The applications of the anti-parallel double crystal X-ray spectrometer to the material science

Y. Ito, T. Tochio\textsuperscript{a}, T. Fujii\textsuperscript{b}, S. Fukushima\textsuperscript{c}

ICR, Kyoto University
\textsuperscript{a} Faculty of Science, Kobe University, Japan
\textsuperscript{b} Faculty of Engineering, Okayama University Japan
\textsuperscript{c} National Institute of Materials Research, Japan

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**The Double crystal x-ray spectrometer**

1. The resolving power of the two-crystal x-ray spectrometer is largely dependent on the perfection of the crystals.

2. The x-ray spectrometer secures high resolving power, intensity, and reproducibility. Therefore,

3. It is possible to make a more detailed study on chemical states using this spectrometer.

Recently, at undulator beam line in the 3\textsuperscript{rd} generation SR,

4. This is focused on its X-ray emission spectra induced by the evolution method. We investigated directly the chemical state of several elements, measuring its emission and partial fluorescence absorption spectra with this two-crystal spectrometer.

Today, as an example, spectral data of several elements in some materials are presented.
The instrumental function which consists of the convolution in rocking curves of the crystal, and slit function of a soller slit in the system can make FWHM of X-ray spectra natural line width. Therefore, in the double crystal method, the only affectivity of the resolution depends on the perfection of the crystal.

1. The second crystal takes an important role as a shutter which cut the extra rays that don‘t satisfy Bragg’s law on the first crystal. And, the first crystal works as the slit before the second crystal.

2. The (++) configuration (anti-parallel) double convolution process between the two instrumental functions of rocking curve and slit function can result in the effective high resolution (Tochio et al. PRA)

Comparison with Single crystal method

This angle moves in tune with the first crystal and the second one.

Unnecessary beam is cut.
We use (+,+)$\,$ setting double crystal x-ray spectrometer

This is the modified RIGAKU spectrometer (System 3580EKI)

This high resolution x-ray spectrometer is in the constant temperature tank to keep a fixed temperature $(35 \pm 0.5\text{degree})$ of the crystal.

Double Crystal Spectrometer
(Rigaku : System 3580E)

Inside of the chamber

Schematic diagram of the double crystal spectrometer
The resolving power of this type spectrometer is largely dependent on the perfection of the crystals.

The x-ray spectrometer secures high resolving power, intensity, and reproducibility: for example, for Ti $K\alpha$ spectra, $E/\Delta E \sim 50000$

Therefore, it is possible to make more detailed studies on satellite structures and chemical states using this spectrometer.

- Measure sample with unbroken
- No more high vacuum, around $\sim 5$ Pa or atmosphere under He.
- Not related to the size of the sample
- Insulator, liquid, organs available
- The effect of the instrumental function is very small, ideally can be ignored
- At present time, no data base (Hyogo prefectural Institute of Technology and our laboratory are constructing the data base)
Reproducibility of double-crystal spectrometer

Repeat measurement of twelve times of Cu-Kα X-rays

Counts/10sec. integration per 0.0005 degree step of Δ2θ

- 1st measurement
- 2nd measurement
- 3rd measurement
- 4th measurement
- 5th measurement
- 6th measurement
- 7th measurement
- 8th measurement
- 9th measurement
- 10th measurement
- 11th measurement
- 12th measurement

Cu-Kα1
Cu-Kα2
Table (1) Reproducibility performances of a goniometer

<table>
<thead>
<tr>
<th>Variation of peak top angle</th>
<th>Cu-Kα₁</th>
<th>Cu-Kα₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ(2θ)° (eV)</td>
<td>0.000051 (0.0087)</td>
<td>0.000250 (0.045)</td>
</tr>
<tr>
<td>Variation of peak top intensity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ(2θ)°</td>
<td>0.49%</td>
<td>0.44%</td>
</tr>
</tbody>
</table>

