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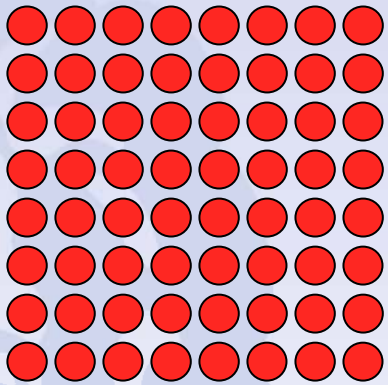
Molecular solids probed by PDF

Stefan Brühne

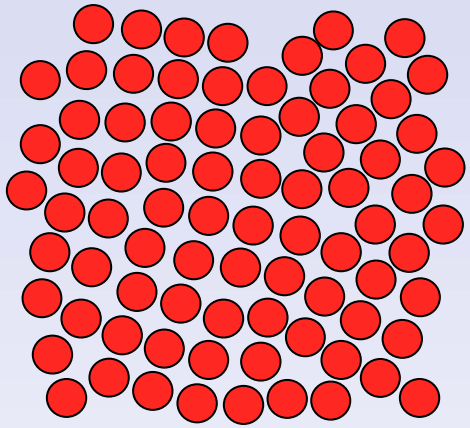
Johann Wolfgang Goethe-Universität, Frankfurt am Main

Physikalisches Institut *and*
Institut für Anorganische und Analytische Chemie

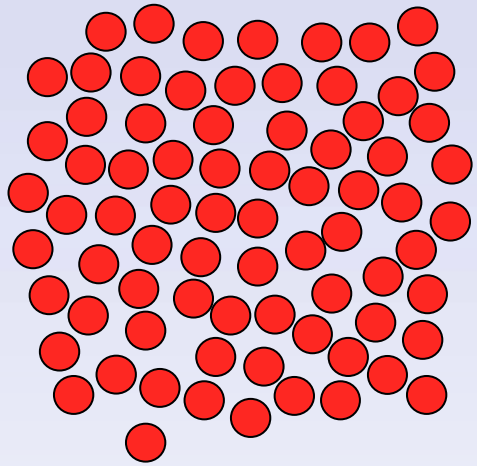
The sold state „in-between“



crystal



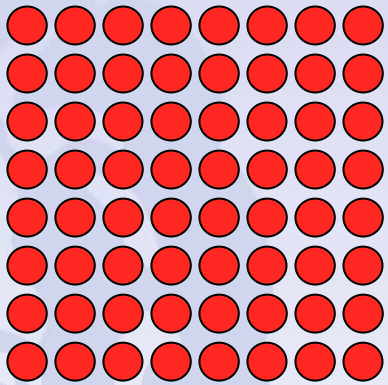
?



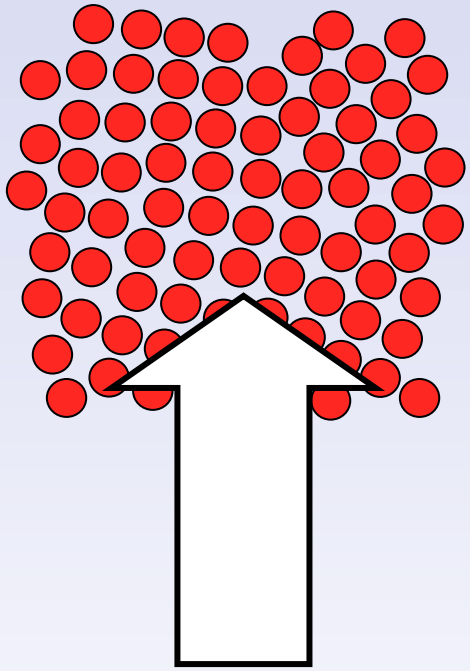
amorphous

Brühne & Glinnemann, *Z. Krist.: Discussion* „What is a crystal?“ (2007) online

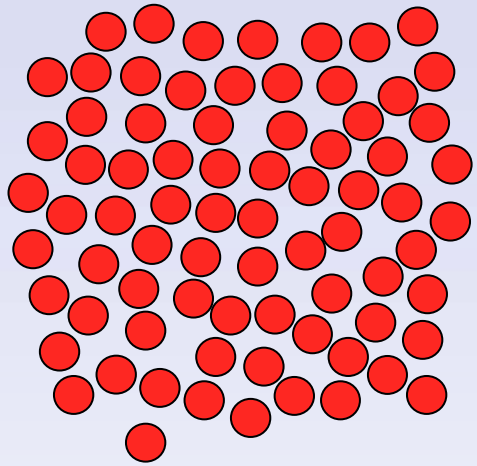
The sold state „in-between“



crystal



this is probed
using PDF !



