APPLICATION OF AUTOMATED ELECTRON DIFFRACTION TO STRUCTURAL INVESTIGATION OF MOLECULAR CRYSTALS

Tatiana E. Gorelik, Galina Matveeva, Ute Kolb

Institute of Physical Chemistry, Johannes-Gutenberg University Mainz, Germany
This document was presented at PPXRD - Pharmaceutical Powder X-ray Diffraction Symposium

Sponsored by The International Centre for Diffraction Data

This presentation is provided by the International Centre for Diffraction Data in cooperation with the authors and presenters of the PPXRD symposia for the express purpose of educating the scientific community.

All copyrights for the presentation are retained by the original authors.

The ICDD has received permission from the authors to post this material on our website and make the material available for viewing. Usage is restricted for the purposes of education and scientific research.

PPXRD Website – [www.icdd.com/ppxrd](http://www.icdd.com/ppxrd)  ICDD Website - [www.icdd.com](http://www.icdd.com)
APPLICATION OF AUTOMATED ELECTRON DIFFRACTION TO STRUCTURAL INVESTIGATION OF MOLECULAR CRYSTALS

Transmission electron microscope (TEM)

Imaging

High-resolution imaging

Electron diffraction

Elemental analysis (EDX)
Powder electron diffraction

Single crystal electron diffraction: tilt series

Pawley and Rietveld refinements using electron diffraction from L1₂-type intermetallic Au₃Fe₁₋ₓ nanocrystals during their in-situ order–disorder transition

Zhiping Luo, Yolanda Vasquez, James F.Bondi, Raymond E.Schaak

Ultramicroscopy, 2011
Single crystal electron diffraction: tilt series

Pawley and Rietveld refinements using electron diffraction from L1₂-type intermetallic Au₃Fe₁₋ₓ nanocrystals during their in-situ order–disorder transition

Zhiping Luo, Yolanda Vasquez, James F. Bondi, Raymond E. Schaak

Ultramicroscopy, 2011
Structure solution using zonal electron diffraction data: historical overview

Organic samples
Rigamonti, R., La struttura della catena paraffinica studiata mediante i raggi di elettroni, *Gazzetta Chimica Italiana* 66 174-182 (1936)


Voigt-Martin et al., The use of simulation methods to obtain the structure and conformation of 10-cyano-9,9'-bianthryl by electron diffraction and high-resolution imaging, *Ultramicroscopy* 57, 29-43 (1995)

Biological samples

2D Protein crystals
Weirich et al. A crystal structure determined with 0.02 Å accuracy with electron microscopy, *Nature* 382, 144 (1996)

Inorganic samples
(Thin)


Solution using structure factor phases derived from HRTEM
Automated electron Diffraction Tomography (ADT):
collection of the complete reciprocal data rather than zonal patterns
Automated electron Diffraction Tomography (ADT):
collection of the complete reciprocal data rather than zonal patterns
Automated electron Diffraction Tomography (ADT): collection of the complete reciprocal data rather than zonal patterns
MORE THAN 30 STRUCTURES ARE SOLVED FROM ADT DATA BY NOW (16 OUT OF THEM - NEW)

**Minerals:**
- Mullite Al$_6$Si$_2$O$_{13}$
- Sarrabusite
- Charoite-96
- Charoite-90

**Intermetallic nanophases:**
- ZnSb, Zn$_8$Sb$_7$

**Metal Organic Frameworks (MOF):**
- MUF-4l
- Basolite

**Organic-inorganic hybrids:**
- ECS3, ECS5

**Organic:**
- NLO-active material
- Organic pigments
- Amides

**Zeolites:**
- ZSM-5 (Na$_x$Al$_x$Si$_{96-x}$O$_{192}$)
- Natrolite Na$_2$Al$_2$Si$_3$O$_{10}$·2H$_2$O
- IM-5
- RKL 040

**Oxides:**
- Na$_2$W$_4$O$_{13}$
- Li$_2$Ti$_3$NiO$_8$
- NaHTi$_3$O$_7$·H$_2$O
- Na$_2$Ti$_6$O$_{13}$

**Ca-compounds:**
- Calcite, Vaterite
- Calcium silicate hydrate Ca$_5$Si$_6$O$_{17}$·5H$_2$O

**Phosphates:**
- SrP$_3$N$_5$O
- Ba$_6$Br$_3$P$_{12}$N$_{17}$O$_9$

**Organic:**
- Organic-inorganic hybrids
- Organic pigments
- Amides

**High pressure phases:**
- HP hydrous Al-pyroxene (Mg$_2$Al(OH)$_2$AlSiO$_6$)
small crystals
$\text{Zn}_8\text{Sb}_7 \sim 40 \text{ nm}$

agglomerated crystals

radiation damage

disorder
Radiation damage: CNBA

E-dose rate: 0.2-0.3 e/A²s

STEM vs. TEM;
Distribute the dose (crystal bending!);
Cool the sample
Orthorombic paracetamol (Pcab)

<table>
<thead>
<tr>
<th>ADT</th>
<th>As given by Haisa et al., 1974</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.4 A</td>
<td>11.805 A</td>
</tr>
<tr>
<td>17.4 A</td>
<td>17.164 A</td>
</tr>
<tr>
<td>7.6 A</td>
<td>7.393 A</td>
</tr>
<tr>
<td>90.1°</td>
<td>90°</td>
</tr>
<tr>
<td>90.0°</td>
<td>90°</td>
</tr>
<tr>
<td>88.1° *</td>
<td>90°</td>
</tr>
</tbody>
</table>

Projection (010): extinctions along c* direction (b-glide plane)

Material provided by Elena Boldyreva, Novosibirsk State University
Orthorombic paracetamol (Pcab)

ADT As given by Haisa et al., 1974

Unit cell parameters:

\begin{align*}
 &a = 11.405 \text{Å} \\
 &b = 17.400 \text{Å} \\
 &c = 7.393 \text{Å} \\
 &\alpha = 90.0^\circ \\
 &\beta = 90.0^\circ \\
 &\gamma = 88.1^\circ \\
\end{align*}

Projection (010): extinctions along c* direction (b-glide plane)

Material provided by Elena Boldyreva, Novosibirsk State University
On the Polymorphism of Aspirin: Crystalline Aspirin as Intergrowths of Two “Polymorphic” Domains**

Andrew D. Bond,* Roland Boese,* and Gautam R. Desiraju*

In the preceding paper, we highlighted the ambiguity that exists in the literature concerning the nature of crystalline aspirin. In 2004, Ouvrard and Price demonstrated computationally that the long-established aspirin crystal structure was amongst those predicted to be most stable, but they identified a slightly more stable structure as the thermodynamic minimum. At the time, it was unclear whether the forms (Figure 1). In form I, the layers are arranged so that C–H–O interactions form centrosymmetric dimers (arrangement A, Figure 1). In the proposed form II, adjacent layers...
Conclusion

Caution during data acquisition

Lattice cell parameters determination is always possible …

Alternative structure solution approaches for medium-resolution data

Direct methods structure solution for high resolution data
Group

Ute Kolb

Galina Matveeva
Enrico Mugnaïoli
Andrew Stewart
Iryna Andrusenko

Sebastian Schlitt
Ulrich Heil

Rudolf Wurfel
Robert Branscheid

Max Otten, FEI, Eindhoven, The Netherlands
Jacco van de Streek, Avant-garde Materials Simulation, Freiburg
Martin U. Schmidt, University of Frankfurt-am-Main
Andreas F.M. Kilbinger, Institute of Organic Chemistry, Mainz

Financial support SFB 625