Reproducibility of 50% intensity angle

<table>
<thead>
<tr>
<th>Cu-Kα₁</th>
<th>low angle side</th>
<th>high angle side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ(2θ)°</td>
<td>0.000084</td>
<td>0.00011</td>
</tr>
<tr>
<td>Intensity gradient</td>
<td>0.035 / 0.0005°</td>
<td>0.025</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu-Kα₂</th>
<th>low angle side</th>
<th>high angle side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ(2θ)°</td>
<td>0.00011</td>
<td>0.00019</td>
</tr>
<tr>
<td>Intensity gradient</td>
<td>0.028</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Cu(Kα₂ - Kα₁)

| Δ(2θ)° | 0.0161 (2.76) | 0.0219 (3.76) | 0.1166 (19.99) |
| Δ(2θ)° | 0.00024 (0.041) | 0.00019 (0.033) | 0.00026 (0.045) |
| asymmetry (error) | 1.09 (0.013) | 1.30 (0.06) |

Note: eV = 171.44 ∙ Δ(2θ)°

Table (2) Spectrometer performances of 50% intensity width and asymmetrical indices

<table>
<thead>
<tr>
<th>50% width</th>
<th>errors of 50% width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ(2θ)° (eV)</td>
<td>Δ(2θ)° (eV)</td>
</tr>
<tr>
<td>Cu-Kα₁</td>
<td>0.0161 (2.76)</td>
</tr>
<tr>
<td>Cu-Kα₂</td>
<td>0.0219 (3.76)</td>
</tr>
<tr>
<td>Cu(Kα₂ - Kα₁)</td>
<td>0.1166 (19.99)</td>
</tr>
</tbody>
</table>

Error: standard deviation in Table (1) and (2)
example 1: V, & Mn in 3d elements

Ca$_3$Mn$_2$O$_7$ Crystal structure
V $K\alpha$ spectra of various oxidation states

Intensity [arbitrary units]

Energy [eV]

V $0.3\text{mol}\%$
VO
$V_2O_3$
$VO_2$
$VOSO_4$
$V_2O_5$

$K\alpha_1$
$K\alpha_2$
V $K\alpha_1$ spectra

![V $K\alpha_1$ spectra graph](image-url)

- Red: V 0.3mol%
- Pink: VO
- Black: $V_2O_3$
- Green: VO$_2$
- Blue: VOSO$_4$
- Orange: $V_2O_5$

Intensity [arbitrary units]

Energy [eV]
Mn $K\alpha$ spectra of various oxidation states
Mn $K\alpha_1$ spectra

Mn $K\alpha$

Intensity [arbitrary units]

Energy [eV]

$\begin{align*}
\text{V 0.3mol\%} & \quad \text{MnCl}_2 \\
\text{MnCl}_2 & \quad \text{MnO} \\
\text{MnO} & \quad \text{Mn}_2\text{O}_3 \\
\text{Mn}_2\text{O}_3 & \quad \text{MnO}_2 \\
\text{MnO}_2 & \quad \text{KMnO}_4
\end{align*}$
Si $K\alpha$ spectra in various Si compounds

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example 2: Si and S
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![Graph showing Si Kα spectra in various Si compounds.]
S Kα spectra of various oxidation states

Q.W.Qi et al., Biological Trace Element Research vol.13, 383 (1987)
example 3: Absorption edge and partial xafs

A schematic apparatus of the double crystal spectrometer and entering synchrotron beam. Pinhole shrinks the beam right spotted to the sample. The beam intensity can be measured as $I_0$ and $I_1$ by meshed Au detector.
Results obtained from Evolution

- Determination of the absorption edge
- Partial XAFS
Peak shift of Fe $K\alpha_{1,2}$ near the $K$ edge

excitation energy [eV]

peak position [eV]

7111.4 eV

7111.2 eV
Cr $K$ partial XAFS obtained from Cr $K\alpha_1$ peak

Cr$^{6+}$ resonant absorption

5992.2 eV
The development of double-crystal x-ray spectrometry has provided the researcher with an invaluable tool in making more precise measurements of x-ray diffraction. The many and wide-spread applications of the two-crystal instrument in investigations of contemporary importance have been considered sufficient justification for design and construction of a double-crystal ionization spectrometer for operation in a vacuum, which would allow this branch of study to be extended to include the soft x-rays of wavelengths greater than two angstroms.

L. G. Parratt, Phys. Rev. 41, 553 (1932)

Thank you for your kind attention!