ISIS User Meeting
July 17, 2018

Superconducting Gap Symmetry in Organic Superconductor λ-$(BETS)_2GaCl_4$ studied by μSR and DFT

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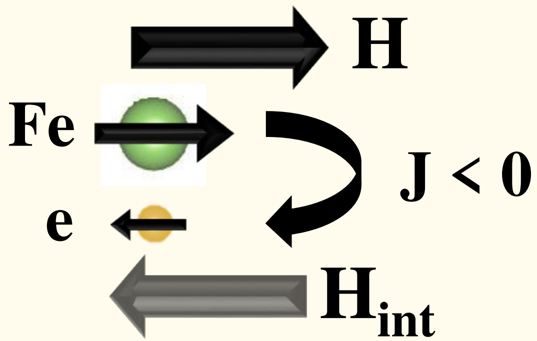
Contents

λ-$(BETS)_2FeCl_4$

Field Induced Superconductor

Parallel to conducting layer (a-c plane)



Magnetic Field (Fe) kills Superconductivity

Pairing Symmetry?

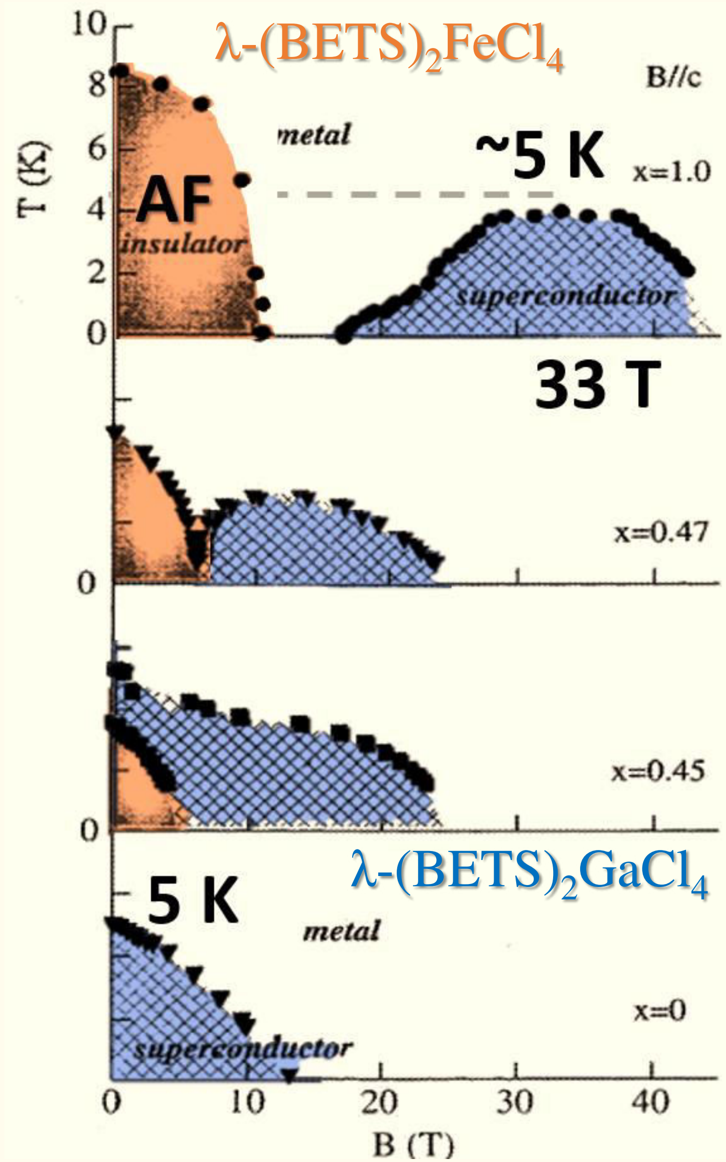
λ-$(BETS)_2GaCl_4$

Iso-structure with Fe system

Superconductor in Zero Field

Pairing Symmetry?

λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$



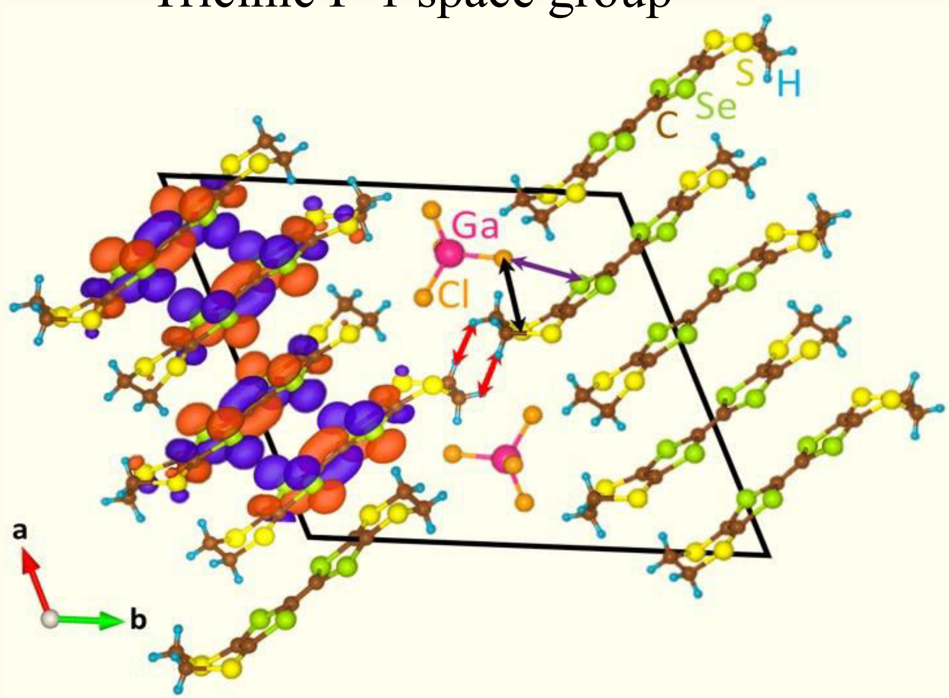
S. Uji and J. Brooks, JPSJ,**75**, 051014 (2006)

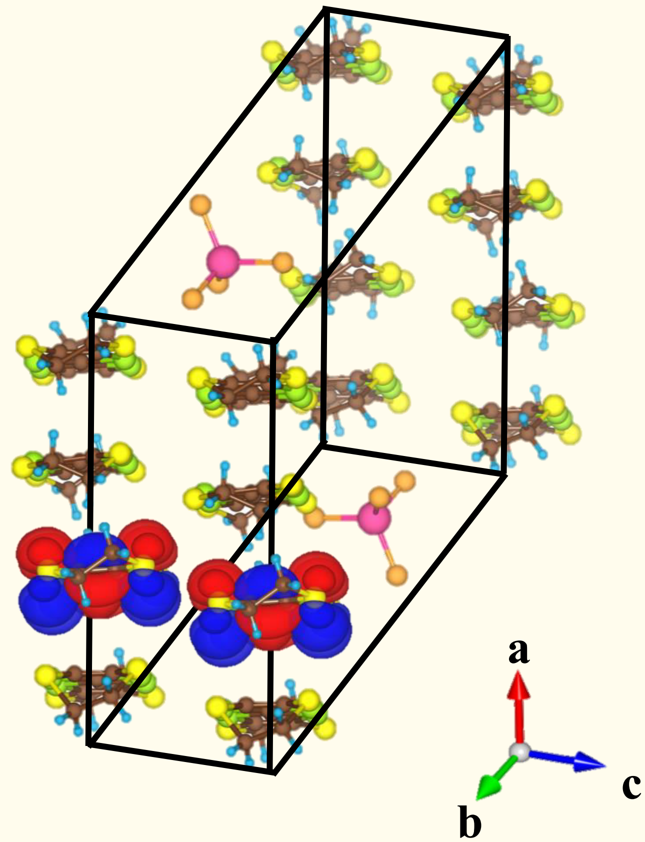
λ-$(BETS)_2GaCl_4$

Isostructural λ-$(BETS)_2FeCl_4$

Low symmetry

Triclnic P-1 space group





Stacking in *a*-direction
Dimerization

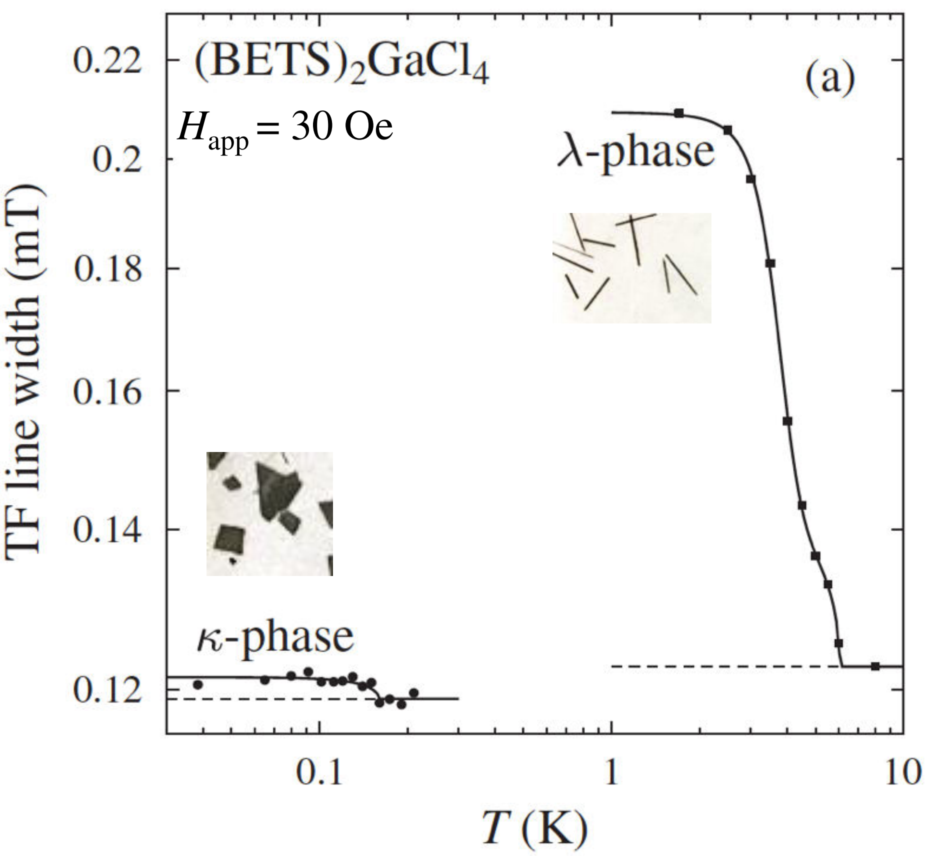
Stacking in *c*-direction
Side-by-side coupling

A. Kobayashi, *et al., Chem. Lett*. 2179-2182 (1993).
H. Kobayashi, *et al., Chem. Lett.* 1559-1562 (1993).
H. Kobayashi, H. Cui, and A. Kobayashi, *Chem. Rev.* **104**, 5265 (2004).

