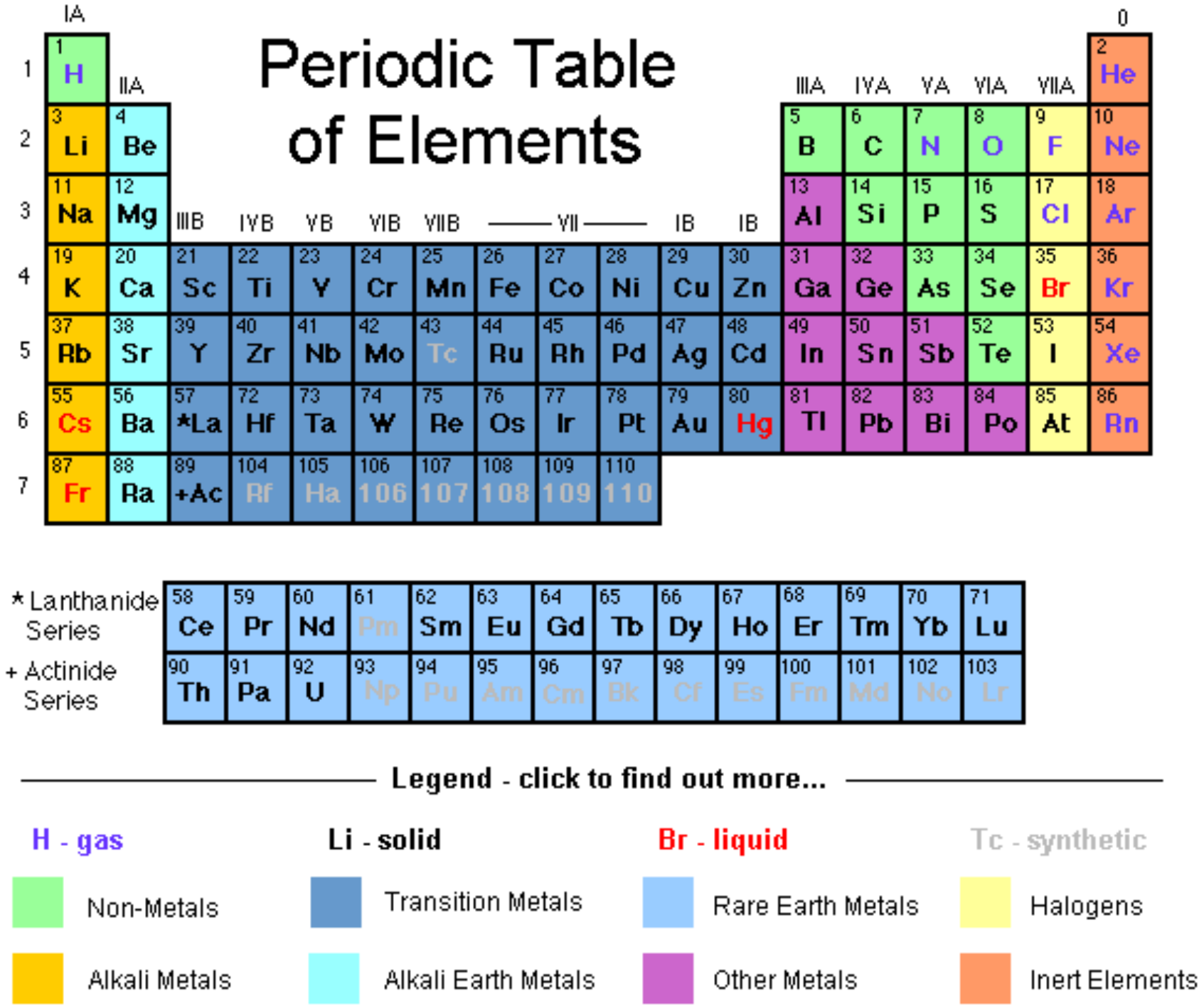
So, the question arises, what else could be reacted with the 122 $(Sr,Ba)Fe_2As_2$ compounds to investigate this ~22 K superconductivity?



