## I. Review of Fe-based Superconductivity II. Disorder effects in unconventional SC

## P. Hirschfeld, U. Florida



Balatsky, Vekhter and Zhu, Rev Mod Phys 78, 373, (2006) Alloul, Bobroff, Gabay, PH, Rev. Mod. Phys. 81, 45 (2009)

Maglab Theory Winter School January 2013



## Anderson's theorem

P. W. Anderson, J.Phys. Chem. Solids 11, 26 (1959)

### THEORY OF DIRTY SUPERCONDUCTORS

#### P. W. ANDERSON

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 3 March 1959)

Abstract—A B.C.S. type of theory (see BARDEEN, COOPER and SCHREIFFER, *Phys. Rev.* 108, 1175 (1957)) is sketched for very dirty superconductors, where elastic scattering from physical and chemical impurities is large compared with the energy gap. This theory is based on pairing each one-electron state with its exact time reverse, a generalization of the k up, -k down pairing of the B.C.S. theory which is independent of such scattering. Such a theory has many qualitative and a few quantitative points of agreement with experiment, in particular with specific-heat data, energy-gap measurements, and transition-temperature versus impurity curves. Other types of pairing which have been suggested are not compatible with the existence of dirty superconductors.

In the presence of dirt one can still pair time-reversed members of Kramer's doublet: thermodynamics (T<sub>c</sub>, gap, sp. ht., ...) are not affected by nonmagnetic impurities

## Abrikosov-Gor'kov theory

SOVIET PHYSICS JETP

VOLUME 35(8), NUMBER 6

JUNE, 1959

ON THE THEORY OF SUPERCONDUCTING ALLOYS

I. THE ELECTRODYNAMICS OF ALLOYS AT ABSOLUTE ZERO

A. A. ABRIKOSOV and L. P. GOR' KOV

Institute for Physics Problems, Academy of Sciences, U.S.S.R.

Submitted to JETP editor July 16, 1958

J. Exptl. Theoret. Phys. (U.S.S.R.) 35, 1558-1571 (December, 1958)

In this paper we give the theory of superconductors containing impurities at the absolute zero. The dependence of the penetration depth on the impurity concentration is considered for small atomic concentrations. We have obtained the electrodynamic equations in an alternating field for superconductors with a mean free path which is smaller than the correlation length.

Many body formulation of disorder problem in superconductor assuming weak scattering agrees with Anderson conclusions

## Abrikosov-Gor'kov theory cont'd Skalski et al PR 136, A1500 1964

Pairbreaking in s-wave SC by magnetic impurities



FIG. 2. The critical temperature  $T_c$ , the order parameter  $\Delta(0)$ , and the half-excitation energy gap  $\Omega_G(0)$  at  $T=0^\circ$ , plotted as a function of the inverse collision time  $\Gamma$ . The superscript P refers to the value when  $\Gamma=0$ .



FIG. 4. The density of states in energy plotted as a function of the reduced energy for several values of the reduced inverse collision time  $\Gamma/\Delta$ .  $\Delta(T)$  is to be understood as  $\Delta(T,\Gamma)$ .

Gapless SC

### Balian-Werthamer: p-wave superconductivity

PHYSICAL REVIEW

#### VOLUME 131, NUMBER 4

#### 15 AUGUST 1963

#### Superconductivity with Pairs in a Relative p Wave\*†

R. Balian

Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette (S.O.), France

AND

N. R. WERTHAMER Bell Telephone Laboratories, Murray Hill, New Jersey (Received 6 March 1963)

These conclusions are not, in general, true for the p-wave pair state. Since the interaction between the conduction electrons and an impurity is short ranged, probably localized to the immediate vicinity of the impurity site itself, the perturbation extends only over a distance comparable to the lattice spacing, and as we remarked earlier very large momentum transfers of order  $2k_F$  are allowed. In fact,  $|\lambda(\mathbf{k}-\mathbf{k}')|^2$  is certainly not such as to restrict  $\hat{k}$  to the vicinity of  $\hat{k}'$  in Eq. (70). The exact cancellation of the two last terms, therefore, occurs only for  $\gamma = 1$ , that is for an s-wave state with nonmagnetic impurities. The prediction for the p-wave pair state, then, is that magnetic impurities would tend to depress the transition temperature to roughly the same degree as for the BCS state, and that in an equivalent concentration nonmagnetic impurities would lower  $T_c$  even more, since  $\lambda^2$  is likely to be a good deal larger in this case.