Experiments for determining superconducting gap symmetry:

Experiments	Results	Gap Symmetry	Reference
Specific Heat	2 – 7 K $\Delta C/\gamma T_c$ =1.37±0.32	*s*–wave	Y. Ishizaki et al., Syn. Met. **133-134**, 219-220 (2003)
Magnetoresistance	Angular dependence of H_{c2} minima of $\Delta(\varphi)$ for $d_{x^2-y^2}$	*d*–wave	T. Kawasaki, *Syn. Met.* **120**, 771-772 (2001)
Microwave-conductivity	$(\sigma_1+i\sigma_2)$ Saturation of **λ** down to T/Tc =0.2	*s*–wave	T. Suzuki et al., *Physica C*, **440**, 17-24 (2006)
STM in thin layer	V-shape spectra	d_{xy}	K. Clark et al., *nat. nanotech.* **5**, 261 (2010)
Flux-flow resistivity	In-plane angular dependence is mainly describe by **two-fold symmetry**	May be **different** with *d*–wave	S. Yasuzuka et al., *J. Phys. Soc. Jpn.* **83**, 013705 (2014)
Specific Heat	Down to 0.6 K	*d*–wave	S. Imajo et al., *J. Phys. Soc. Jpn.* **85**, 043705 (2016)
ARPES			
NMR	Spin Fluctuation at metalic state		T. Kobayashi and A. Kawamoto, *Phys. Rev. B.* **96**, 125115 (2018)
Neutron Scattering			
***μ*SR**	Penetration depth **λ** = 0.72(2) μm		F. L. Pratt, *et al. Polyhedron* **22**, 2307 (2003)

Muon spin relaxation (μSR) study on $(BETS)_2GaCl_4$



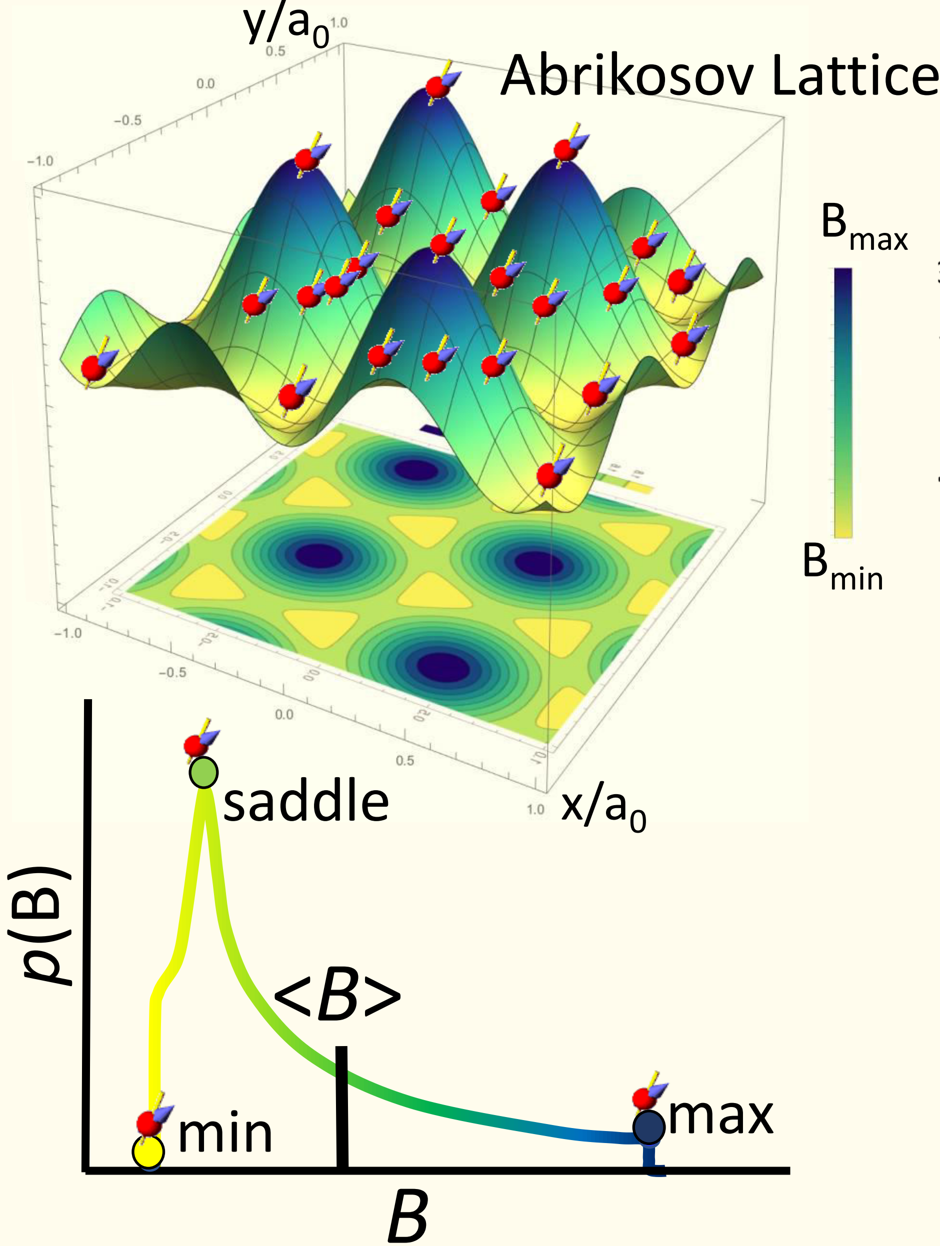
λ-$(BETS)_2GaCl_4$: Increasing of TF-linewidth → formation of the vortex state

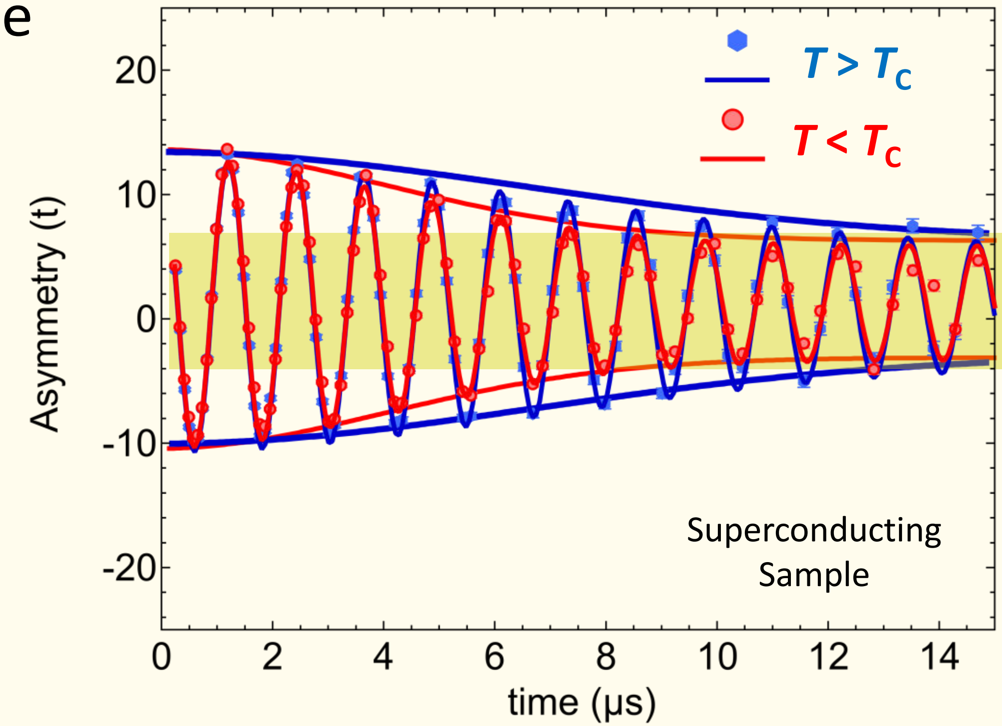
$T_c = 5.5$ K

κ-$(BETS)_2GaCl_4$: $T_c \sim 150$ mK.

F. L. Pratt, *et al. Polyhedron* **22**, 2307 (2003).

TF-μSR for studying superconductivity





$T > T_C$:
Normal State
Nuclear Dipole Moment

$T < T_C$:
Superconducting State
Nuclear Dipole Moment+
Magnetic Penetration Depth

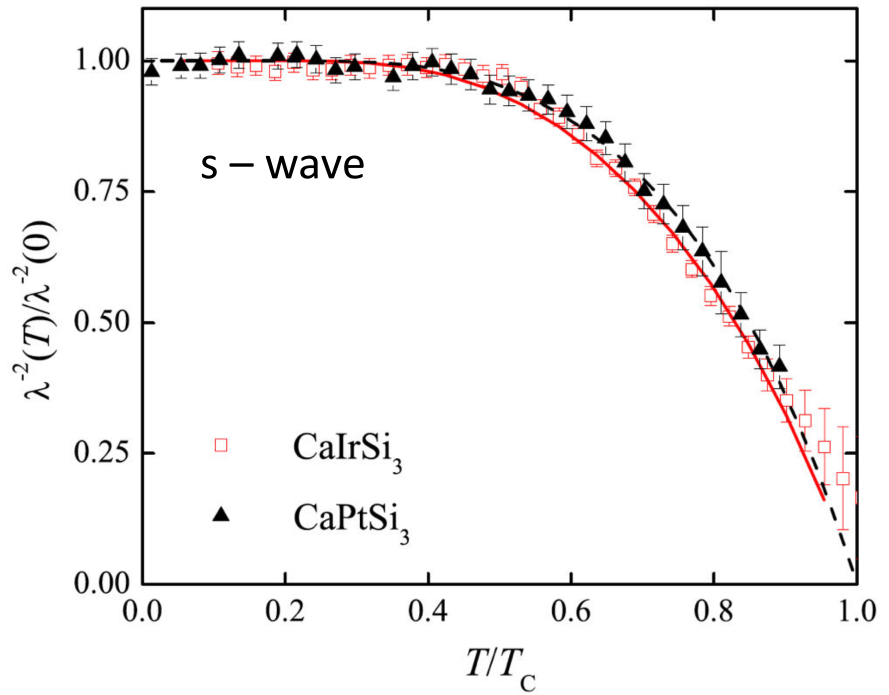
Gaussian distribution p(B)

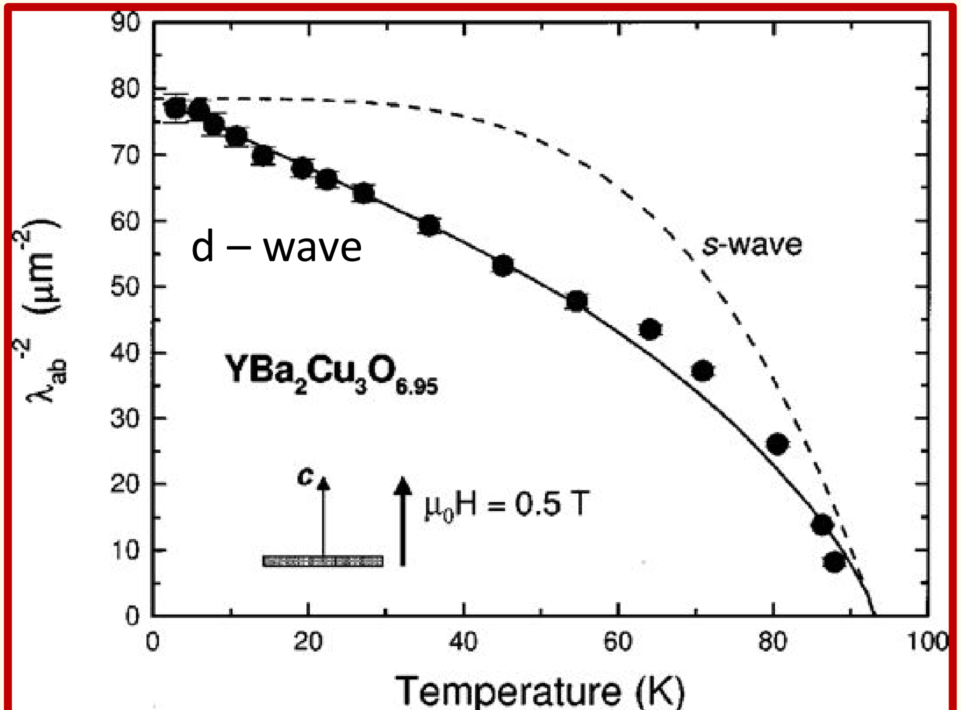
$\sigma \propto \langle \Delta B^2 \rangle^{1/2} \propto 1/\lambda^2 \propto n_s/m^*$

σ: μSR Relaxation ra

TF-μSR for determining superconducting gap symmetry

Temperature dependence of Penetration depth λ related to the quasiparticle excitation



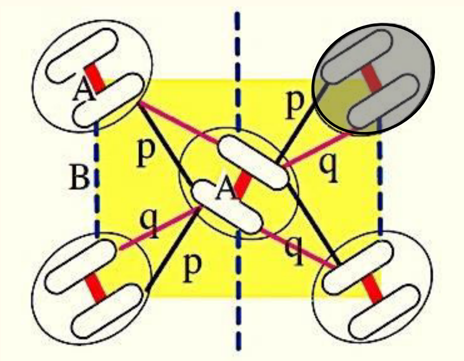


- s-wave with a full gap around Fermi surface
- Increasing of λ^{-2} just below T_C
- round shape behavior
- saturation at low temperature