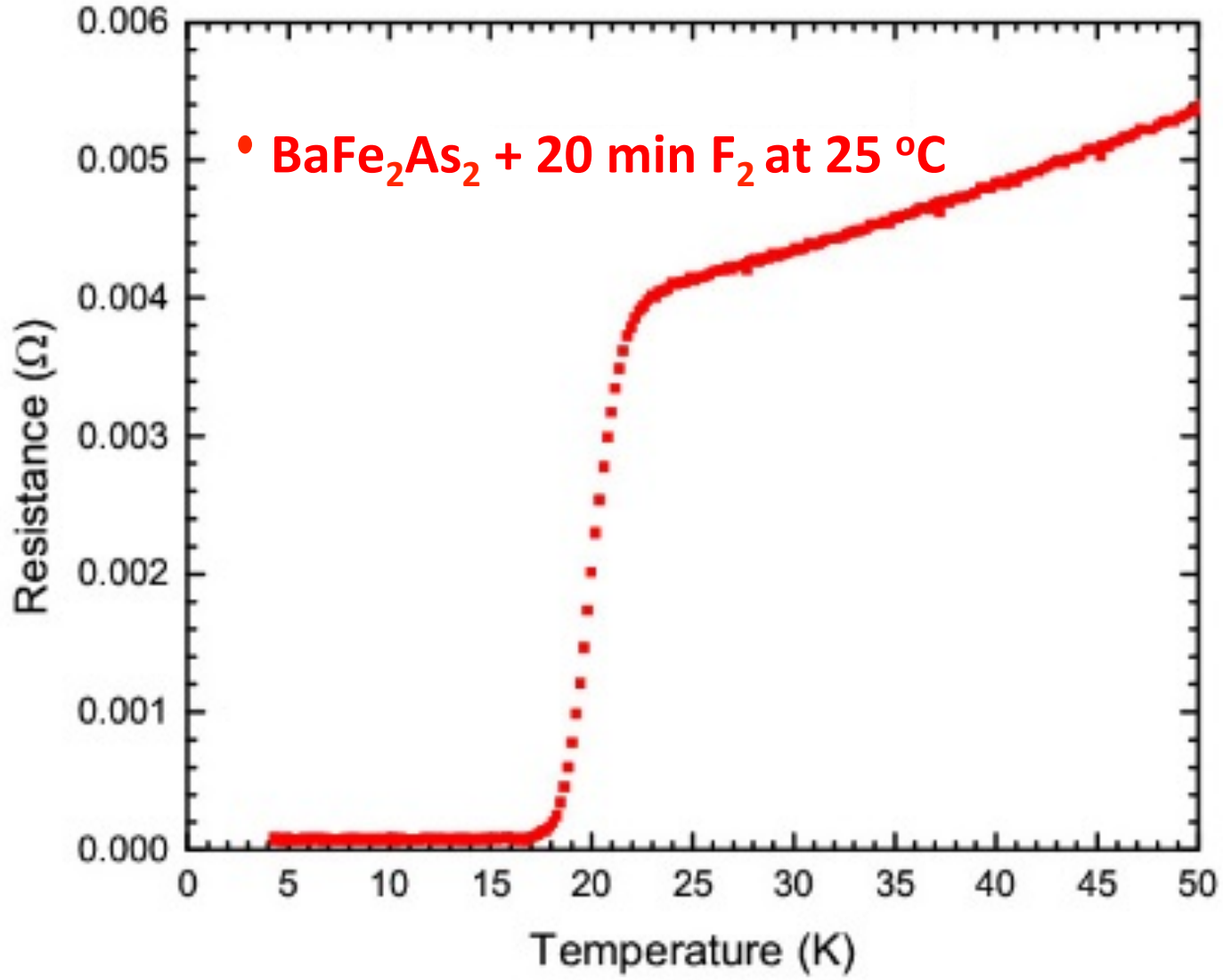
$T_c \approx 22$ K in $BaFe_2As_2$ Exposed to Cl_2 (our work)