amorphous

Brühne & Glinnemann, *Z. Krist.: Discussion* „What is a crystal?“ (2007) online

outline

traditionally, ‚hard' solids are probed by PDF – *e.g.* alloys

- Co_2Nb

outline

traditionally, ‚hard' solids are probed by PDF – *e.g.* alloys

- Co_2Nb

molecular solids, are they different?

outline

traditionally, ‚hard' solids are probed by PDF –
e.g. alloys

- Co_2Nb

molecular solids, are they different?

exploratory tour:

- organic superconductor
- organic Na-salt
- organic pigment
- pharmaceuticals

Co_2Nb

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FRANKFURT AM MAIN

G. Kreiner

a Laves C15 phase,
cF24, *Fd*-3*m*, $a \approx 6.8$Å

Phase width > 5at%: $Co_{2+x}Nb_{1-x}$

Co_2Nb

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G. Kreiner

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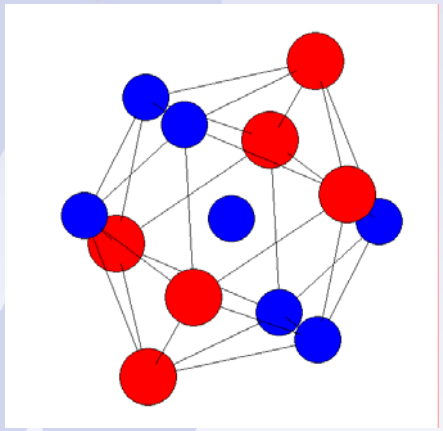
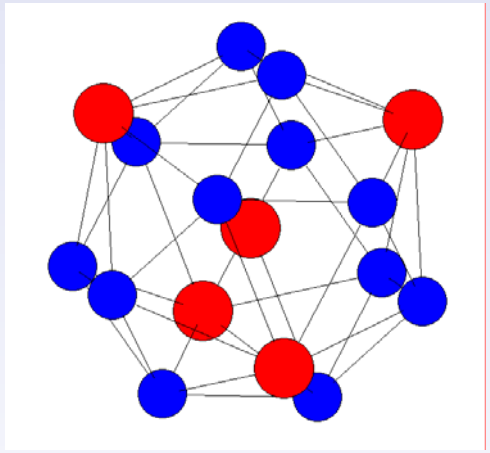
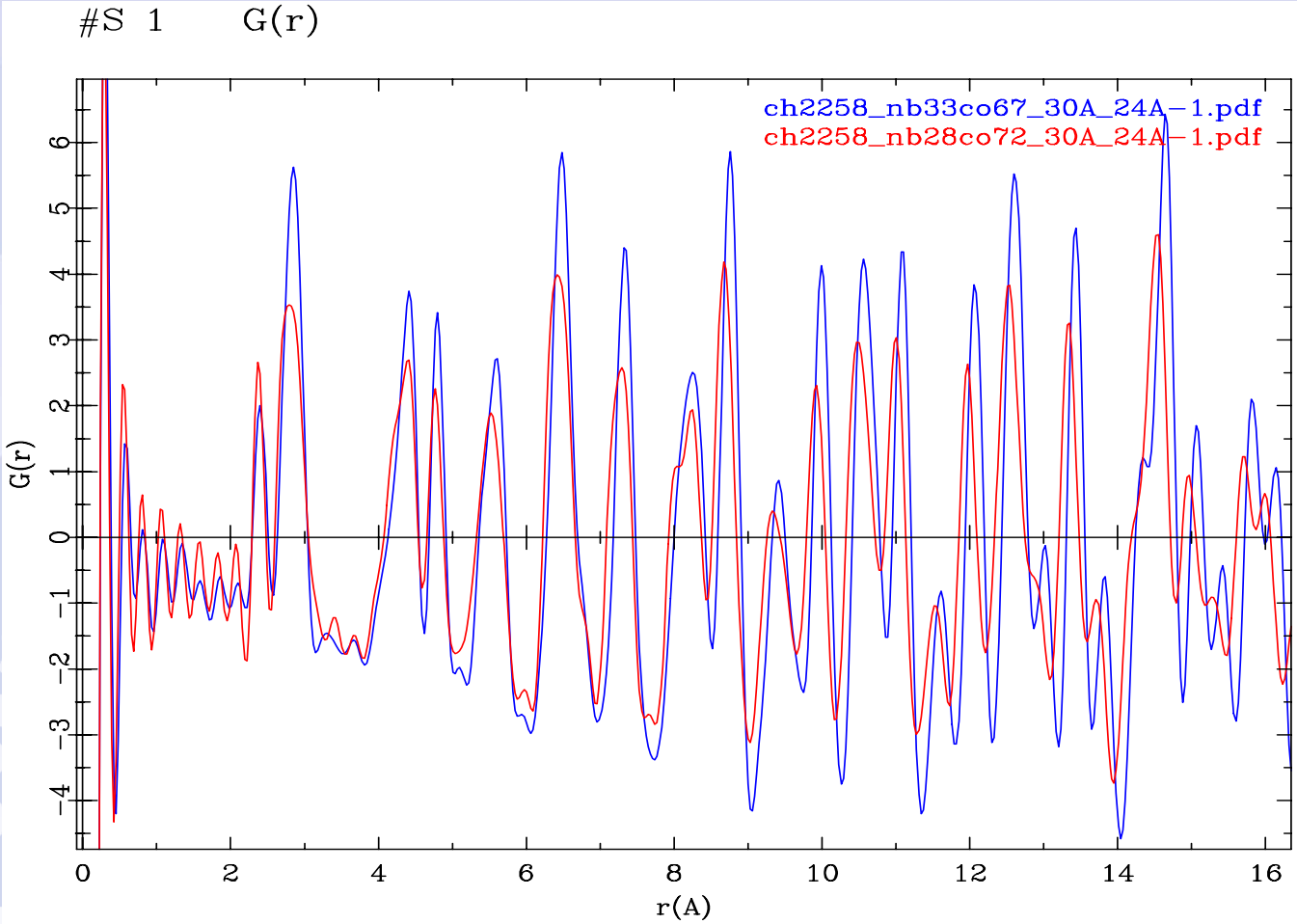