Nonmagnetic impurities are pairbreaking in unconventional superconductors

#### Strong magnetic impurity creates bound state in s-wave SC

#### BOUND STATE IN SUPERCONDUCTORS WITH PARAMAGNETIC IMPURITIES

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#### Abstract

A generalized canonical transformation and a SCF method have been used to investigate the influence of isolated impurity atoms on the properties of superconductors. It has been found that a bound state of excitation exists around a paramagnetic impurity with its energy level in the energy gap. An analytical expression has been obtained for the corresponding wave function. The effect of electromagnetic absorption due to the bound state should appear as a precursory peak. The possible experimental verifications of the bound state through tunnelling effect and infrared absorption are discussed.

Futhermore, the excitations of continuous spectra around a nonmagnetic impurity and the spatial variation of the energy gap parameter have been considered.

Yu Lu, Acta Physica Sinica 21, 75 (1965)

see also

H. Shiba, Prog. Theor. Phys. 40, 435 (1968).

A. I., Rusinov, 1969, Zh. Eksp. i Teor. Fiz. 56, 2047, [Sov. Phys. JETP 29, 1101 (1969)].

### 7-matrix for *single* nonmagnetic impurity



**Onsite potential** 

$$U(i) = u_0 \delta(i - i_0)$$
  
$$T(\omega) = \frac{1}{u_0^{-1} - \sum_k G^0(k, \omega)}$$



Magnetic impurity bound state in s-wave SC

 $\underline{G}^{0} = (\omega \tau_{0} - \xi_{k} \tau_{3} - i\sigma_{2} \Delta \tau_{1})^{-1}$ 

$$\underline{U} = u_s \vec{S} \cdot \vec{\alpha} = u_s \vec{S} \cdot \left[\frac{1 + \tau_3}{2}\vec{\sigma} + \frac{1 - \tau_3}{2}\sigma_2\vec{\sigma}\sigma_2\right]$$

$$\underline{T} = \underline{U} + \underline{U}\underline{G}^0\underline{T} = u_s \frac{\overline{G}_0 (1 + u_s^2) \tau_0 + \overline{G}_1(1 - u_s^2) \tau_1}{1 - 2u_s^2 \left(\frac{\Delta^2 + \omega^2}{\Delta^2 - \omega^2}\right) + u_s^4}$$
subgap state

正常 起导 有亲质

$$\underline{G}^{0} = \begin{bmatrix} \langle cc^{\dagger} \rangle & \langle cc \rangle \\ \langle c^{\dagger}c^{\dagger} \rangle & \langle c^{\dagger}c \rangle \end{bmatrix} = \frac{\omega\tau_{0} + \xi_{k}\tau_{3} + \Delta\tau_{1}}{\omega^{2} - \xi_{k}^{2} - \Delta^{2}}$$

"Nambu propagator"

$$\underline{G}^{0} = \begin{bmatrix} \langle cc^{\dagger} \rangle & \langle cc \rangle \\ \langle c^{\dagger}c^{\dagger} \rangle & \langle c^{\dagger}c \rangle \end{bmatrix} = \frac{\omega\tau_{0} + \xi_{k}\tau_{3} + \Delta\tau_{1}}{\omega^{2} - \xi_{k}^{2} - \Delta^{2}}$$

 $\underline{T} = \underline{U} + \underline{U}\underline{G}^{0}\underline{T} \qquad \underline{U} = u_{0}\tau_{3}\delta(i-i_{0})$  $= u_{0}\tau_{3} + u_{0}\tau_{3}\left[\Sigma_{k}\underline{G}^{0}(k,\omega)\right]\underline{T}$ 

$$\underline{G}^{0} = \begin{bmatrix} \langle cc^{\dagger} \rangle & \langle cc \rangle \\ \langle c^{\dagger}c^{\dagger} \rangle & \langle c^{\dagger}c \rangle \end{bmatrix} = \frac{\omega\tau_{0} + \xi_{k}\tau_{3} + \Delta\tau_{1}}{\omega^{2} - \xi_{k}^{2} - \Delta^{2}}$$

$$\underline{T} = \frac{G_0 \tau_0 - G_1 \tau_1 - u_0^{-1}}{u_0^{-2} + G_1^2 - G_0^2};$$

$$G_{\alpha}(\omega) = \frac{1}{2} \operatorname{Tr} \Sigma_{k} \tau_{\alpha} \underline{G}^{0}(k, \omega)$$
$$= \begin{cases} \frac{-i\omega}{\sqrt{\omega^{2} - \Delta^{2}}} & \alpha = 0\\ \frac{i\Delta}{\sqrt{\omega^{2} - \Delta^{2}}} & \alpha = 1 \end{cases}$$

$$\underline{G}^{0} = \begin{bmatrix} \langle cc^{\dagger} \rangle & \langle cc \rangle \\ \langle c^{\dagger}c^{\dagger} \rangle & \langle c^{\dagger}c \rangle \end{bmatrix} = \frac{\omega\tau_{0} + \xi_{k}\tau_{3} + \Delta\tau_{1}}{\omega^{2} - \xi_{k}^{2} - \Delta^{2}}$$

$$\underline{T} = \frac{G_0 \tau_0 - G_1 \tau_1}{\underbrace{u_0^{-2} + G_1^2 - G_0^2}_{u_0^{-2} + 1}};$$