Note that $\rho \rightarrow 0$ is quite broad


Periodic Table of Elements
IA
IIA
IIIB
IVB
VB
VIB
VIIB
VII
IB
IB
IIIA
IVA
VA
VIA
VIIA
0
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
57 *La
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
89 +Ac
104 Rf
105 Ha
106 106
107 107
108 108
109 109
110 110
* Lanthanide Series
58 Ce
59 Pr
60 Nd
61 Pm
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu
+ Actinide Series
90 Th
91 Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100 Fm
101 Md
102 No
103 Lr
Legend - click to find out more...
H - gas
Li - solid
Br - liquid
Tc - synthetic
Non-Metals
Transition Metals
Rare Earth Metals
Halogens
Alkali Metals
Alkali Earth Metals
Other Metals
Inert Elements

$T_c \approx 22$ K in $BaFe_2As_2$ Exposed to F_2



Note that $\rho \rightarrow 0$ is fairly narrow. Note also the large amount of work* on this effect in 'as-prepared' xtals.

*e. g. Paglione et al. as well as our group

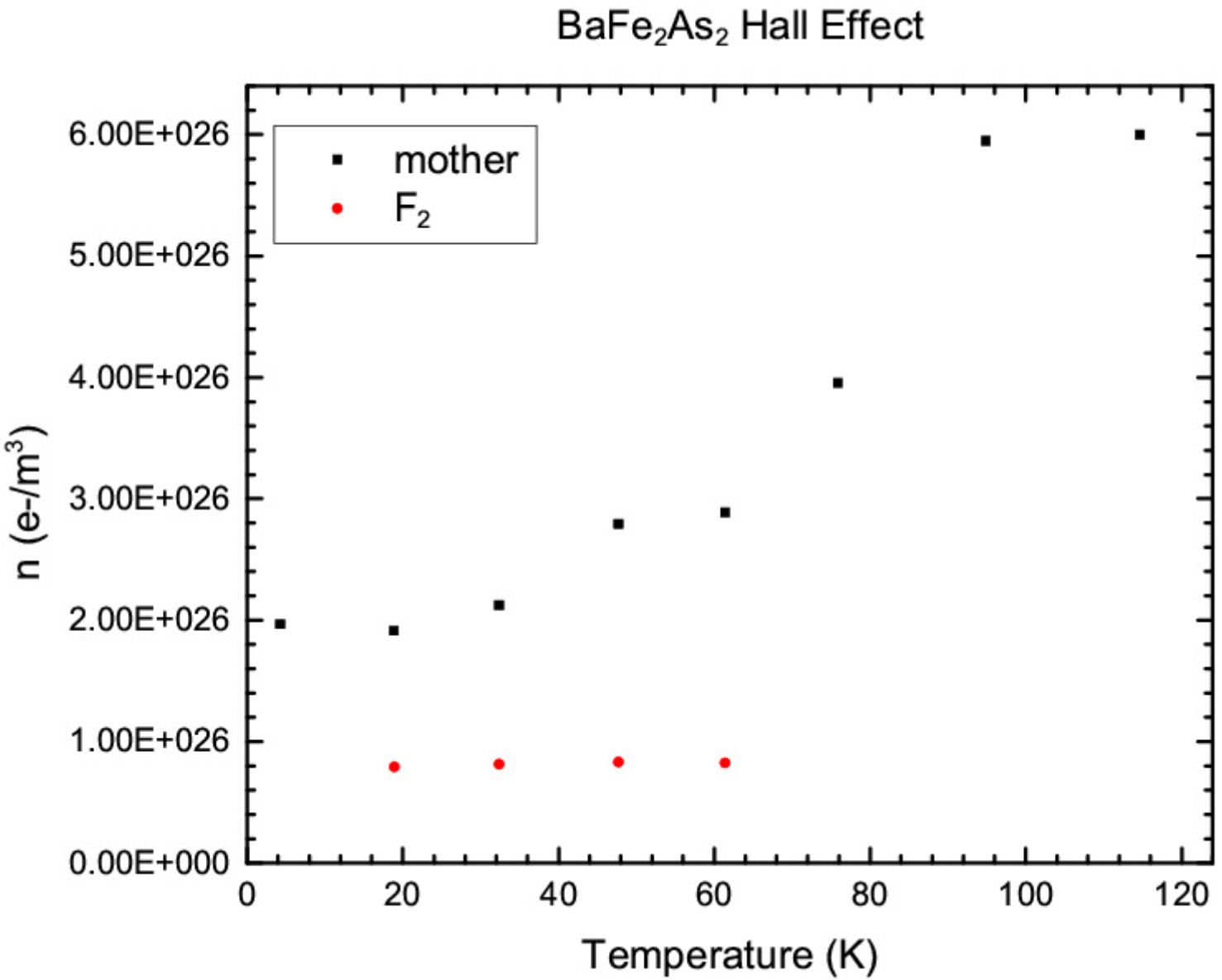
Focus on Fluorinated $BaFe_2As_2$ and Its Properties
-What are the Important Questions?-