Co: CN12, icosahedron Nb: CN16, Frank-Kasper-polyhedron „P“

tcp: tetrahedrally close packed

Co_2Nb



ID31 data

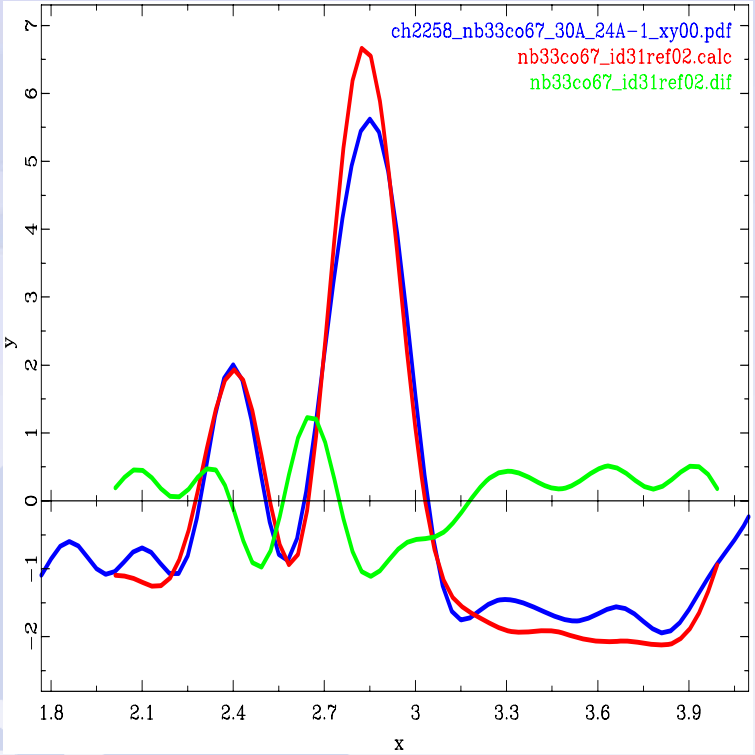
J. Glinnemann
J. Brüning

Co_2Nb

$Co_{2.2}Nb_{0.8}$

- shift in lattice constant
- first peak Nb-Nb, Co-Nb

Co_2Nb