No! no pole... (Anderson, AG)

$$G_{\alpha}(\omega) = \frac{1}{2} \operatorname{Tr} \Sigma_{k} \tau_{\alpha} \underline{G}^{0}(k, \omega)$$
$$= \begin{cases} \frac{-i\omega}{\sqrt{\omega^{2} - \Delta^{2}}} & \alpha = 0\\ \frac{i\Delta}{\sqrt{\omega^{2} - \Delta^{2}}} & \alpha = 1 \end{cases}$$

### What about in *d*-wave superconductor?



$$\underline{G}^{0} = \frac{\omega\tau_{0} + \xi_{k}\tau_{3} + \Delta(\phi)\tau_{1}}{\omega^{2} - \xi_{k}^{2} - \Delta(\phi)^{2}}$$

 $\Delta(\phi) = \Delta_0 \cos 2\phi$ 

## What about in *d*-wave superconductor?



$$\underline{G}^{0} = \frac{\omega\tau_{0} + \xi_{k}\tau_{3} + \Delta(\phi)\tau_{1}}{\omega^{2} - \xi_{k}^{2} - \Delta(\phi)^{2}}$$

$$\Delta(\phi) = \Delta_0 \cos 2\phi$$

$$\underline{T} = \frac{G_0 \tau_0 - G_1 \tau_1 - u_0^{-1}}{u_0^{-2} + G_1^2 - G_0^2}$$

$$G_{0}(\omega) = \left\langle \frac{-i\omega}{\sqrt{\omega^{2} - \Delta(\phi)^{2}}} \right\rangle_{\phi}$$
$$G_{1}(\omega) = \left\langle \frac{i\Delta(\phi)}{\sqrt{\omega^{2} - \Delta(\phi)^{2}}} \right\rangle_{\phi}$$

## Nonmagnetic impurity in *d- or s* -wave superconductor?



Possible pole...

$$\underline{G}^{0} = \frac{\omega\tau_{0} + \xi_{k}\tau_{3} + \Delta(\phi)\tau_{1}}{\omega^{2} - \xi_{k}^{2} - \Delta(\phi)^{2}}$$

$$\Delta(\phi) = \Delta_0 \cos 2\phi$$

$$G_{0}(\omega) = \left\langle \frac{-i\omega}{\sqrt{\omega^{2} - \Delta(\phi)^{2}}} \right\rangle_{\phi}$$
$$G_{1}(\omega) = \left\langle \frac{i\Delta(\phi)}{\sqrt{\omega^{2} - \Delta(\phi)^{2}}} \right\rangle_{\phi} = 0!$$
for d-wave

Bound states of nonmagnetic impurity in *d*-wave SC

Byers et al (1993): Local DOS shows 4fold pattern

Balatsky et al.(1995):

Bound state in resonant limit at

$$\Omega_0 = \Delta_0 \left( 2N_0 u_0 \log 8N_0 u_0 \right)^{-1}$$



see also Stamp, 1986 (p-wave)

 $\rho(\mathbf{x},\mathbf{y},\mathbf{E}=1.1\Delta_0)$ 



### Nonmagnetic impurity bound states in various systems



## Finite nonmagnetic disorder in unconventional superconductors





Anisotropy smeared out:



d-wave: Mix  $\Delta_{\mathbf{k}}$ ,  $\Delta_{\mathbf{k}'}$  with signs  $\pm$ :



Gap supressed:



(Weak nonmagnetic) disorder and unconventional superconductors: destruction of gap nodes

> Gor'kov and Kalugin, Sov. Phys. JETP 41, 253 (1985) Rice and Ueda, *Theory of Heavy Fermions and Valence Fluctuations (Springer, 1985)*

Self-consistent treatment of average G:



self-consistent Born

predictions for residual dos N(0) in p-wave states

``polar state"  $\Delta(\theta) = \cos \theta$  N(0)>0 for infinitesimal disorder

``axial state"  $\Delta(\theta) = \sin \theta$  N(0)>0 for critical disorder strength

triplet classes with point nodes (with moment) are `topologically stable'

Schmitt-Rink et al, PRL 57, 2575 (1986)

Disorder: self-consistent *t*-matrix approx. ("SCTMA", "CPA"...)