- How deep is the superconductivity?
- Any change in lattice parameters?
- Hall Effect
- X-ray Photoemission Spectroscopy: Input as to where F goes in the lattice?
- DFT calculations: where might the F be going?

Focus on Fluorinated $BaFe_2As_2$ and Its Properties -What are the Important Questions?-

- How deep is the superconductivity? 5 – 10 μ
- Any change in lattice parameters? No (c-axis, discussion)
- Hall Effect (see next slide)
- X-ray Photoemission Spectroscopy: Input as to where F goes in the lattice?
- DFT calculations: where might the F be going?

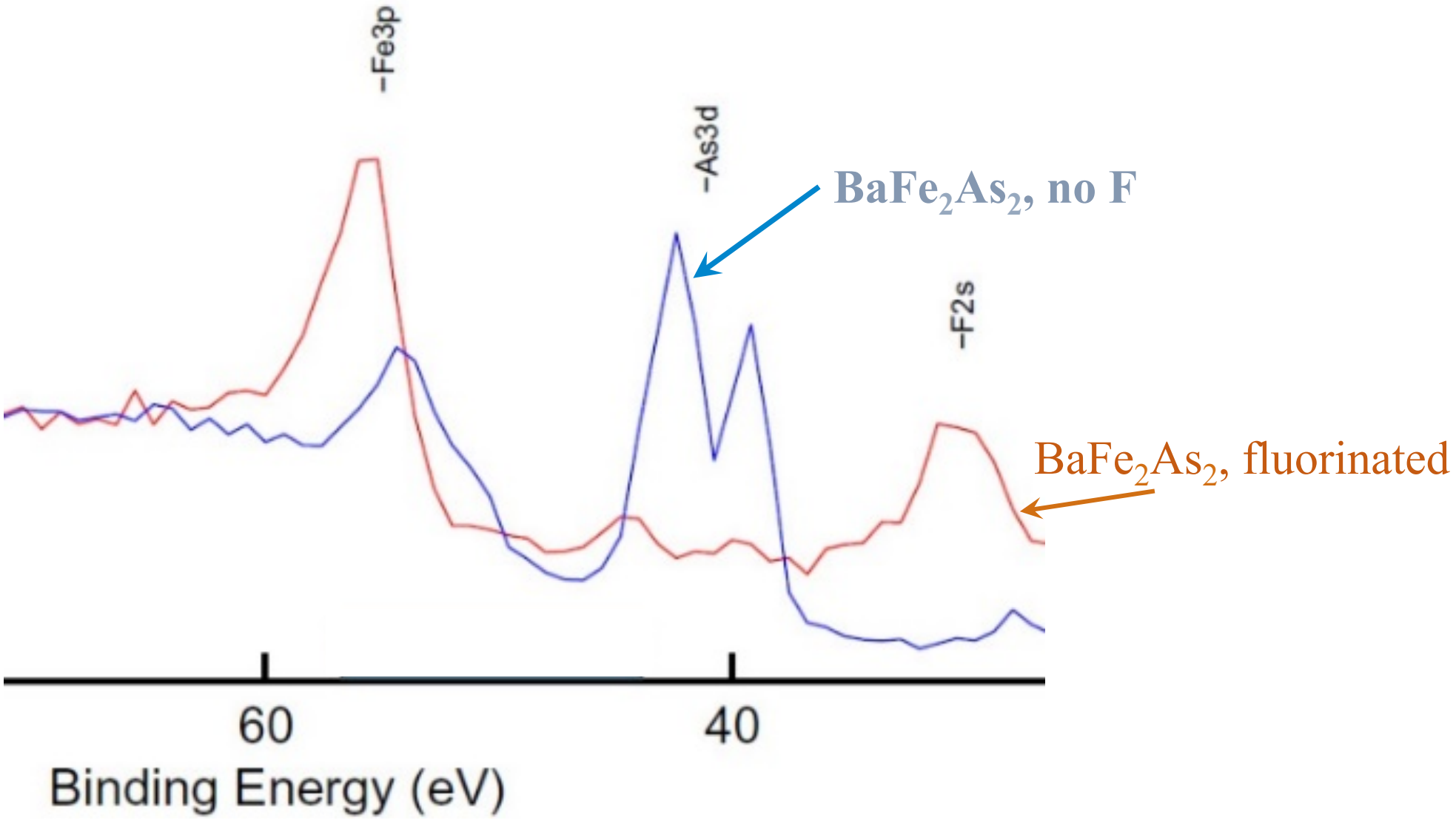
Hall Effect of Fluorinated $BaFe_2As_2$



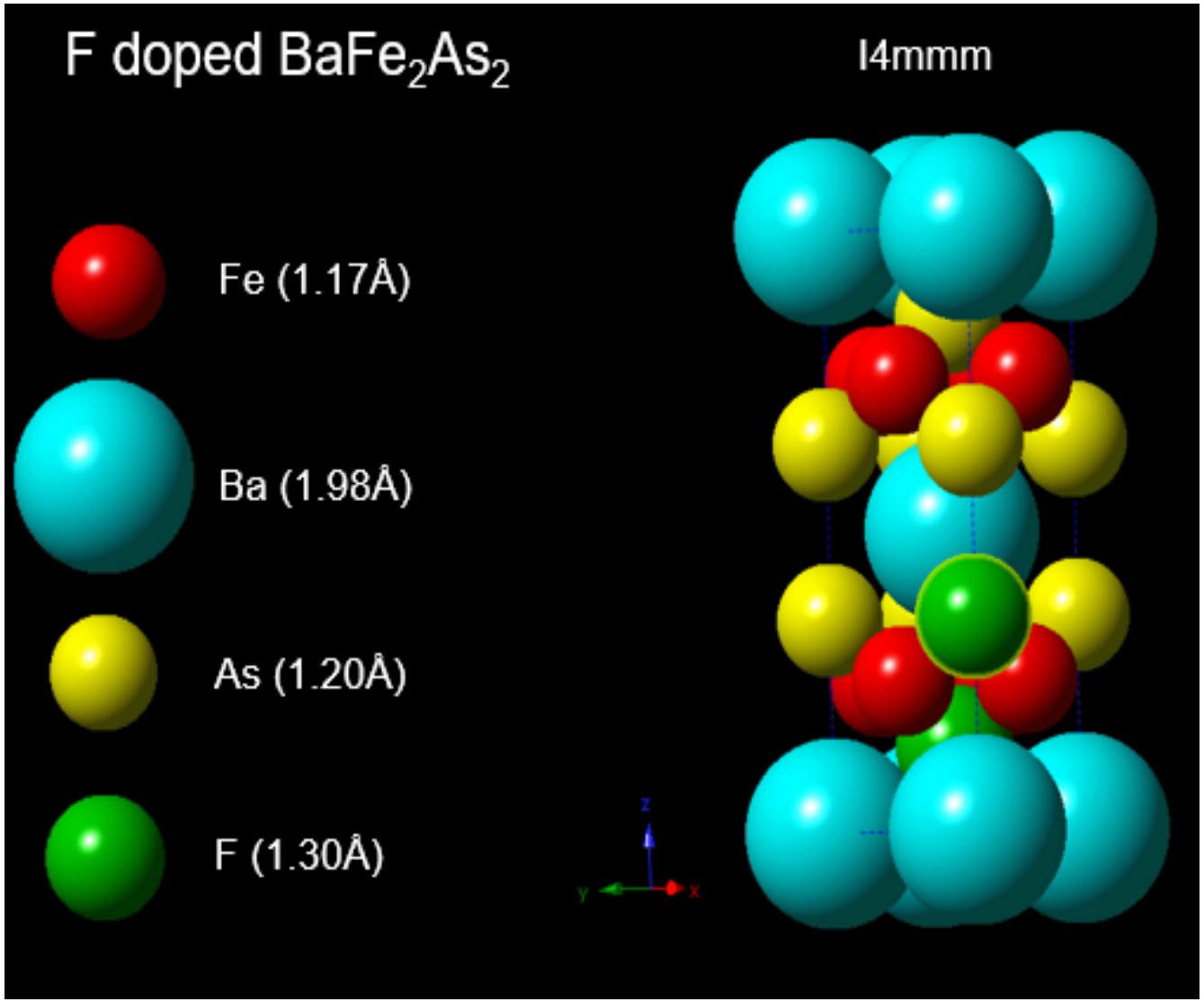
Focus on Fluorinated $BaFe_2As_2$ and Its Properties -What are the Important Questions?-

