Ultra-high-resolution photoemission study of superconductors and strongly correlated materials using quasi-CW VUV laser

S. Shin,1,2 T. Kiss,1 S. Tsuda,1 K. Ishizaka,1 T. Yokoya,1 and T. Togashi,2 C. Chen,3 S. Watanabe1

1Institute for Solid State Physics, University of Tokyo
2RIKEN
3Beijing Center for Crystal R&D, Chinese Academy of Science
Research of Superconductors by PES

Resolution Temperature

100 meV

HgCaBaCuO 133K

100K

10 meV

MgB₂ 39K

High T_c’s

Simple metal

Metal alloy

Borocarbide

10K

1 meV

LiTi₂O₄ 13.7K

κ-(ET)₂Cu[N(CN)₂]Br 11.6K

Transition metal oxide

Organic molecular

1K

p, d, f-wave superconductor

100 μeV

CeRu₂ 6.0K

0.1K

10 μeV

Heavy fermions

Target of this study
1. Development of Laser photoemission system
   • High resolution Photoelectron analyzer
   • Quasi-CW VUV laser
   • Low temperature Cooling system

2. High resolution PES study on superconductors
   Nb ; simple metal superconductor
   CeRu$_2$ ; 4f electron superconductor with Onuki et al
   MgB$_2$ ; intermetallic compound with Tajima et al
   -(ET)$_2$Cu[N(CN)$_2$]Br ; organic superconductor with Kanoda et al
   -(ET)$_2$Cu (SCN)$_2$

3. High resolution PES study on Kondo material
   LiV$_2$O$_4$ ; Kondo state in TMO with Ueda et al

4. Bulk sensitive PES in low photon energy region
   SrVO$_3$ ; comparison with DMFT with Inoue et al

5. Conclusion and Future of Laser-Photoemission
What limits the photoemission resolution?

1. Line width of light source
2. Electron analyzer
   - Slit width
   - Engineering precision
   - Disorder of work function
   - Instability of power source
3. Residual magnetism
4. Ripple in ground level
5. Space charge effect

- It will be settled by developing laser
- They have been resolved. Recent progress is in energy region below 1 meV
- CW or quasi-CW light source should be necessary (= weak peak intensity, but strong average intensity)

Space charge effect by pulsed light
Laser system

6th harmonic (6.994eV) of Nd:YVO₄ laser using KBBF crystal

## Specification of new Laser

### Highest photon energy quasi CW Laser

<table>
<thead>
<tr>
<th>Laser</th>
<th>HeIα</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photon energy</td>
<td>6.994eV</td>
</tr>
<tr>
<td>FWHM</td>
<td>0.26meV (0.09meV with etalon)</td>
</tr>
<tr>
<td>Frequency</td>
<td>80MHz (quasi CW)</td>
</tr>
<tr>
<td>Total Photon flux</td>
<td>2.2x10^{15} photons/sec</td>
</tr>
<tr>
<td>polarization</td>
<td>vertical, horizontal, circular</td>
</tr>
<tr>
<td>Size of spot</td>
<td>0.2µm – 0.5mm</td>
</tr>
</tbody>
</table>

**Microscopy**
- Bulk sensitive
- High energy resolution
- Polarization dependent
- Low damage of sample

Photon flux of SR is weak, and becomes weak in proportion to the increase of the monochromator resolution

Cf. \( \sim 10^9 \) phs./sec (1 meV resolution at 100eV)
Laser excitation photoemission spectrometer

Gammadata-R4000 analyzer

Sample chamber

Cryopump

Laser

Mirror

Lens

Sample bank

Mirror

Cryostat

XYZ stage

Preparation chamber

Mirror

SHG crystal

Lens
Performance of the experimental system

Au
T = 5.3 K
He Iα (21.218 eV)
(SES2002)

Resolution 1.4 meV

Intensity (arb. units)
Binding energy (meV)

Au
Laser
hv = 6.994 eV
(R4000)
T = 2.9 K

ΔE = 360 μeV

Intensity (arb. units)
Binding energy (meV)
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5. Conclusion and Future of Laser-Photoemission
We can measure superconducting gap without clean surface
Another example
Without surface cleaning, we can measure superconducting gaps of new materials whose crystal size is quite tiny.