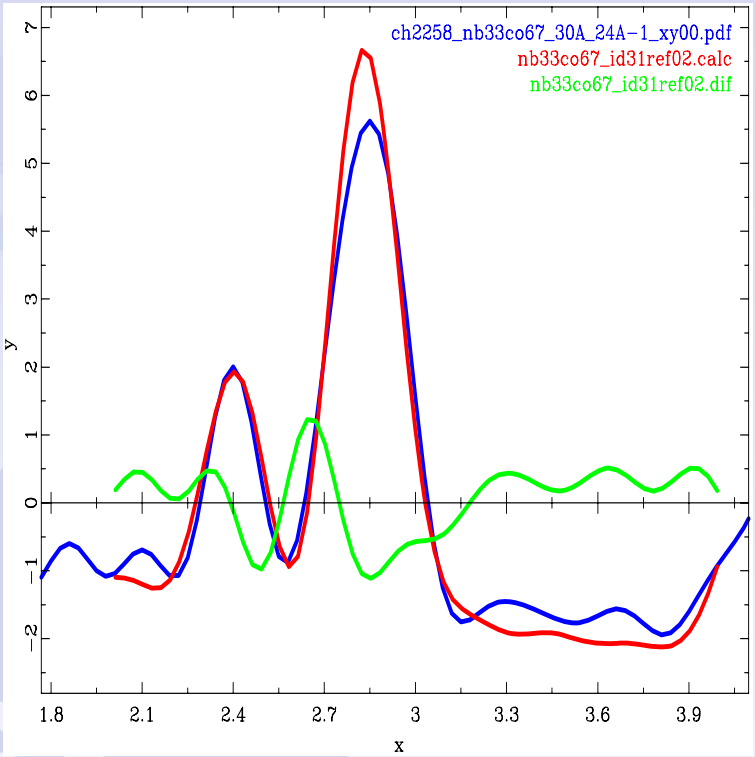
Co_2Nb

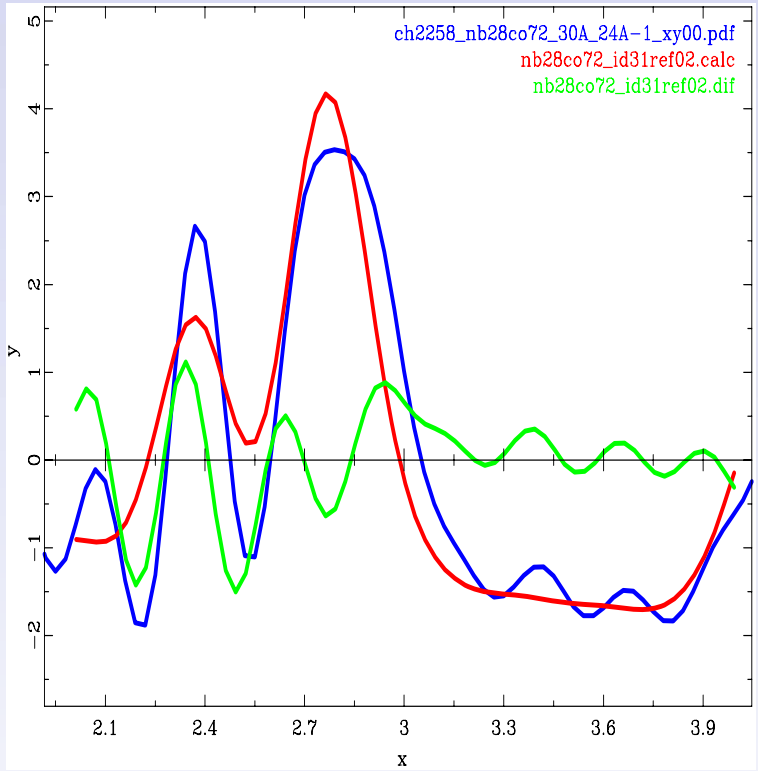
measured

refined

difference

Co_2Nb





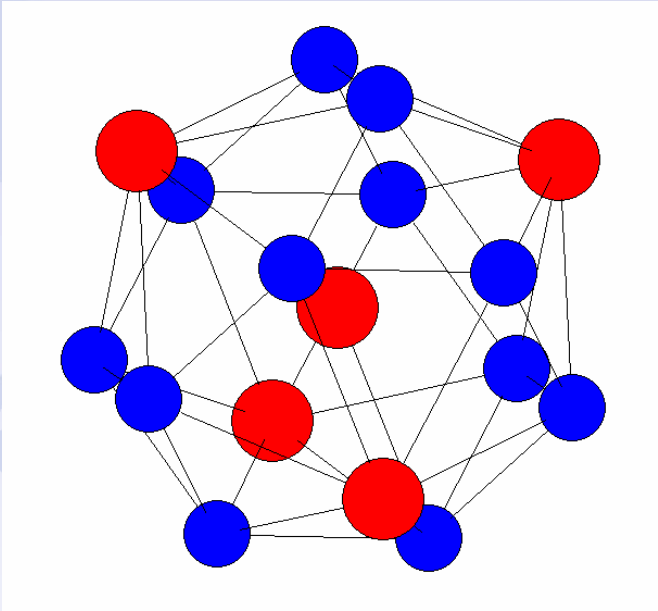
Co_2Nb $Co_{2.2}Nb_{0.8}$

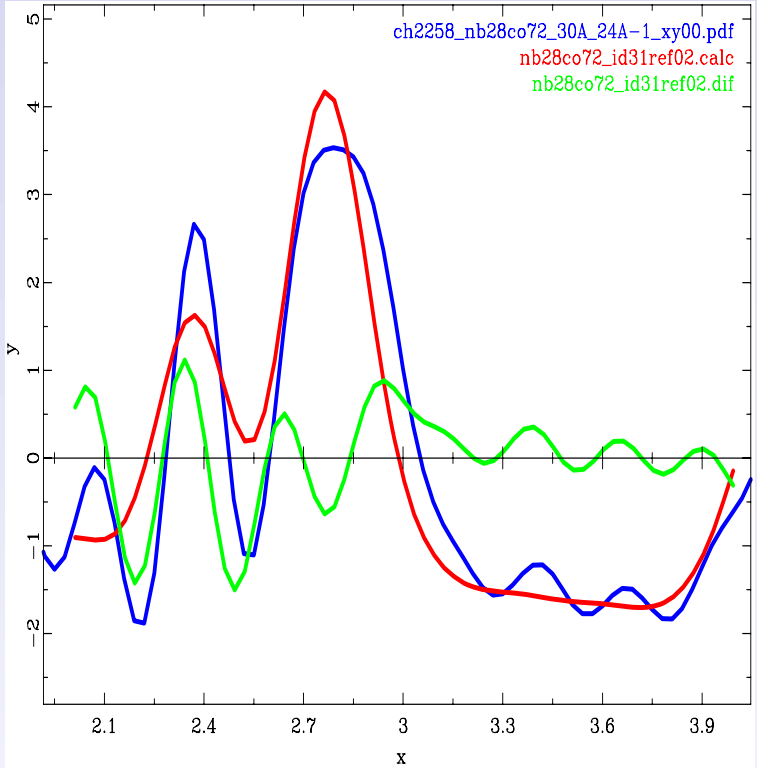
measured

refined

difference