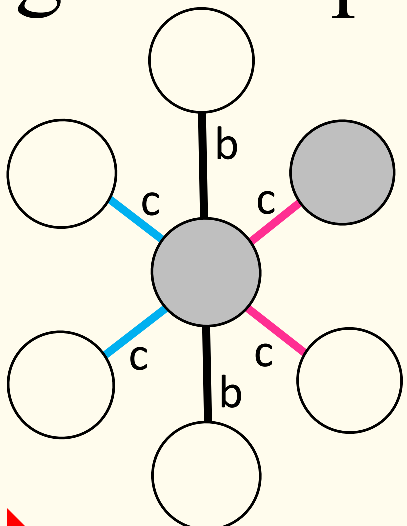
- d-wave with node at Fermi surface
- Increasing of λ^{-2} just below T_C
- linear behavior
- keep increasing at low temperature

R. P. Singh, *et al., Phys. Rev.* B **90,** 104504 (2014)
J. E. Sonier, J. H. Brewer, and R. F. Kiefl, *et al., Rev. Mod. Phys.* **72**, 769 (2000)

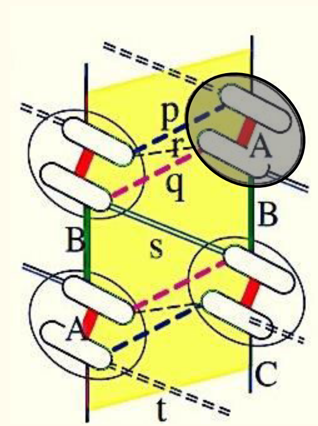
Polytypes organic superconductors



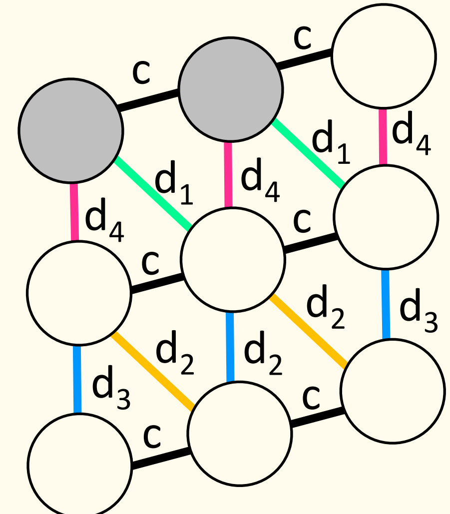
molecular
¾ – filled



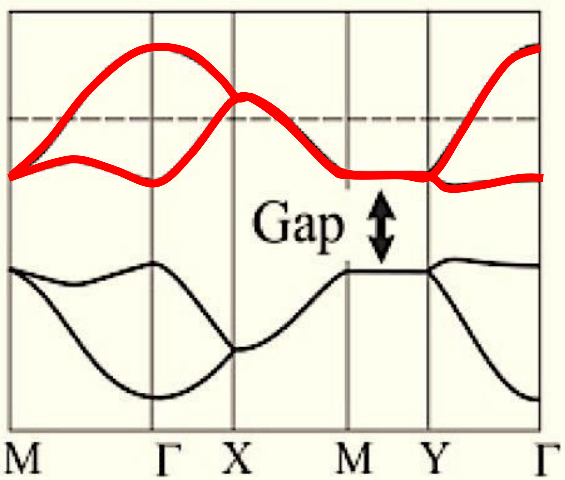
dimer
½ – filled



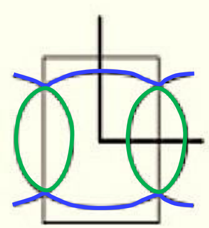
molecular
¾ – filled



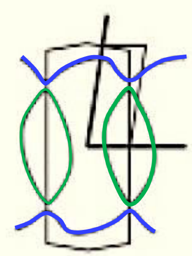
dimer
½ – filled

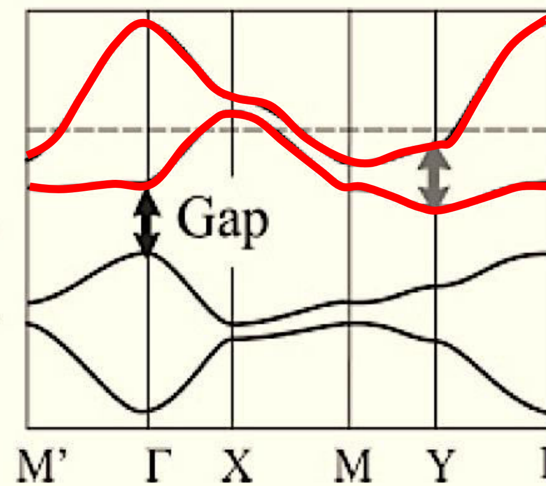


κ



λ



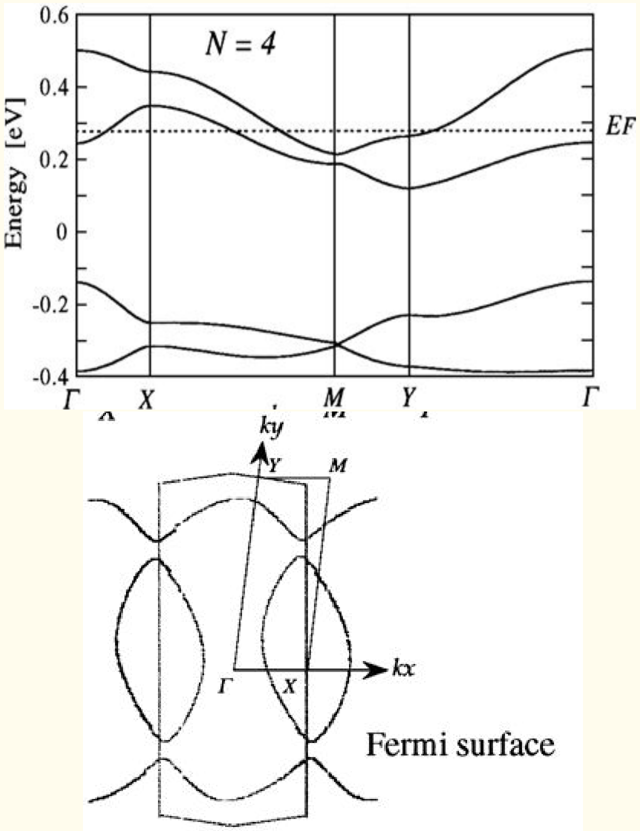


cf. Shubnikov de Haas experiment
Huckel tight binding approximation
first principle calculation

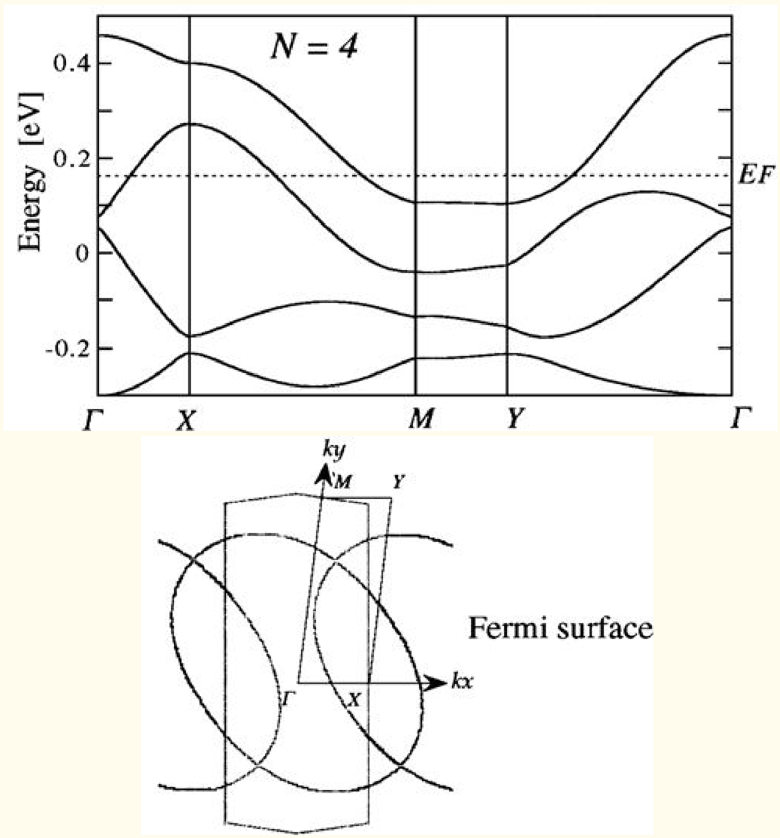
cf. Shubnikov de Haas experiment

Theoretical work
Band energy calculated by extended Hückel tight-binding appr.

“Kobayashi”



“Mori”



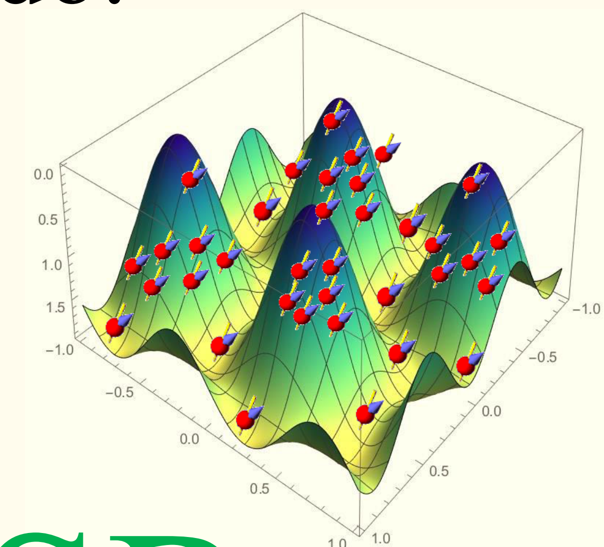
Transfer Integral *t* = -*Es* = (-10 eV) × s
s = overlap integral

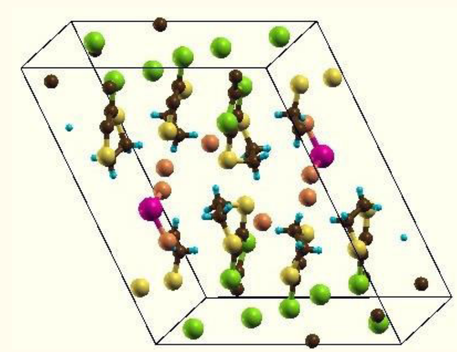
C. Hotta and H. Fukuyama, *J. Phys. Soc. Jpn.* **69**, 2577 (2000).

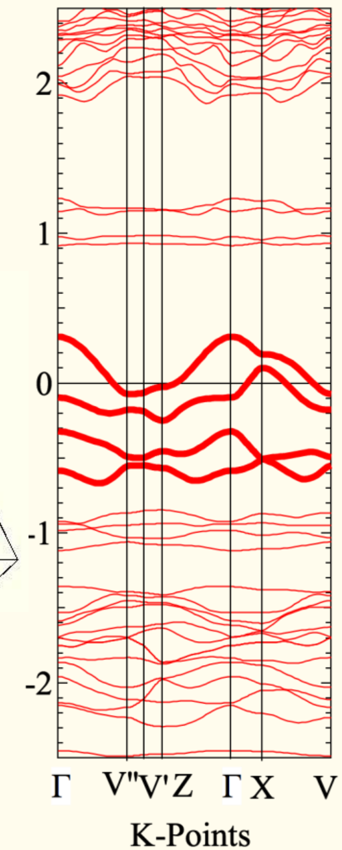
Research Purpose:

To determine superconducting gap symmetry in λ-$(BETS)_2GaCl_4$ by μSR

How to do:

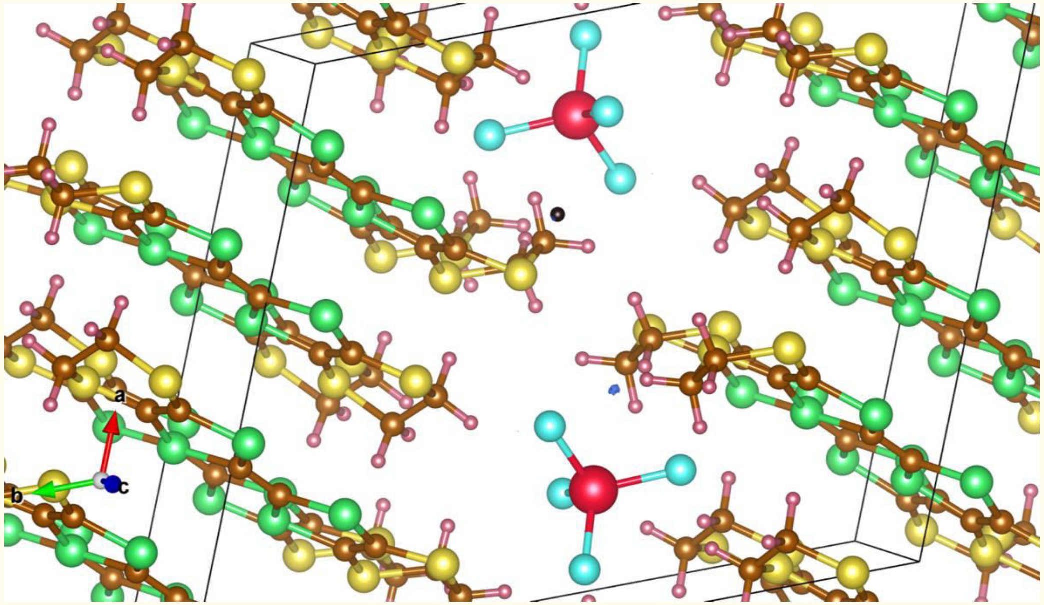






μSR + DFT

Muon Site Calculation



Minimum Potential Calculation Isosurface ~25 eV

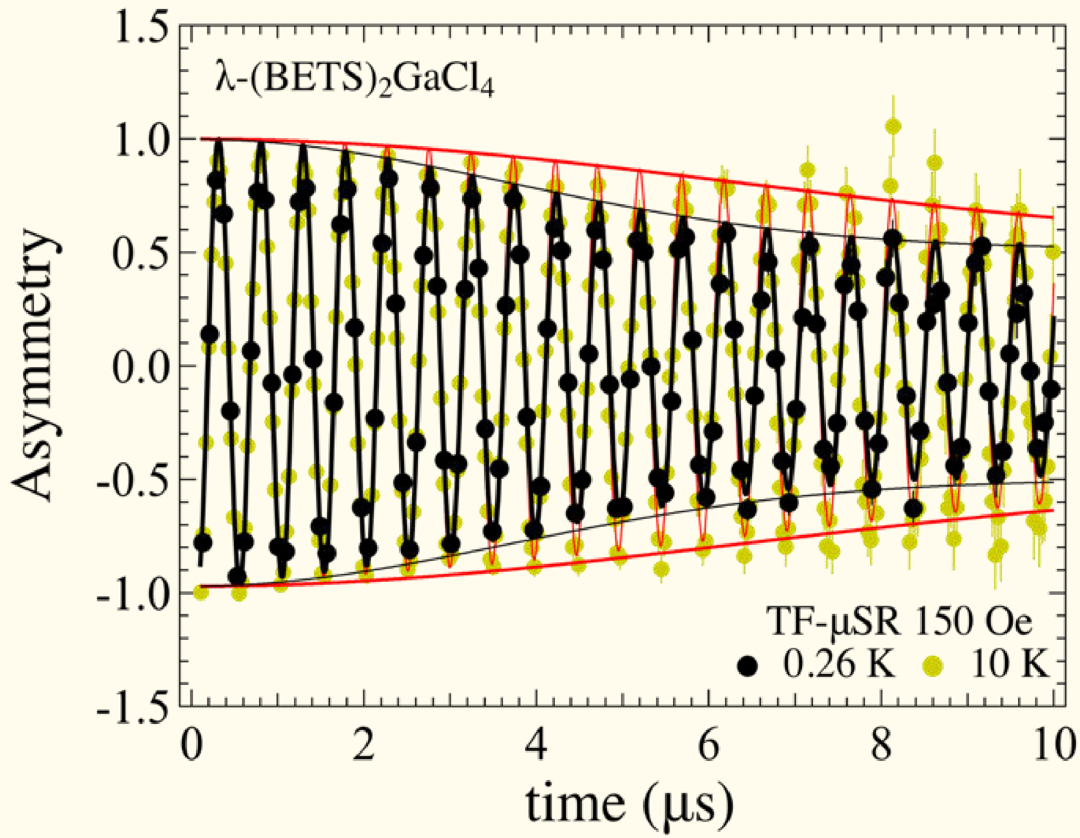
- Muon Position
  - X= 0.675
  - Y= 0.605
  - Z= 0.915

Close to the edge of BETS molecules

To determine superconducting gap symmetry in λ-$(BETS)_2GaCl_4$ by μSR and DFT

Transverse Field μSR

T_c	$H_{c1\ (T=1.8K)}$	$H_{c2\ (T=0K)}$
5.3(1) K	11(1) Oe	63(1) kOe



$$A\,(t) = 0.486\, e^{(-\sigma^2 t^2)} \cos\left(\gamma_\mu H_1 t + \phi\right) + 0.514 \cos(\gamma_\mu H_2 t + \phi)$$

Phenomenological model analysis of SUPERFLUID DENSITY

$$\frac{1}{\lambda^2} = \frac{4\pi n_s e^2}{m^* c^2} x \frac{1}{1+\xi/l}$$

$$\frac{\lambda^{-2}(T)}{\lambda^{-2}(0)} = 1 + \frac{1}{\pi}\int_0^{2\pi}\int_{\Delta(\varphi,T)}^{\infty}\left(\frac{\partial F}{\partial E}\right)\frac{E}{\sqrt{E^2 - \Delta_i^2(\varphi,T)}}dEd\varphi$$

- Numerical Fitting
- $F = \frac{1}{1+\exp(E/k_B T)}$ Fermi function
- $\Delta_i(\phi,T) = \Delta_{0,i}\Gamma(T/T_C)g(\phi)$ Δ_i: gap function; i: index of component; $\Delta_{0,i}$:gap amplitude

$\Gamma(T/T_C)\Delta(\varphi,T) = tanh\{1.82[1.018(^{T_C}/_T - 1)]^{0.51}\}$ BCS Approximation

T_C = 5.3 K

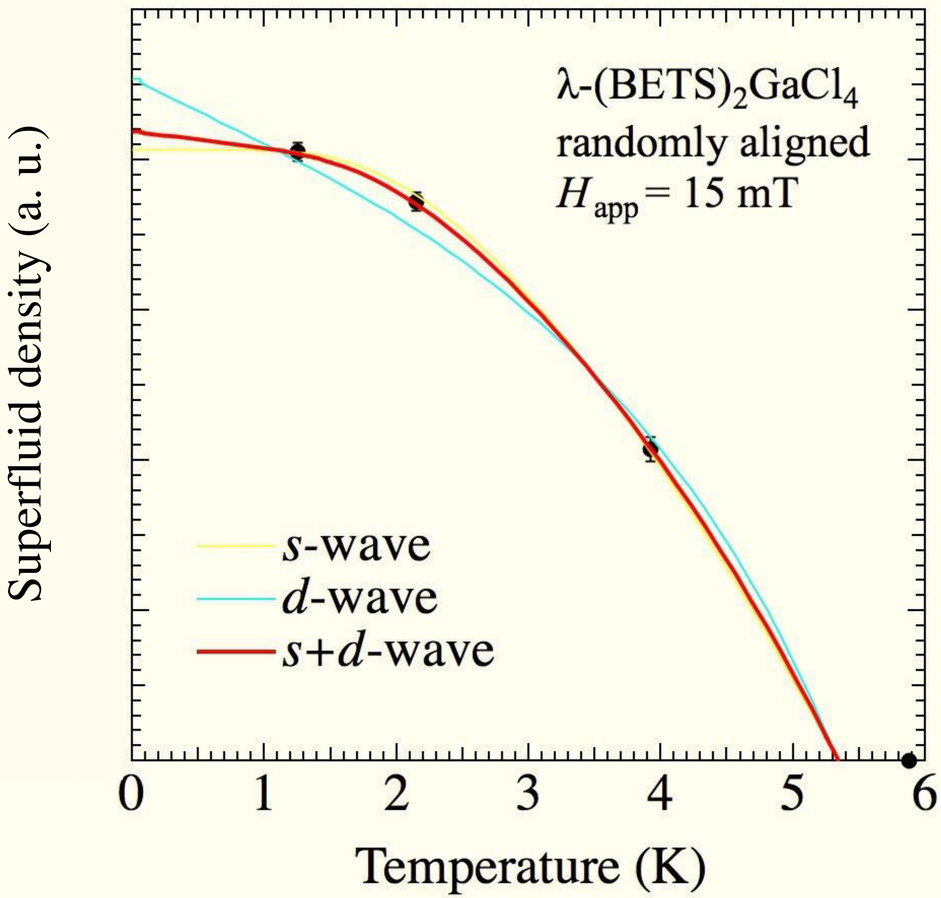
$g(\phi) = 1$	for *s* – wave
$g(\phi) = \cos(2\phi)$	for *d* – wave
$g(\phi) = 1 + a\cos(4\phi)$	for *anisotropic s*–wave

S. Chandrasekhar and D. Einzel, Ann. Phys. **505**, 535 (1993) A. Suter and B. M. Wojek, Physics Procedia **30** 69 (2012)
A. Carrington and F. Manzano, Physica C **385,** 205 (2005)

How is the gap symmetry?

neither simple *s–wave* nor simple *d*–wave

s+d wave model best explained the μSR results



$\lambda(0)$	691(7) nm
s-wave	71.4%
d-wave	28.6%
T_c	5.3(1) K
Reduced χ^2	1.19
P-value	0.016

D. P. Sari, Ph. D. Thesis, Osaka University March 2018
D. P. Sari *et al.*, in preparation

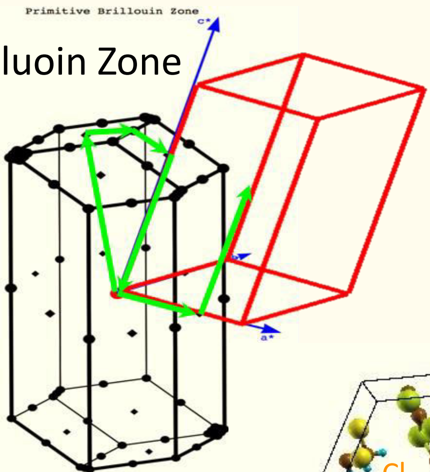
s+d–wave??

How can we understand from theoretical view point?