Sum all multiple scattering diagrams from 1 impurity:

$$\underline{\Sigma} = n_i \underline{\mathsf{T}}$$
$$\underline{\mathsf{T}} = \underline{\mathsf{V}} + \underline{\mathsf{V}} \underline{\mathsf{G}} \underline{\mathsf{T}}$$





where  $\gamma$  is residual scattering rate,  $\Delta_0$  gap max,  $\rho_0$  normal state DOS.

Experiments exhibit effect of residual DOS (YBCO):



 $\rho(0) \sim \gamma \simeq \sqrt{n_i \Delta_0 E_F}$  unitarity scattering limit  $u_0 \gg E_F$  $\delta\lambda(T=0), \sqrt{1/T_1 T} \sim \rho(0)$ 

### Origin of "impurity band": hopping through tails of impurity states



Semiconductor

d-wave SC

### Experiments require near-unitarity impurity scattering

(cuprates, heavy fermions)

• Strong effect on low-T properties with little  $T_c$  supression

 Strong *T*-dependence of transport coefficients Pethick
 & Pines 1986

"Universal"

σ, κ/Τ, ...

Unitarity

Born



## Impurities in cuprates

Probe the response of SC to a spin/charge local perturbation

Dilute Cu in-plane substitutions

- Ni<sup>2+</sup> 3d<sup>8</sup> spin 1
- Zn<sup>2+</sup> 3d<sup>10</sup> no spin
  - Li<sup>+</sup> no spin

*Out-of-plane* defects: missing O, cation switching, ...



## Zn On-site LDOS spectrum: $\Omega_0$ =-1.5 meV



Pan et al, Nature 403, 746 (2000).



Data contrast with naïve expectation: |Y|<sup>2</sup> should be a four-fold symmetric 'star' oriented with gap-nodes, maximum amplitude on nearest neighbor sites!

# Spatial structure of these $|\Psi|^2$ not well understood.





## Theories of impurity resonance spatial pattern

•"Chemistry": M.E. Flatté et al. 2001, 03. Assume generalized extended impurity potential.

 "Filter": C.S. Ting et al. 2001, Martin & Balatsky
 2002. STM probes LDOS of neighboring Cu's due to k-dependent tunneling matrix elements.

• "Correlations": Polkovnikov et al 2001, account for Kondo screening of correlation-induced local moment

## Back to FeSC: intriguing defect states whose structure may reveal SC gap

those shown believed to be Fe vacancies (J.E. Hoffman)



#### Sometimes no impurity bound states are seen



l=1.0 eV

6

8

far away

onsite

n.n.n.

3rd n.n.

(b)

n.n.

Na(Fe<sub>1-x</sub>Co<sub>x</sub>)As

Yang et al, PRB 86, 214512 (2012)

#### bound states are hard to tune to low E

#### but it is not surprising!

#### 5-orbital BdG: Kariyado and Ogata, JPSJ 79, 083704 (2010).

far away

onsite

n.n.n.

3rd n.n.

-0.08-0.06-0.04-0.02 0 0.02 0.04 0.06 0.08 Energy (eV)

(a)

n.n.

12

10

8

2

ő ő

I=0.5 eV

PH et al, ROPP 74, 124508 (2011) Beaird et al PRB 86, 140507 (2012)



### How to simplify many-parameter problem II: use ab initio methods to determine intra/interband character of scattering?

- Ratio V<sub>inter</sub>/V<sub>intra</sub> important
- Impurity diagonal in orbital space has generically large interband component (Kontani 2009)
- Answer question with ab initio calculations for specific defects

|                | Mn     | Co    | Ni    | Zn    | Ru    |
|----------------|--------|-------|-------|-------|-------|
| xy             | 0.32   | -0.39 | -0.97 | -7.88 | -0.10 |
| yz             | 0.27   | -0.34 | -0.84 | -8.10 | 0.03  |
| $z^2$          | 0.29   | -0.36 | -0.93 | -7.96 | -0.21 |
| zx             | 0.27   | -0.34 | -0.84 | -8.10 | 0.03  |
| $x^2 - y^2$    | 0.25   | -0.33 | -0.75 | -8.22 | 0.16  |
| Average        | 0.28   | -0.35 | -0.87 | -8.05 | -0.02 |
| Ref. <u>36</u> | 1.27   | -1.23 | -2.42 | -     | 1.95  |
| $\Delta E_F$   | -0.004 | 0.011 | 0.032 | 0.084 | 0.062 |
|                |        |       |       |       |       |

Kemper et al 2009 for Co

band space:

$$\frac{U_{12}}{U_{11}} \approx \frac{1}{3}$$

Kemper et al 2009, Nakamura et al 2010

Disagreement between Kemper, Nakamura, Elfimov... on Co potential?