Co_2Nb

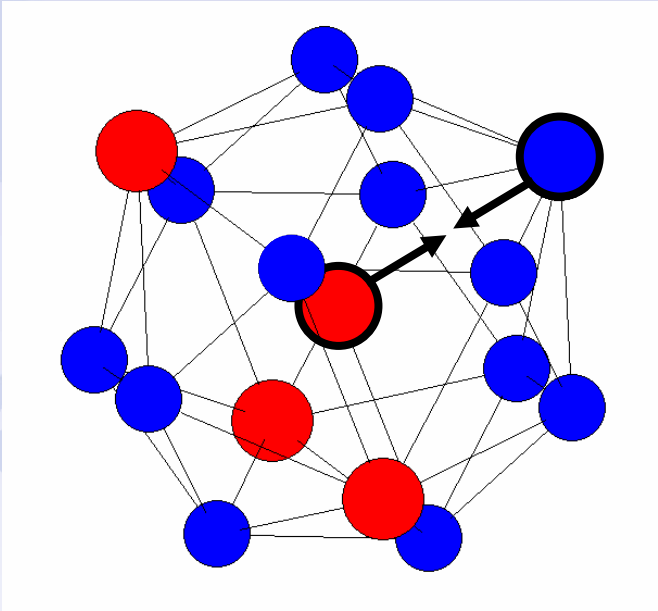


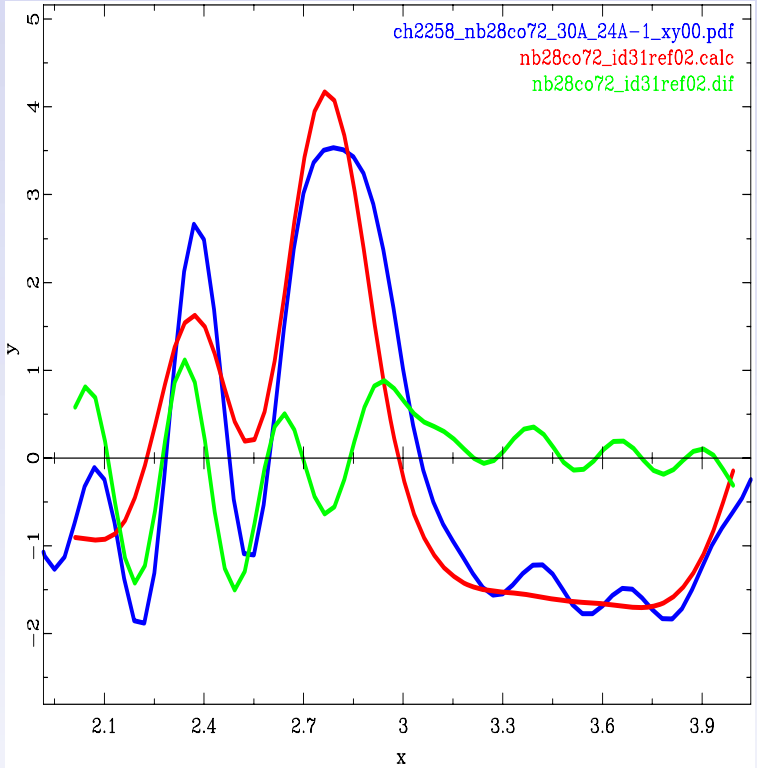


$Co_{2.2}Nb_{0.8}$

the first peak is affected only,
the rest virtually <u>not</u>

Co_2Nb





$Co_{2.2}Nb_{0.8}$

a very local effect (r < 3.5Å),
refinements under way...