DFT calculation

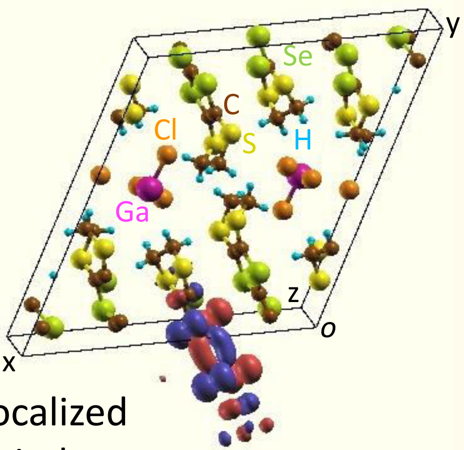
Band Structure

Brillouin Zone

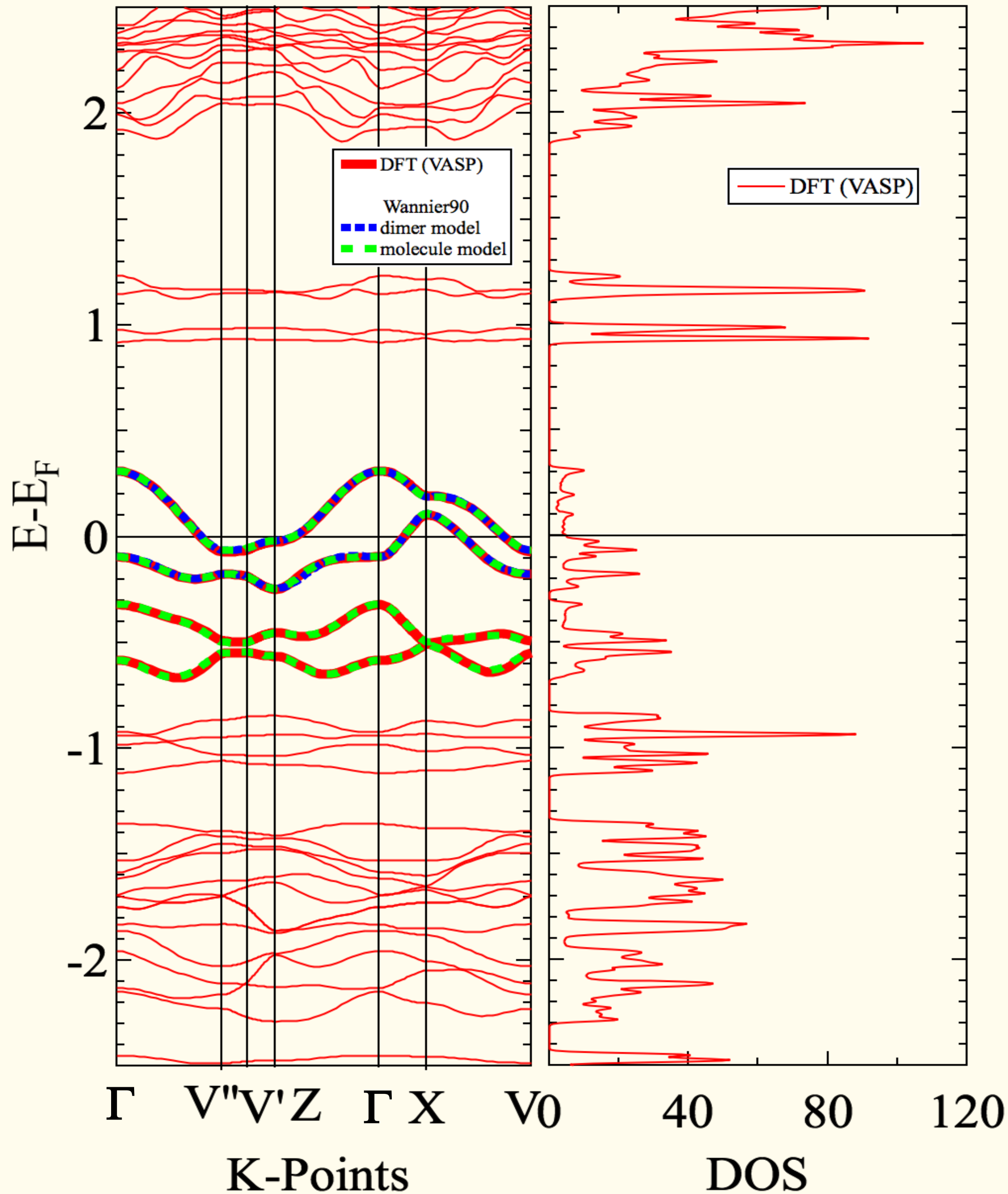


k-Path Selection

unit cell



Maximally localized Wannier Orbital



Calculation condition:

VASP 5.3

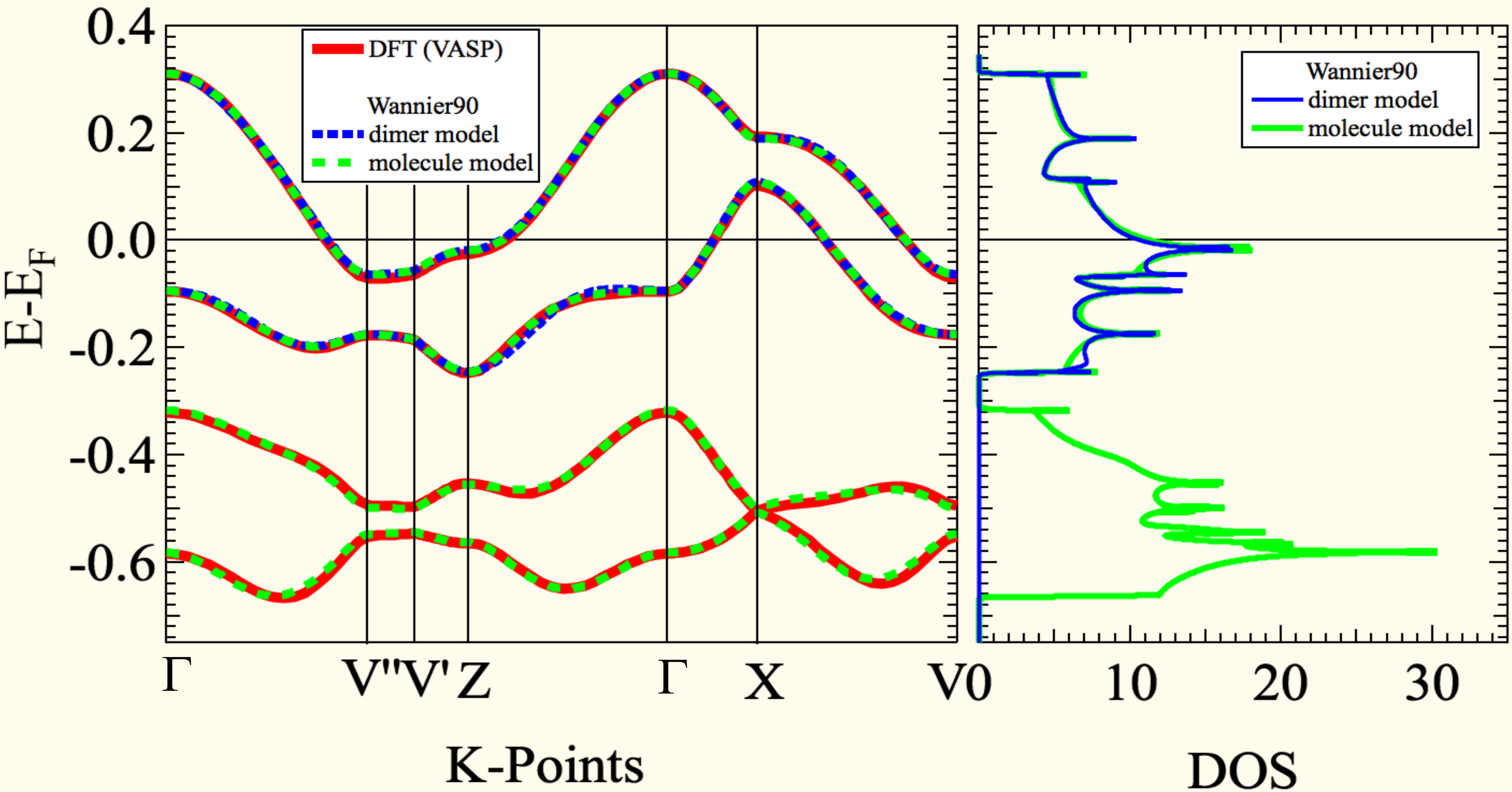
GGA Pseudopotential

4x4x4 *k*-point sampling

Cutoff energy = 500 meV

Wannier90

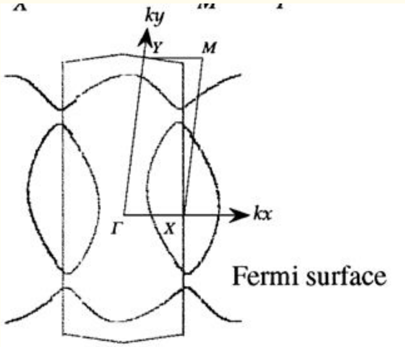
Band Structure, DOS

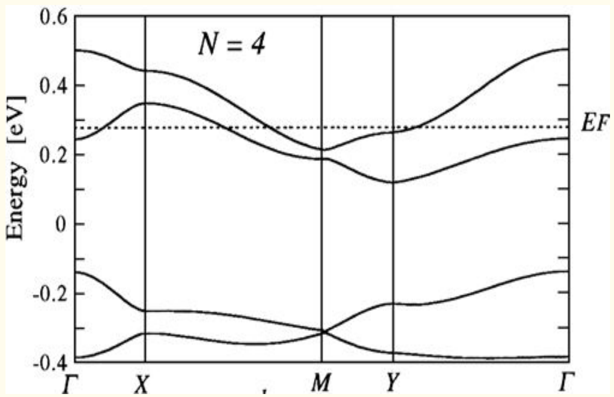


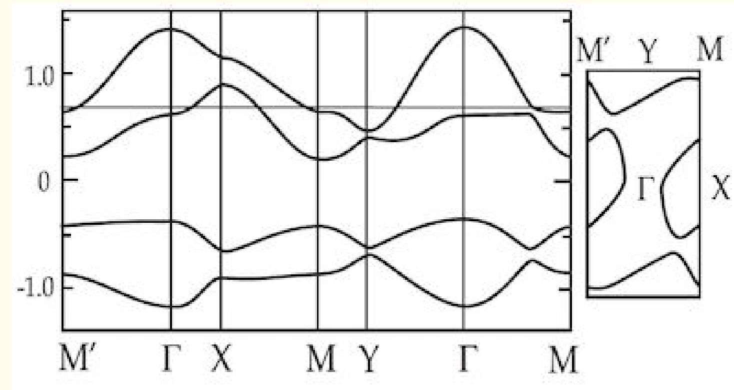
Flat band at the Z-point gives rise to the large DOS around the Fermi surface

Comparison to the extended Hückel tight-binding appr.

“Kobayashi”



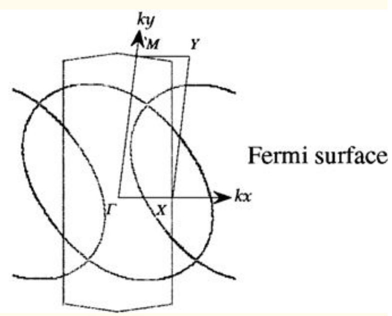


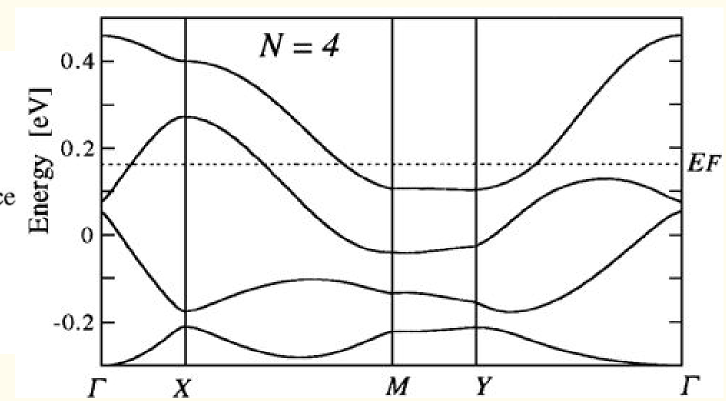


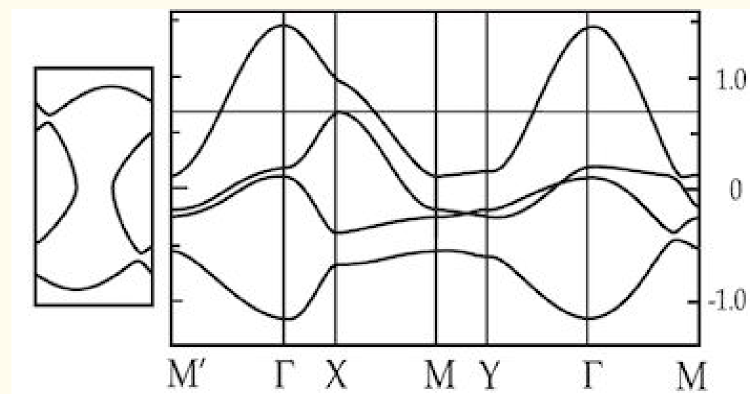
molecular

dimer

“Mori”







molecular

dimer

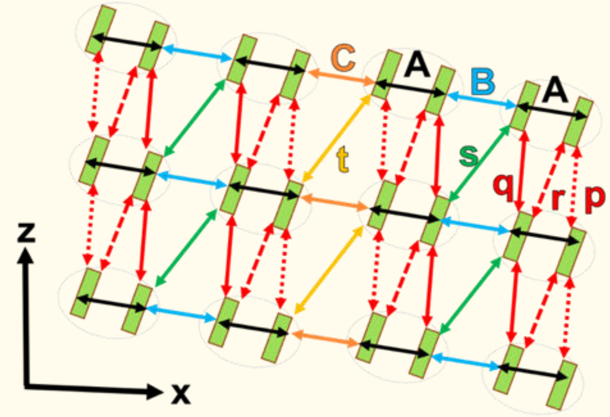
Dimer approximation does not hold

C. Hotta, *J. Phys. Soc. Jpn.* **72**, 840 (2003).

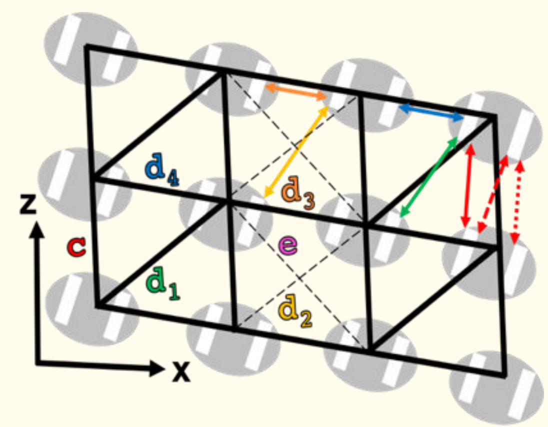
Transfer integrals

Dimer approximation

	Transfer Integral t (meV)	Mori-Katsuhara	Kobayashi et al	DFT (VASP) Wannier 4-band	DFT (VASP) Wannier 2-band
MOLECULAR MODEL (4-BAND)	A	336	238	**235**	
	p	28	13	**15**	
	q	93	31	**59**	
	r	130	37	**64**	
	s	-171	-48	**-81**	
	t	-26	-4	**-16**	
	C	-148	-57	**-137**	
	B	-183	-98	**-129**	
DIMER MODEL (2- BAND)	c	126	41	69	**64**
	d_1	86	24	40	**52**
	d_2	13	2	8	**13**
	d_3	74	29	69	**76**
	d_4	96	49	65	**64**
	e				**-17**