- How deep is the superconductivity? 5 – 10 μ
- Any change in lattice parameters? No (discussion)
- Hall Effect electron concentration *decreases* with F doping (??)
- X-ray Photoemission Spectroscopy: Input as to where F goes in the lattice? (see next slide)
- DFT calculations: where might the F be going?

Photoemission Data on Fluorinated $BaFe_2As_2$ ⇒As is replaced by F



This XPS result matched our thinking at the time

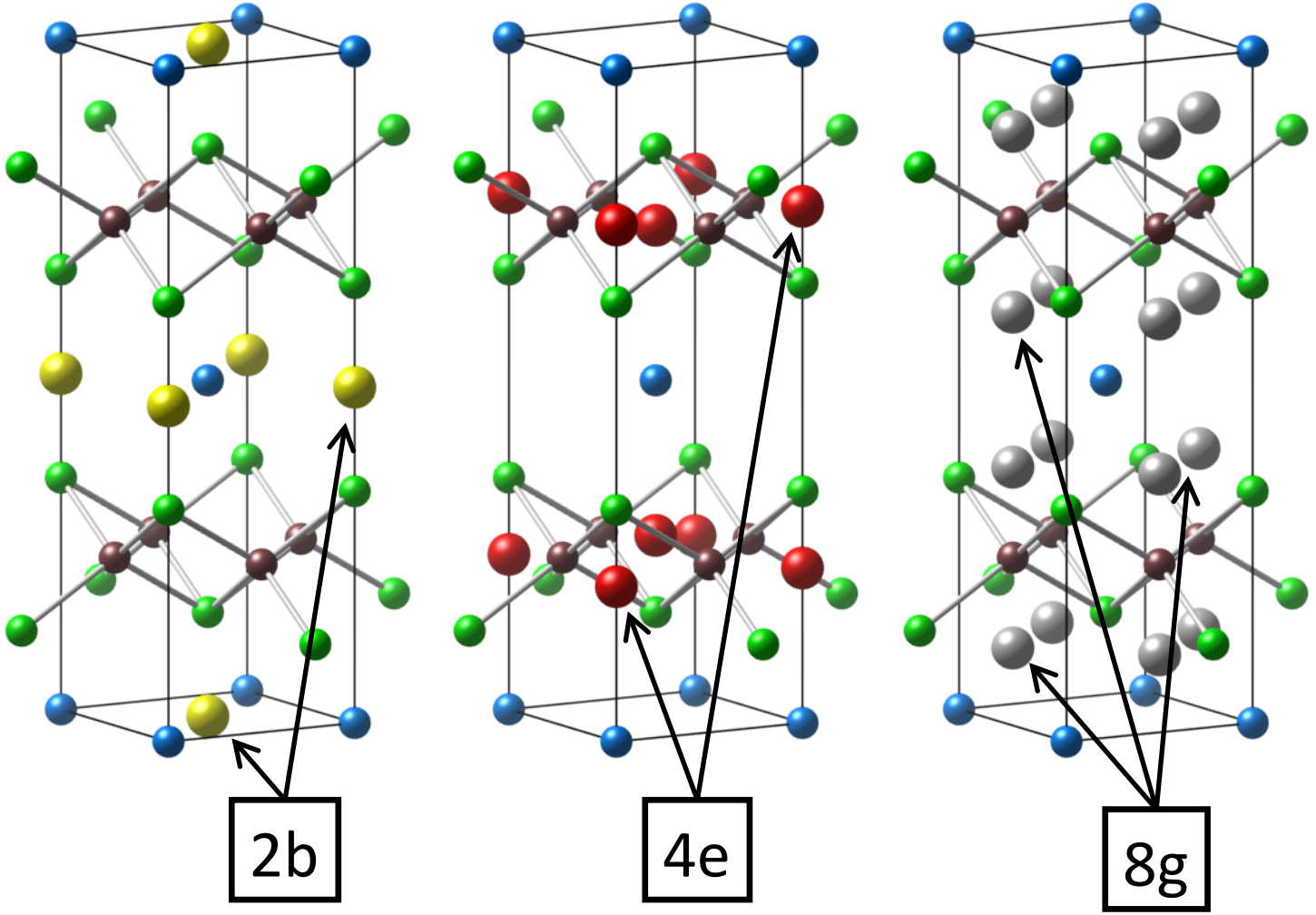


Focus on Fluorinated $BaFe_2As_2$ and Its Properties -What are the Important Questions?-

- How deep is the superconductivity? 5 – 10 μ (definitely not 2-d, does not obey Kosterlitz-Thouless)
- Any change in lattice parameters? No (c-axis; discussion)
- Hall Effect electron concentration *decreases* with F doping
- X-ray Photoemission Spectroscopy: Input as to where F goes in the lattice? Arsenic 3d, 4s lines missing near surface
- calculations: where might the F be going?

Interstitial sites for F in t-$BaFe_2As_2$

- Search for possible interstitial sites for F defect
  1. Create 3D mesh over irreducible part of cell with 0.1 Å spacing