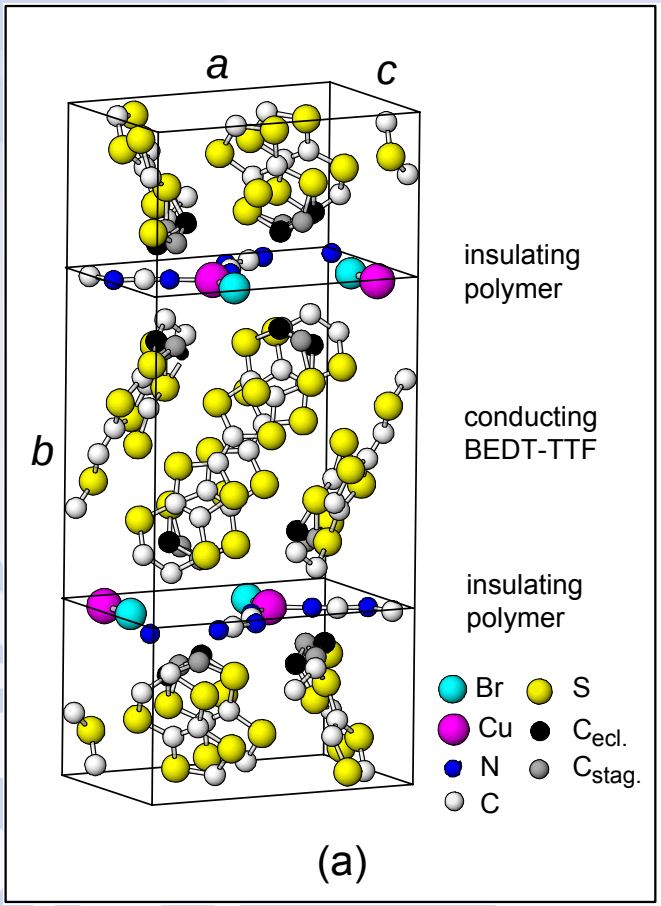
but:

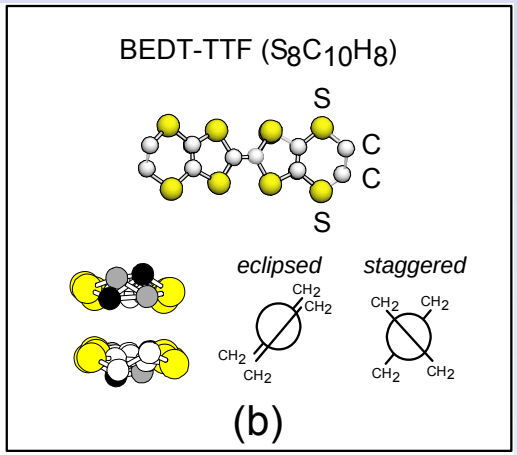
molecular solids,
are they different?

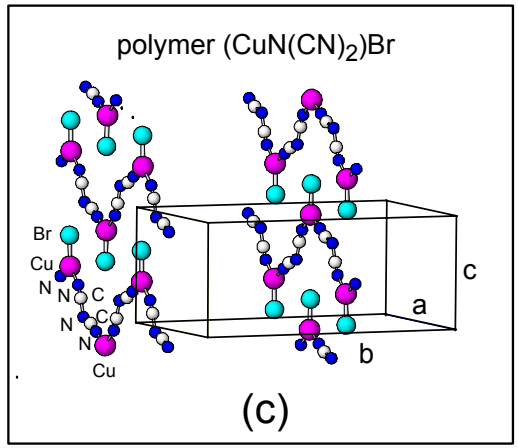
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ – an organic superconductor

C. Strack,
M. Lang

T_c = 10.4K







κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ – an organic superconductor

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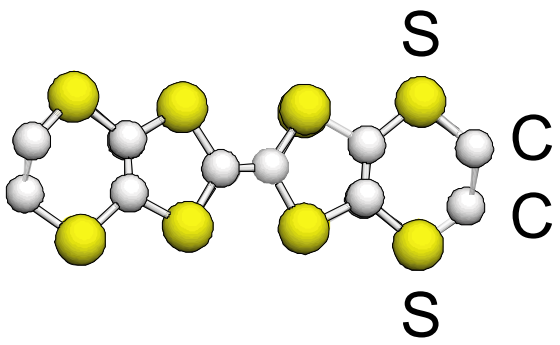
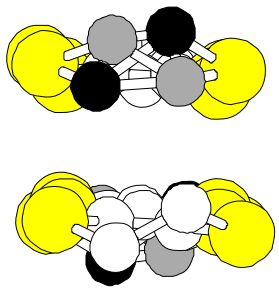
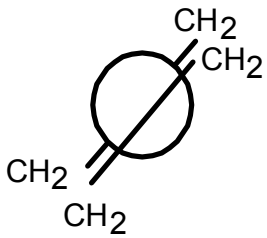
C. Strack,
M. Lang