Molecular 4-band model



Dimer 2-band model

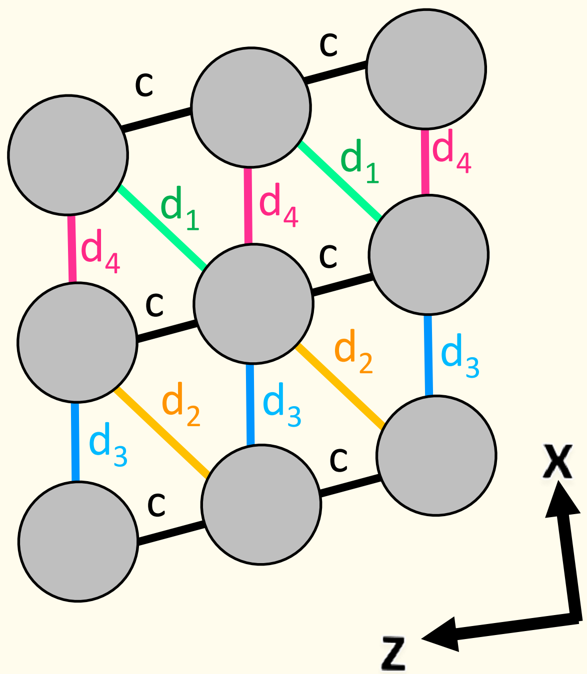
Dimer approximation:

$t_c = \frac{1}{2}(t_p + t_q + t_r)$, $t_{d4} = -\frac{1}{2} t_B$, $t_{d1} = -\frac{1}{2} t_s$,

$t_{d2} = -\frac{1}{2} t_t$, $t_{d3} = -\frac{1}{2} t_C$

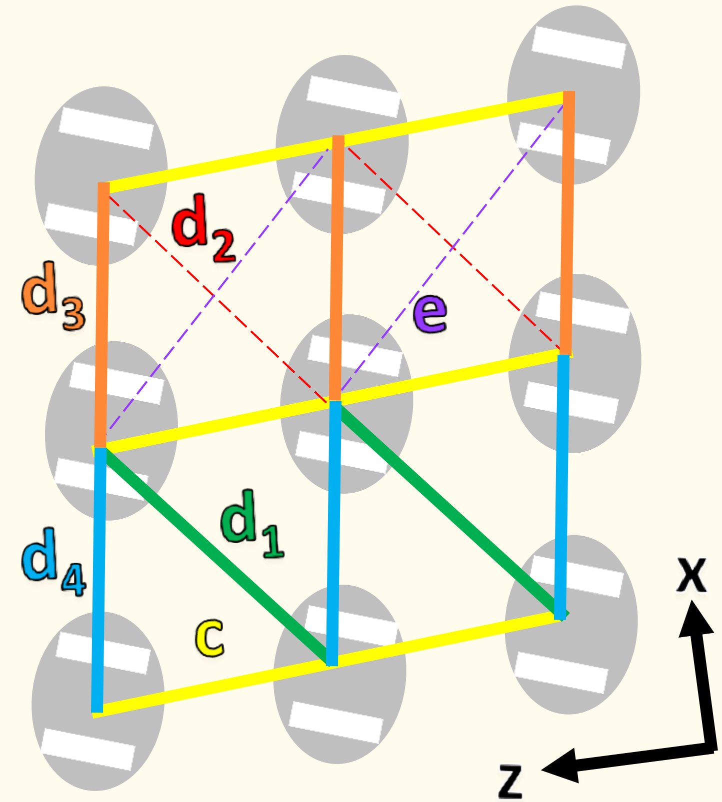
C. Hotta, *J. Phys. Soc. Jpn.* **72**, 840 (2003)

Transfer integrals



t_c, t_{d1}, t_{d2}, t_{d3}, t_{d4}

anisotropic triangular lattice

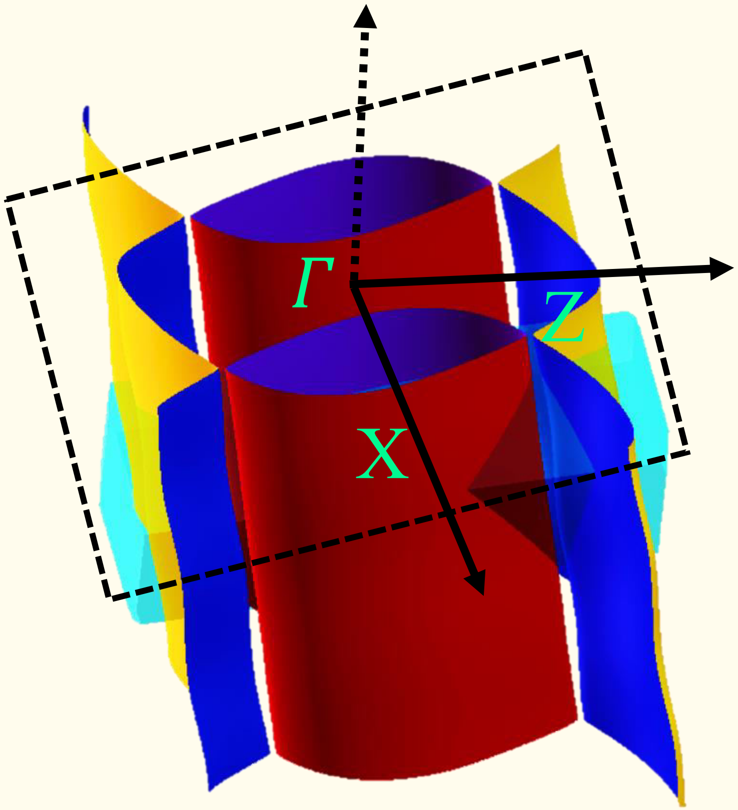


t_c, t_{d1}, t_{d2}, t_{d3}, t_{d4}, t_e

DFT calculation dimer 2-band model

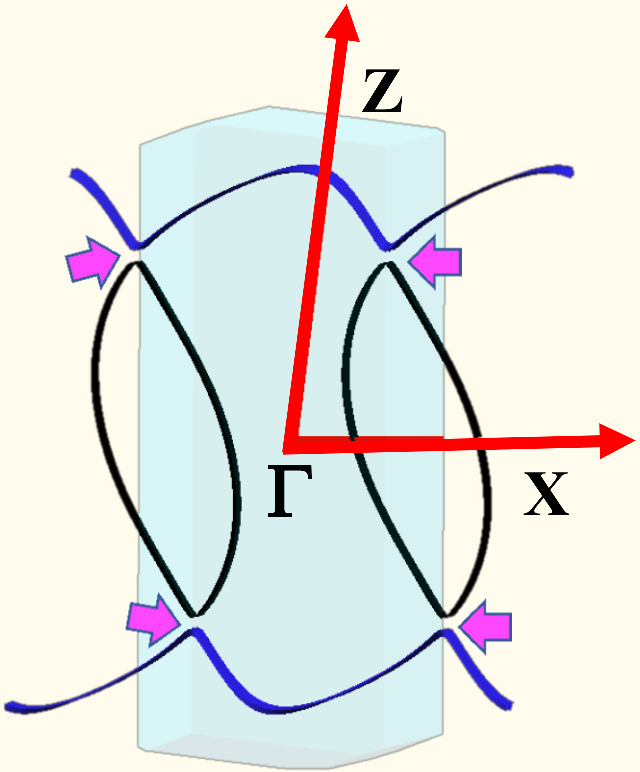
C. Hotta, *J. Phys. Soc. Jpn.* **72**, 840-853, (2003)

Fermi Surface



$51 \times 51 \times 51$
grids

in Brilluoin zone



Point-like gaps, low crystal symmetry

Not simple gap structure neither *s* nor *d* (mixed) is expected

Work done by H. Aizawa – Kanagawa Univ

Random Phase Approximation

Spin Fluctuation mediated superconductor

Spin-singlet channel

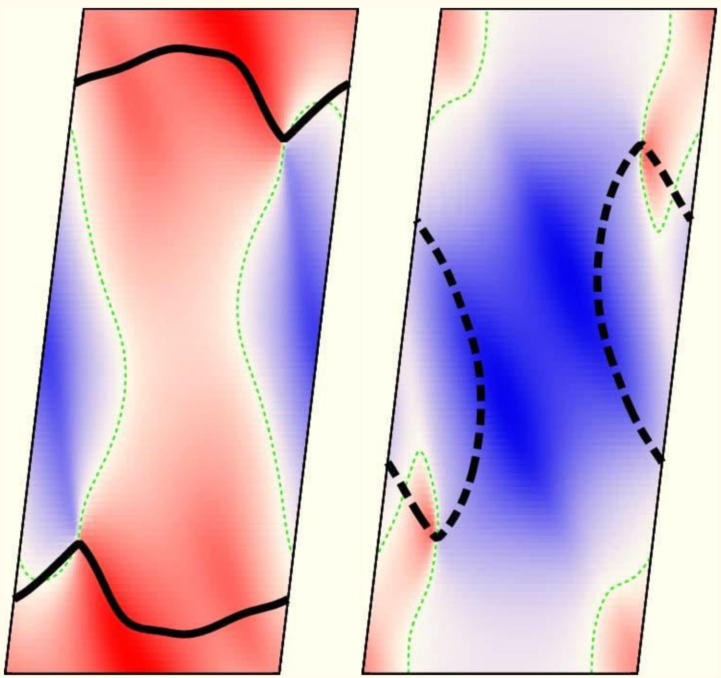
Hubbard Hamiltonian

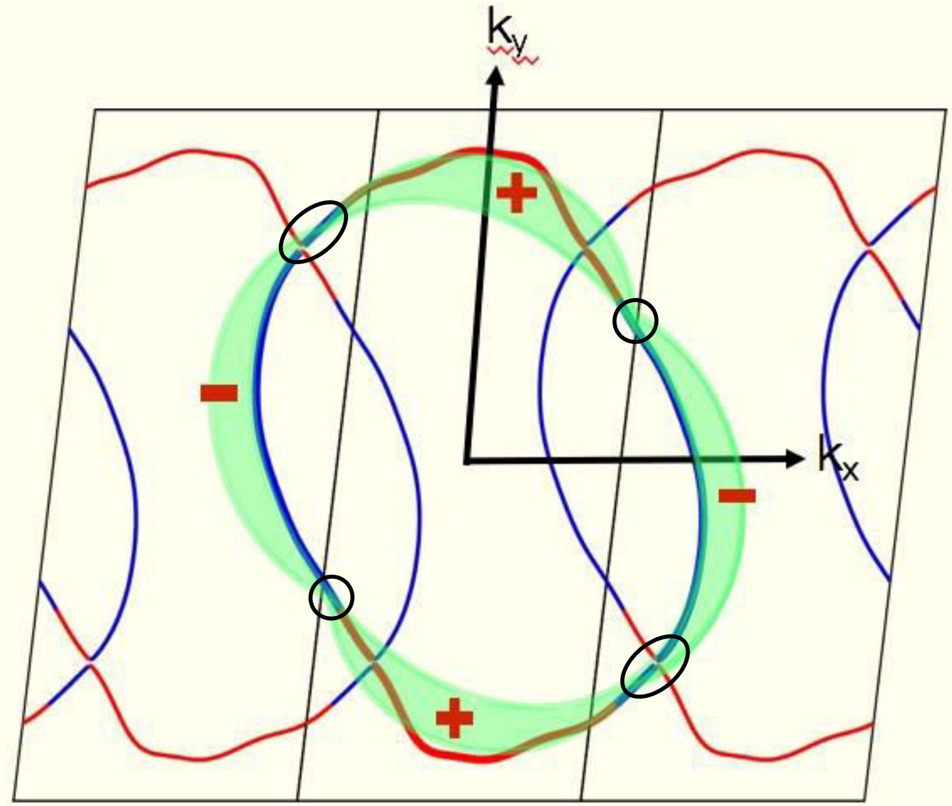
Dimer 2-band model

$$H = \sum_{\langle i,j \rangle} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_{i} U n_{i\uparrow} n_{i\downarrow}$$

t_{ij} from DFT calculations

Spin-singlet gap function in ***k***-space



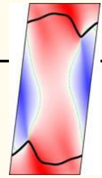
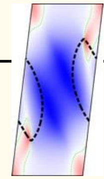