$KO\text{S}_2\text{O}_6$

As-grown surface!

Hiroi Group (2003)
- Geometrically Frustrated Pyrochlore
- Unconventional superconductor?
Laser-PES is the most bulk sensitive PES

Electron escape depth

Electron kinetic energy (eV)

New VUV laser PES

SPRING-8

VUV-SX SR ring

He Iα

Hard X-ray PES

VUV laser

Hundred
CeRu$_2$

1. Valence fluctuation \( (T_K>1000\text{K}) \), Ce valence ~ 3.7
2. Superconductor that has the highest Tc = 6.2K in Ce compounds

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(\frac{2\Delta(0)}{k_B T_C})</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Break-junction $^1$</td>
<td>4.1-4.4</td>
<td>s-wave</td>
</tr>
<tr>
<td>NMR $^2$</td>
<td>4</td>
<td>s-wave(anisotropic)</td>
</tr>
<tr>
<td>Specific Heat $^3$</td>
<td>3.7</td>
<td>s-wave</td>
</tr>
<tr>
<td>NMR $^4$</td>
<td>3.7</td>
<td>s-wave (large anisotropy)</td>
</tr>
<tr>
<td>STS $^5$</td>
<td>3.3-6.6</td>
<td>s-wave</td>
</tr>
<tr>
<td>Specific Heat $^6$</td>
<td>-</td>
<td>line node (largest anisotropy)</td>
</tr>
</tbody>
</table>

6) J. G. Sereni et al., Mod. Phys.Lett. 3(1989)1225
Valence band spectrum of CeRu$_2$

- Bulk sensitive in high energy region
- Bulk sensitive in low energy region
- 0.4 eV peak

Superconducting gap of CeRu$_2$

Superconducting gap was clearly observed by laser-PES

Kiss et al., PRL 94 (2005)57001
Anisotropic Superconducting gap of CeRu$_2$

Fit

$$(\Delta_{\text{max}}, \Delta_{\text{min}}, \Gamma) =$$

- (1.12, 0.50, 0.07)
- (0.98, 0.98, 0.13)
- (1.18, 0.00, 0.001)

Temperature dependence

Kiss et al., PRL 94 (2005) 57001
Superconducting gap of organic superconductor $(\text{ET})_2\text{Cu}[\text{N(CN)}_2]\text{Br}$, $(\text{ET})_2\text{Cu} (\text{SCN})_2$
d-wave superconductor?

Previous works
- No intensity at $E_F$; They look like insulators
- All the ET-materials have the similar spectra and are inconsistent with the band calculation

Why?
- Surface effect?
- or
- Electron correlation effect?

Comparison with the band calculation

\[ \text{-\textbf{(ET)}\textsubscript{2}Cu[N(CN)\textsubscript{2}]Br, \text{-\textbf{(ET)}\textsubscript{2}Cu (SCN)\textsubscript{2}}} \]

1. The band calculation has been quite important for the materials design of new organic materials

2. But bulk-sensitive PES spectra are inconsistent with the band calculation in
   - DOS
   - Fermi edge

Electron correlation effect is essential, rather than the Surface effect?

H. Mori, Private communication
By using strong laser light
- First observation of Fermi edge and superconducting gap.
- Inconsistent with band calculation

1. Low carrier density
2. Strong correlation effect
The spectrum was measured by He lamp and show the two gap structure for the first time. Tsuda et al., PRL87,17006(2001)
"sub meV" resolution spectra on MgB$_2$ by laser-PES

Carbon substitution effect

- Carbon concentration
- Strong increase of the interband coupling
- $2\Delta_L/k_B T_c \approx 4.1$
- $T_c$ increase by the interband coupling

\[
\Delta_L \leftrightarrow \sigma \text{ band}
\]

\[
\Delta_S \leftrightarrow \pi \text{ band}
\]

\[
\begin{align*}
\text{Intensity (arb. units)} & \\
\text{Binding Energy (meV)} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Mg(B$_{1-x}$C$_x$)$_2$} & \\
x = 0\% & \\
x = 2\% & \\
x = 5\% & \\
x = 7.5\% & \\
\end{align*}
\]

\[
\begin{align*}
\text{Gap size (meV)} & \\
\text{Carbon concentration (%)} & \\
\text{T}_c (K) & \\
\end{align*}
\]
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5. Conclusion and Future of Laser-Photoemission
Ultra-high resolution photoemission; Kondo peak

The case of Ce compounds

The Kondo peak becomes sharper and stronger as the temperature decreases

Hüfner, “Photoelectron spectroscopy”
Bulk sensitive spectra using VUV laser; typical coherent and incoherent peaks have been observed in Sr\textsubscript{x}Ca\textsubscript{1-x}VO\textsubscript{3} PES spectra.