# s<sub>++</sub> or s<sub>+-</sub>? Few phase-sensitive expts.

#### Chen et al, Nature 2010

# 

#### $NdFeAsO_{0.88}F_{0.12}$

Half-integer fluxes detected (in a small fraction of loops)

#### Christianson et al Nature 2008



#### Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub>

20

20

10

Energy Transfer [meV]

Enhanced susceptibility at Q below Tc  $\Rightarrow$  sign change of order parameter

# Hanaguri et al Science 2010



#### Fe(Se,Te)

Field dependence of quasiparticle interference peaks depends on order parameter sign



Various critiques of all experiments, alternate scenarios: where is the

10

## Hiroshi Kontani, M2S 2012

# impurity effect in single crystal (Ba,K)Fe<sub>2</sub>As<sub>2</sub>

J.Li et al. PRB 85, 214509 (2012).



✓ Vegard's law: good crystal



other experiments:

1111 systems: Sato et al, JPSJ('08) Ba122: Paglione et al, arXiv('12) irradiation: Nakajima et al, PRB ('10)

> local impurity on Fe-sites



Inter- and intraband impurity scattering in 2-band s<sub>+/-</sub> system



#### Scenario 1: isotropic $s_{+/-}$ state + **interband** impurity scattering $\Rightarrow$ low-E power laws



 $s_{+/-}$  state has full gap but **interband** scattering is pairbreaking due to bound state

#### Scenario 2: anisotropic states with intraband scattering



Mishra et al PRB 2009



recall Fletcher et al 2008 LaFePO T<sub>c</sub>=6K  $\lambda \sim T \Rightarrow nodes!$ 



intraband scattering averages gap anisotropy, "lifts" nodes! Simplest problem:  $T_c$  suppression in  $s_{+/-}$  state

naïve expectations:

- interband scattering will suppress T<sub>c</sub> faster
- T<sub>c</sub> suppression will depend on interband/intraband scattering potential ratio u/v
- $T_c$  suppression will depend on ratio/signs of interband/intraband pairing  $\lambda_{inter}/\lambda_{intra}$  as well

## 2-band disorder problem self-consistent t-matrix approx.





 $\gamma = 2n\sigma/N(0)$  is the normal-state scattering rate,  $\sigma = \frac{\left(\pi \sqrt{N_a N_b v}\right)^2}{1 + \left(\pi \sqrt{N_a N_b v}\right)^2}$  is the impurity concentration, *v* is the interband impurity potential,  $\sigma$  is the impurity strength  $(\sigma \rightarrow 0$ : Born limit,  $\sigma = 1$ : unitary limit)

Preosti, Muzikar PRB 54, 3489 1996; Golubov, Mazin, Phys. Rev. B 55, 15146 1997 M.L.Kulic<sup>'</sup>, O.V.Dolgov, PRB, **60**, 13062 (1999); Y. Ohashi, Physica C, **412-414**, 41(2004)

## Electron irradiation at LSI (Irradiated Solids Lab)--Paris



http://emir.in2p3.fr/LSI

http://www.lsi.polytechnique.fr/accueil/equipements/accelerateur-sirius/

- vacancy interstitial (Frenkel) pairs
- different sublattices are affected, depending on beam energy
- initial paper: arXiv:1209.3586 with 2.5MeV electrons: dominant Fe vacancies





Shibauchi Matsuda also: C. van der Beek, M. Konczykowski







Prozorov

Thanks: C. van der Beek

## e- irradiation experiments





## e- irradiation of BaFe<sub>2</sub>(As,P)<sub>2</sub>



Nonmonotonic change of low T dependence:  $T \rightarrow \exp(-\Delta/T) \rightarrow T^2$ 

## DOS, $\Delta\lambda$ , T<sub>1</sub><sup>-1</sup>with increasing disorder: mixed inter and intraband scattering

disorder→





Theory of nonmonotonic  $\lambda(T)$ -variations

Wang et al 2012 (unpublished)





Only s+/- can explain data!

## Comparison: expt vs. theory





- Unconventional superconductors are generically sensitive to nonmagnetic disorder
- impurity bound states may be good probes of superconducting gap structure; mysteries remain
- e- irradiation experiments: T<sub>c</sub> suppression, penetration depth experiments strong evidence for sign-changing ∆ in FeSC
- To use disorder analysis to determine order parameter structure, need to reduce # parameters – ab initio methods?