The SC gap phase changes its sign, but has the same sign within the same Fermi surface

D. P. Sari, Ph. D. Thesis, Osaka University March 2018

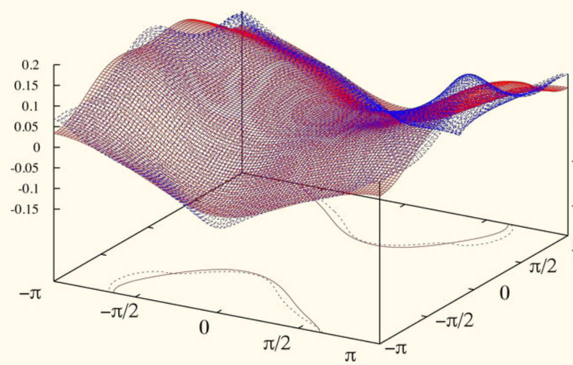
H. Aizawa *et al*., J. Phys. Soc. Jpn. **87**, 093701 (2018)

Work done by H. Aizawa – Kanagawa Univ

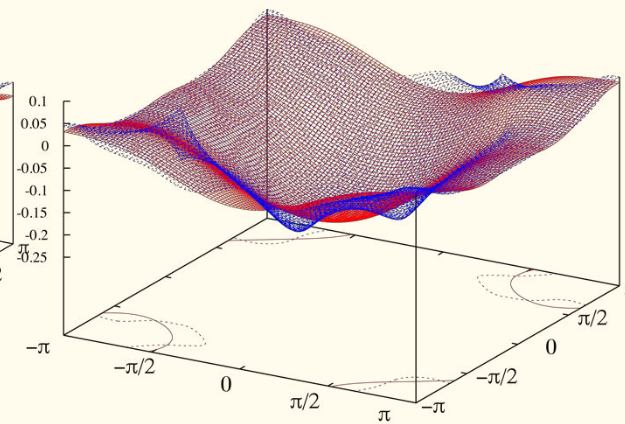
band-index α	α=1 	α=2 
$C^{\alpha}{}_{s0}$	**0.0308**	**-0.0666**
$C^{\alpha}{}_{s1}$	-0.0025	**-0.0303**
$C^{\alpha}{}_{s2}$	0.0025	-0.0061
$C^{\alpha}{}_{dx2\text{-}y2}$	**-0.0261**	-0.0037
$C^{\alpha}{}_{dxy}$	0.0064	-0.0040

Finite $d_{x^2-y^2}$ - wave component
Extended s-wave component

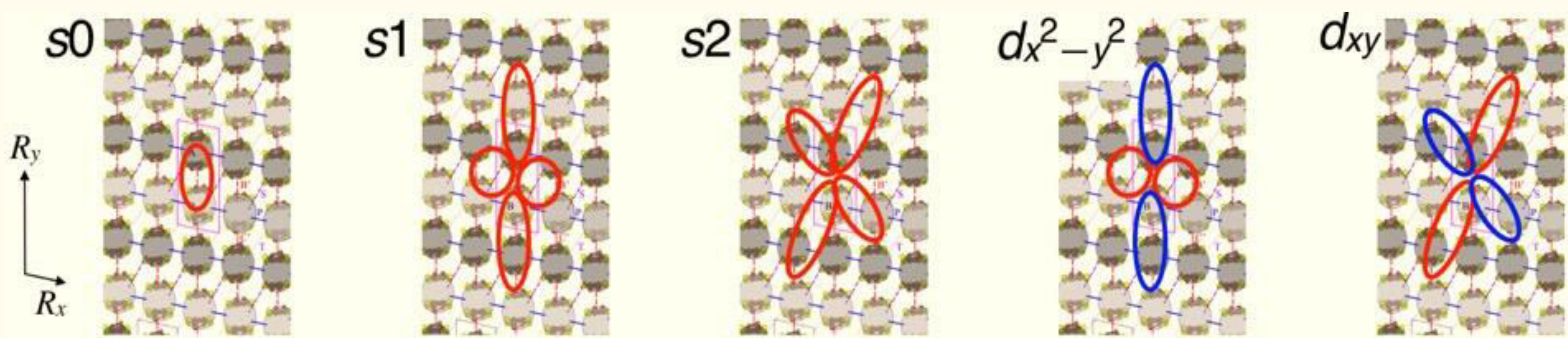
α=1



α=2



Gap function around the Fermi surface
red: RPA results, blue: fitting



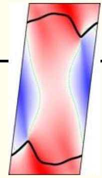
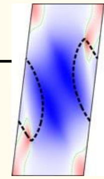
Basis function defined in the k-space:

- Isotropic *s*-wave: $f_{s0}(k_x, k_y) = 1$
- extended s_1-wave: $f_{s1}(k_x, k_y) = 2\left[\cos(k_x) + \cos(k_y)\right]$
- extended s_2-wave: $f_{s2}(k_x, k_y) = 2\left[\cos(k_x + k_y) + \cos(k_x - k_y)\right]$
- $d_{x^2-y^2}$-wave: $f_{d_{x^2-y^2}}(k_x, k_y) = 2\left[\cos(k_x) - \cos(k_y)\right]$
- d_{xy}-wave: $f_{d_{xy}}(k_x, k_y) = 2\left[\cos(k_x + k_y) - \cos(k_x - k_y)\right]$

The gap function then was fitted by

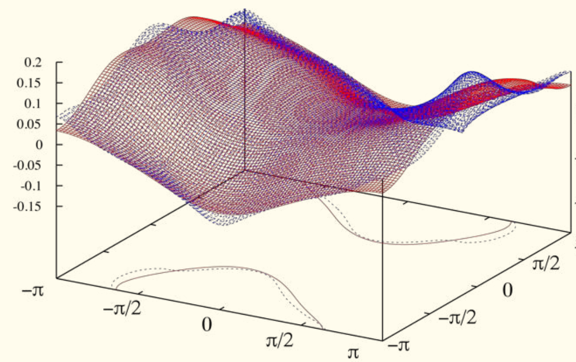
$$\frac{\Delta^{\alpha}(k_x, k_y)}{\Delta_0} = C^{\alpha}_{s0} f_{s0}(k_x, k_y) + C^{\alpha}_{s1} f_{s1}(k_x, k_y) + C^{\alpha}_{s2} f_{s2}(k_x, k_y) + C^{\alpha}_{d_{x^2-y^2}} f_{d_{x^2-y^2}}(k_x, k_y) + C^{\alpha}_{d_{xy}} f_{d_{xy}}(k_x, k_y) + \cdots \text{ (up to } N = 25 \text{ neighbors)}$$

Work done by H. Aizawa – Kanagawa Univ

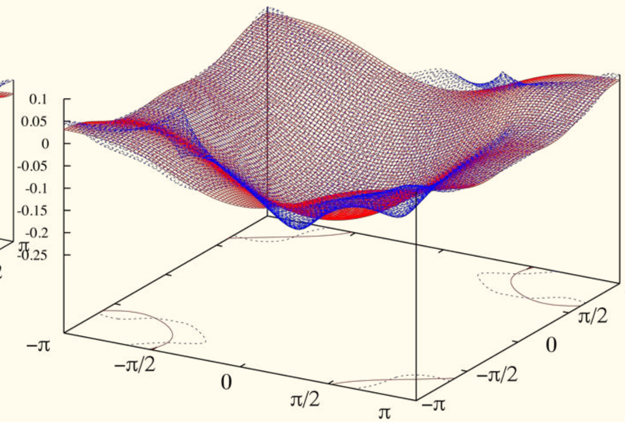
band-index α	α=1 	α=2 
$C^{\alpha}{}_{s0}$	**0.0308**	**-0.0666**
$C^{\alpha}{}_{s1}$	-0.0025	**-0.0303**
$C^{\alpha}{}_{s2}$	0.0025	-0.0061
$C^{\alpha}{}_{dx2-y2}$	**-0.0261**	-0.0037
$C^{\alpha}{}_{dxy}$	0.0064	-0.0040

Finite $d_{x^2-y^2}$ - wave component
Extended s-wave component

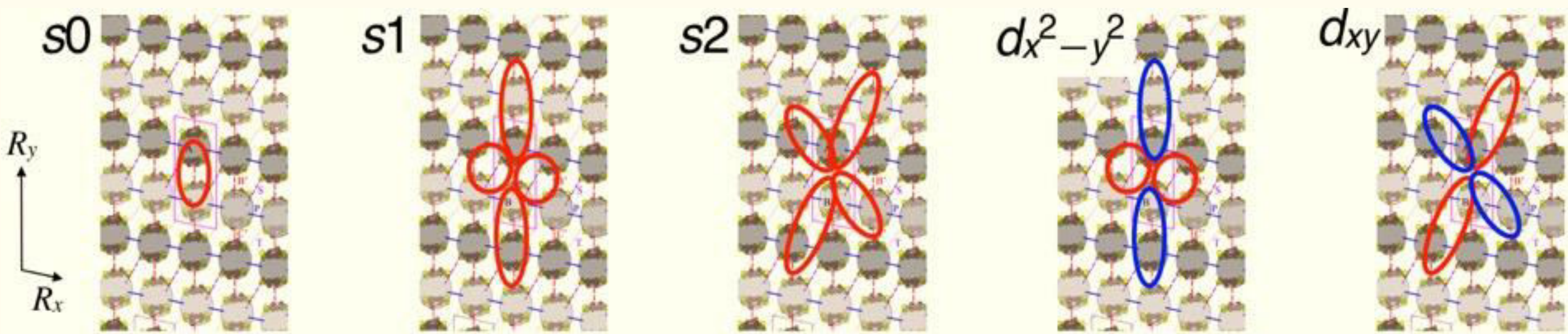
α=1



α=2



Gap function around the Fermi surface
red: RPA results, blue: fitting



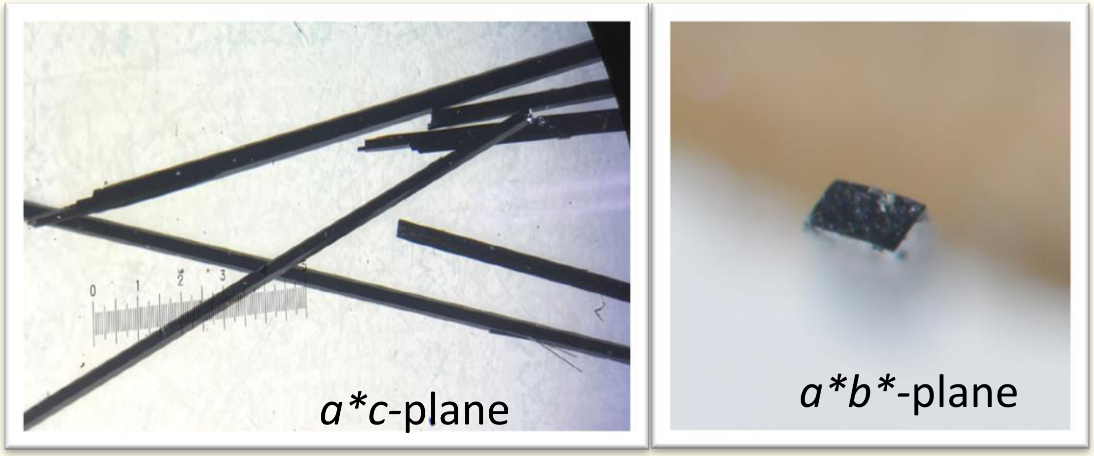
Summary:

1. μSR result of London penetration depth is well explained by *s*+*d*-wave gap symmetry.