  2. Add F atom to cell at coordinates of mesh point
  3. Calculate single point energy of cell using UFF method
  4. Repeat for each mesh point
  5. Sort coordinates with lowest energies
- Found three low-energy interstitial sites



F impurity calculation results

Impurity site	$\Delta E\downarrow raw$ (eV)	$\Delta E\downarrow true$ (eV)	$V\downarrow imp$ (Å^3)	$d\downarrow ideal$ (Å)
Ba sub.	-4.28, -1.58	1.98, 6.04	12.6	0.00
Fe sub.	2.96, -1.61	3.30, 6.01	8.6	0.00
As sub.	-2.06, -0.71	4.20, 6.91	-5.9	0.13
2b int.	-4.51	1.76, 3.11	18.8	0.00
4e int.	-2.82	3.44, 4.80	21.6	1.14
8g int.	-4.20	2.06, 3.41	19.8	1.43

What have we learned; what are remaining questions?

- Not 2-d, not Kosterlitz Thouless behavior
- Fluorine gives reproducible (over 200 samples, always the same T_c with 1 or 2 K) filamentary superconductivity. No diamagnetic shielding
- At least according to XPS, fluorine replaces arsenic in the lattice
- According to calculations, fluorine replacing arsenic is most consistent with the calculated volume of the impurity, V_{imp}.