FIG. 1. Top: DOS $D(\varepsilon^0)$ of CaVO\textsubscript{3} and SrVO\textsubscript{3} calculated by the APW method. Bottom: measured photoemission spectra $\rho_{\text{exp}}(\omega)$ of Ca\textsubscript{1-x}Sr\textsubscript{x}VO\textsubscript{3} taken with $h\nu = 50$ eV. A spectrum of Au is also shown as a reference to $E_F$ and the instrumental resolution.

Inoue et al., PRL74,2539(1995)

Density of states $\rho(\omega)=-\text{Im} G$ by the $d=\square$ approach at $T=0$ for the half-filled Hubbard model at $U/t^*=1$, 2, 2.5, 3, and 4 from top to bottom. The calculation is done by iterative perturbation in terms of $U$. The bottom one ($U/t^*=4$) is an insulator.

Georges, Kotliar, Krauth, and Rozenberg, PRL1996.
Photon-energy dependence of the V 3d spectral weights for Sr$_{1-x}$Ca$_x$VO$_3$. The V 3d spectra are normalized by the integrated intensities of the incoherent part ranging from 0.8 to 2.6 eV.


What happens in the bulk sensitive spectra using VUV laser?

- More bulk sensitive
- Much higher resolution

- Incoherent peak becomes weak in SX PES
- CaVO$_3$ and SrVO$_3$ spectra are similar in SX PES
Excitation energy dependence of coherence peak

Contrary to the SX spectra, coherent peaks become weaker
The temperature dependence is well reproduced by the Surface and Bulk spectra.

\[ I(E) = \exp\left(-\frac{s}{\lambda}\right) I_{\text{bulk}}(E) + \left[1 - \exp\left(-\frac{s}{\lambda}\right)\right] I_{\text{surface}}(E) \]

where:
- \( I(E) \) is the intensity as a function of binding energy.
- \( s \) is the thickness of the surface layer.
- \( \lambda \) is the mean free path.

Parameters:
- SrVO\(_3\)
  - \( s = 5 \) Å
  - \( E = \{21.218, 13.7, 9.18, 6.994\} \) eV
- CaVO\(_3\)
  - \( s = 5 \) Å
  - \( E = \{21.218, 13.8, 9.2, 6.994\} \) eV

<table>
<thead>
<tr>
<th>( E(\text{eV}) )</th>
<th>( \lambda(\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.218</td>
<td>3</td>
</tr>
<tr>
<td>13.8</td>
<td>6</td>
</tr>
<tr>
<td>9.2</td>
<td>20</td>
</tr>
<tr>
<td>6.994</td>
<td>100</td>
</tr>
</tbody>
</table>

\( d_{x^2-y^2}(\text{surface}) \) and \( d_{xy}(\text{bulk}) \) represent the coherent part.
Summary

- Development of Quasi CW VUV-laser ;
  Highest $h\nu$ of 7eV with 0.26meV line width

- Development of analyzer with high energy resolution at low temperature ;
  Highest energy resolution of 0.36 meV, Lowest temperature of 2.7K

- Laser PES is powerful for the study on low Tc superconductors and strongly correlated materials

  High resolution PES and Bulk sensitive Fermiology
  - CeRu$_2$ ; 4f electron system, gap anisotropy
  - MgB$_2$ ; multigap, interband interactions
  - $(\pi$-(ET)$_2$Cu (SCN)$_2$ ; d-wave superconductor
  - LiV$_2$O$_4$ ; Kondo state in TMO
  - SrVO$_3$ ; comparison with DMFT(Surface and bulk)

Laser-PES has solved the weaknesses of PES

- Low resolution → High resolution
- Surface sensitive → Bulk sensitive
- High temperature → Low temperature
- Large spot size → Small spot size