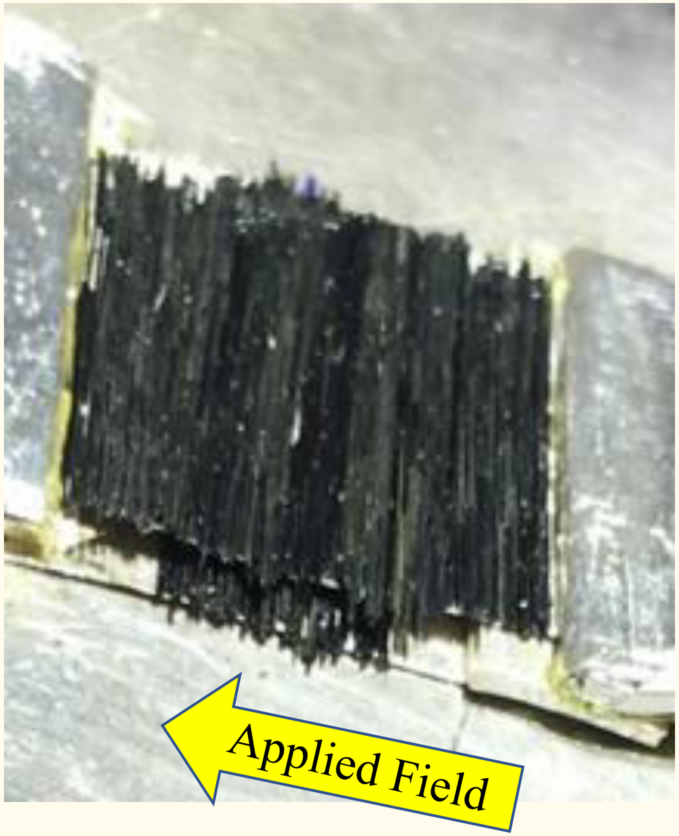
2. From the DFT and RPA calculations, it is revealed that the superconducting phase is changing a sign along the extended Brilluoin zone but does not change sign within the same Fermi surface → give rise to that a large *s*-wave component.

3. Next step → Single crystal alignment measurement

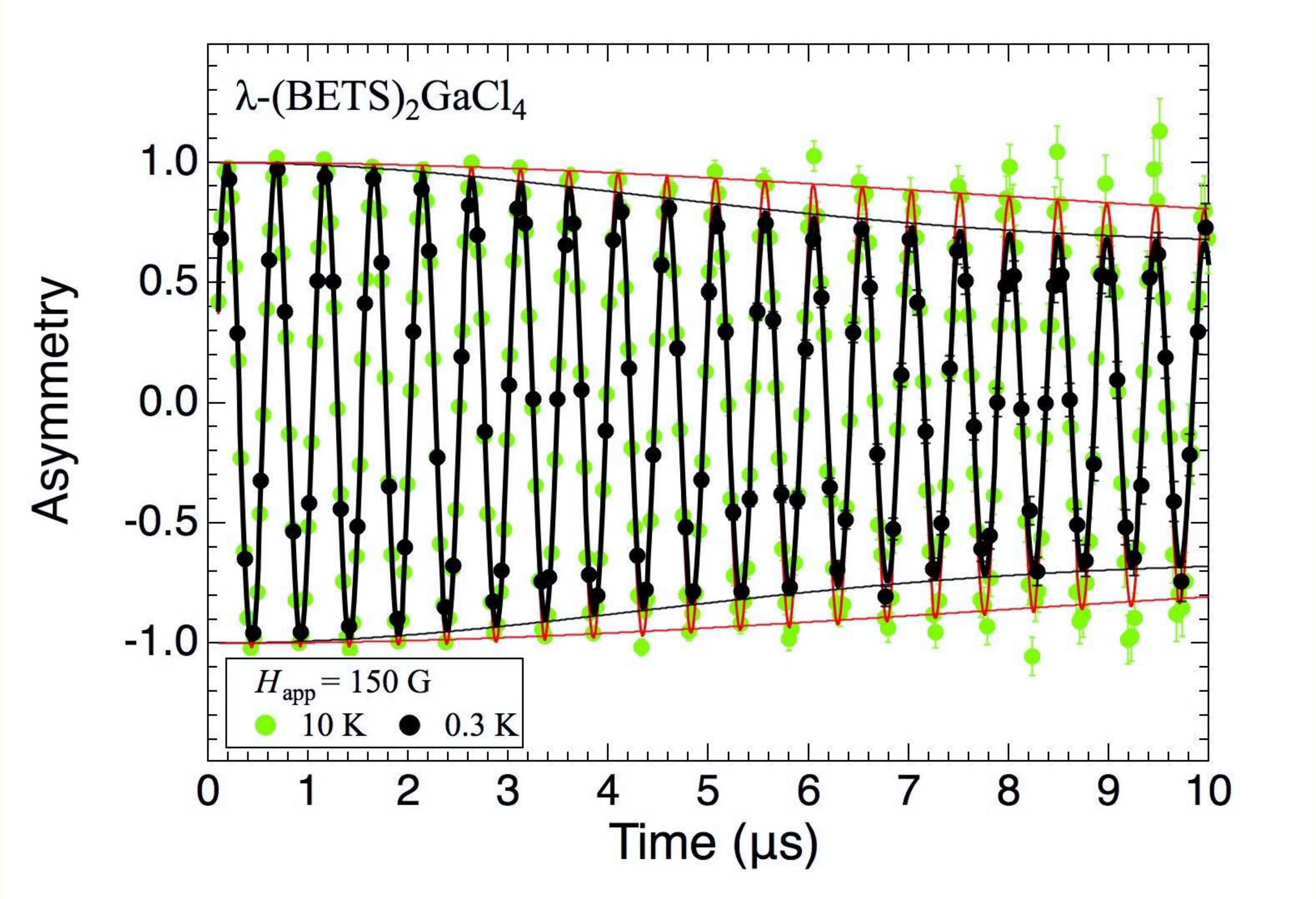
Aligning the single crystals



Typical crystals
Champion crystal: 0.3 x 0.22 x ~6 mm



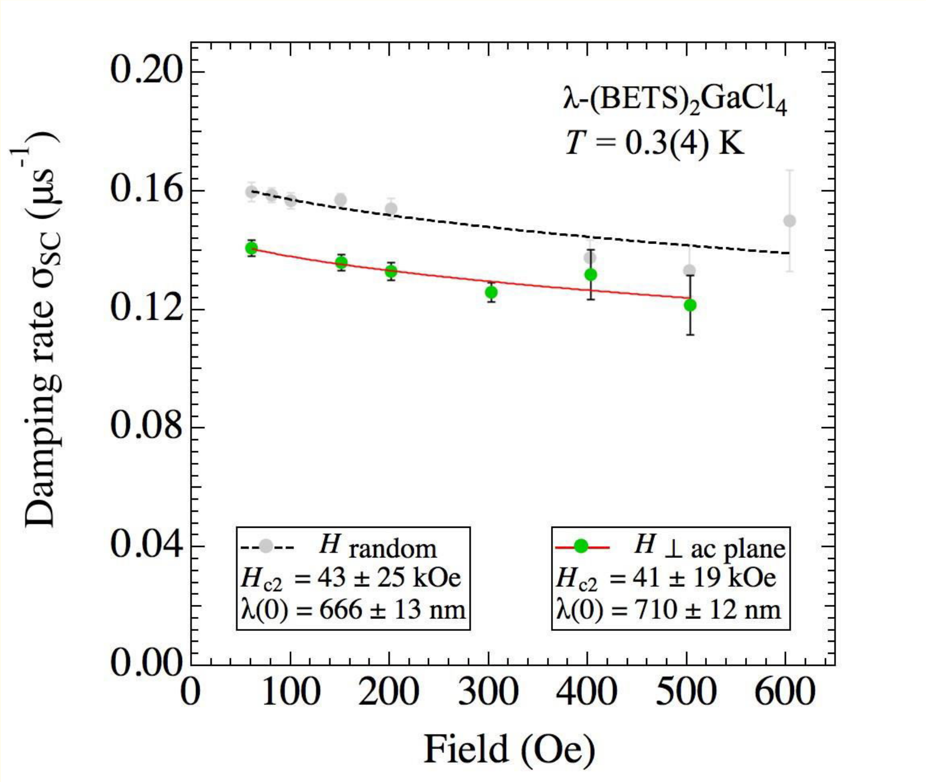
Time Spectra

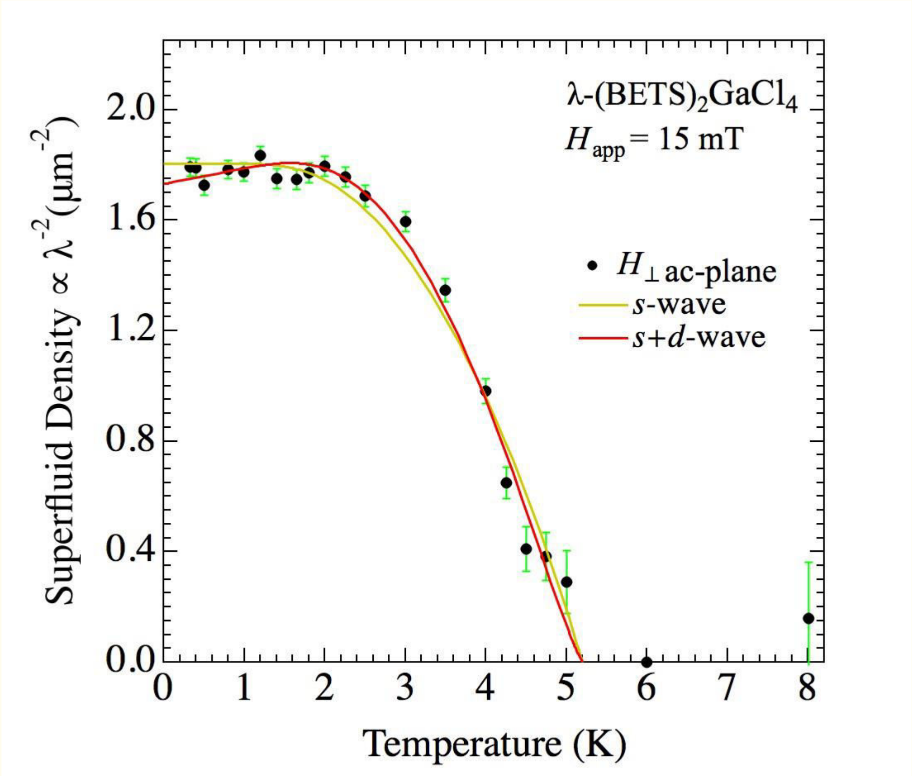


$$A_{(t)} = 0.3438\, e^{(-(\sigma t)^2)} \cos\left(\gamma_\mu H_{int_1\,(sample)} t + \phi\right)$$

$$+\, 0.6562\, \cos\left(\gamma_\mu H_{int_2\,(Ag\ foil)} t + \phi\right)$$

Temperature Dependence





$$\sqrt{2}\,\sigma_{SC}(H) = 4.83\ \times 10^4 \times\left(1-\frac{H_{app}}{H_{c2}}\right)\left[1+1.21\left(1-\sqrt{\frac{H_{app}}{H_{c2}}}\right)^3\right]\lambda^{-2}$$

where σ_{SC} is in μs^{-1} and λ is in nm

I need further investigation (another crystal orientation?)
I do need the SuperMUSR

COLLABORATION

Experiment

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