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- Hall effect
- According to calculations, As substitution is energetically much less favorable that interstitial placement of the fluorine.
- Mechanism for the superconductivity:
  - T_{SDW} is ~ unchanged (caveat)
  - Charge doping?
  - Defect mechanism

Mechanism for Superconductivity – Defects?

- Paglione group (Saha et al. PRL 103, 037005 (2009)) proposed defects as being important in their $SrFe_2As_2$ as-prepared crystal work: "internal crystallographic strain originating from c-axis-oriented planar defects plays a central role in promoting the appearance of superconductivity under ambient pressure conditions in ~ 90% of as-grown crystals."
- Paul Chu's group (Wei et al., Phil Mag 94, 2562 (2014)) Explanation of T_c=49 K (filamentary but some (≤3%) low field (H<1 G) diamagnetic shielding) in Pr-doped $CaFe_2As_2$:
  - enhanced T_c *up to* 49 K – doping independent T_c, rules out T_c= f(carrier density)
  - may have occurred at the interfaces associated with strains and/or defects

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  - . . . . . .

Comments, Suggestions?

Raw and true defect formation energies

- Substitutional raw defect formation energy:

  $\Delta E\downarrow raw\ [F\downarrow X\ ]=E[F\downarrow X\ ]-E[bulk]+\mu\downarrow X$

  - $E[F\downarrow X\ ]$ - energy of supercell with fluorine at X = As, Fe, B
  - $E[bulk]$ - energy of the perfect supercell (without defect)
  - $\mu\downarrow X$ - reference chemical potential for X = As, Fe, Ba
- Interstitial raw defect formation energy:

  $\Delta E\downarrow raw\ [F\downarrow i\ ]=E[F\downarrow i\ ]-E[bulk]$

  - $E[F\downarrow i\ ]$ - energy of supercell with fluorine at interstitial sit
- True defect formation energy:

  $\Delta E\downarrow true=\Delta E\downarrow raw-\mu\downarrow F$

  - $\mu\downarrow F$ - reference chemical potential for fluorine

Chemical potentials:

$\mu\downarrow X\ [\mathrm{BaFe}\downarrow 2\ \mathrm{As}\downarrow 2\ ]\leq\mu\downarrow X\leq\mu\downarrow X\ [bulk]$

$-4.614\leq\mu\downarrow\mathrm{Ba}\leq-1.908$

$-9.589\leq\mu\downarrow\mathrm{Fe}\leq-8.237$

$-6.022\leq\mu\downarrow\mathrm{As}\leq-4.669$

Fluorine reservoir:

$-\infty\leq\mu\downarrow\mathrm{F}\leq\mu\downarrow\mathrm{F}\ [\mathrm{F}\downarrow 2\ ]$

Using BaF_2 as a reference:

$\mu\downarrow F=1/2\ (E[\mathrm{BaF}\downarrow 2\ ]-\mu\downarrow\mathrm{Ba}\ )$

- The two values for "E_{raw}" for the substitution sites are upper and lower bounds depending on the chemical potential of the atom that will be removed. The lower bound represents the chemical potential for the atom in BaFe2As2 and the upper bound represents the chemical potential for the atom in its elemental ground state structure. The "E_{raw}" values for the interstitial sites are a single value as the sites are initially empty.
- "E_{true}" are then calculated by subtracting the fluorine chemical potential from "E_{raw}". The range of fluorine chemical potentials is calculated using the compound BaF2 as a reference, which gives an upper or lower bound depending on the chemical potential for Ba.
- "Vimp" is the impurity volume and is defined as Vimp = V(with F) – V(bulk), where V(with F) is the volume of the BaFe2As2 cell with fluorine at a given site and V(bulk) is the volume of the bulk BaFe2As2 cell.
- "d_ideal" is the distance the fluorine atom has displace from the ideal site, interstitial or substitutional, after relaxation of the atoms/cell.