BEDT-TTF ($S_8C_{10}H_8$)

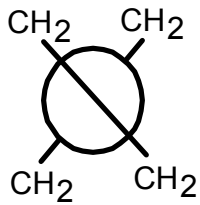




eclipsed



staggered



(e) (s)

T_c = 10.4K

$T_{glass} \approx 90K$

glass transition corresponds "somehow" to conformations e and s

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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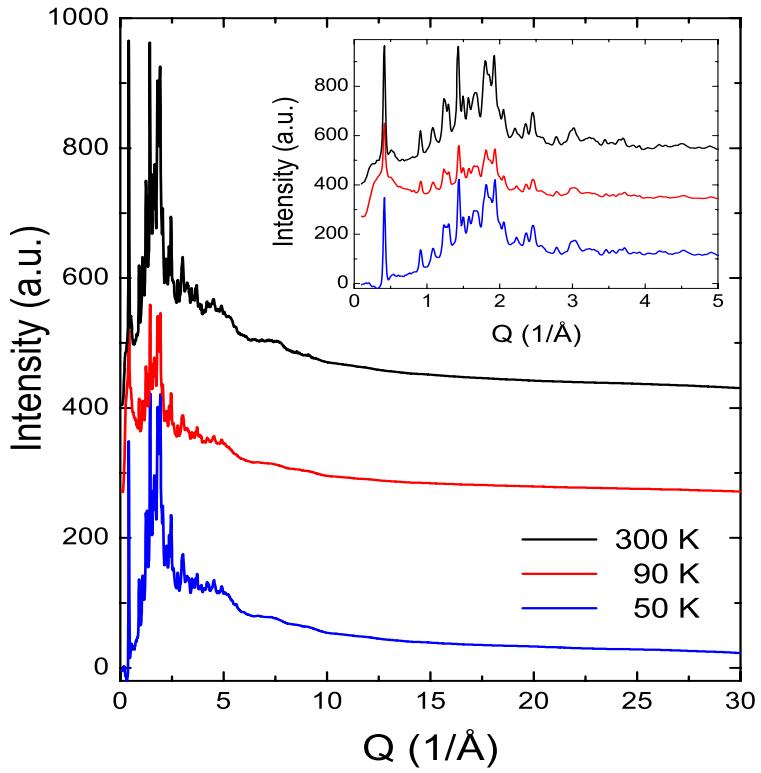
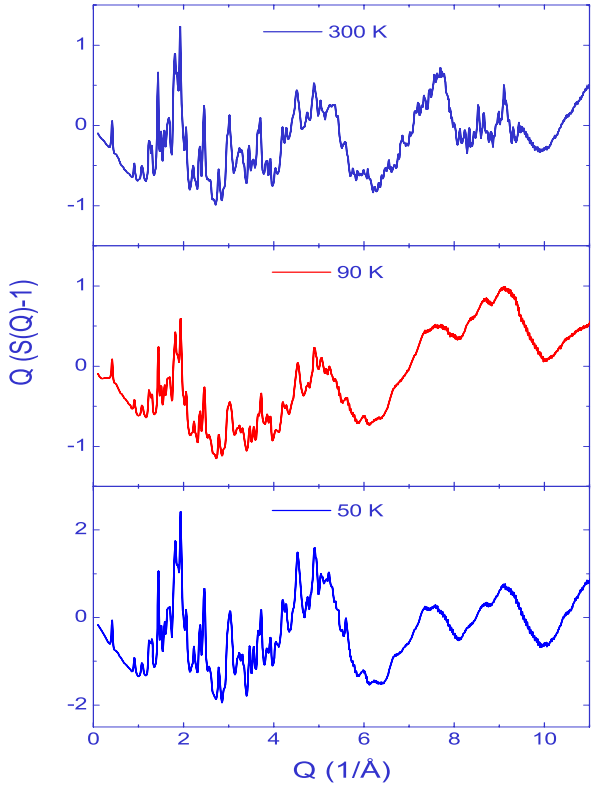
ID15B data: *f*(T)

A. Wolter,
S. Süllow,
G.G. Aviles, T. Buslaps

I(*Q*)



F(*Q*)



κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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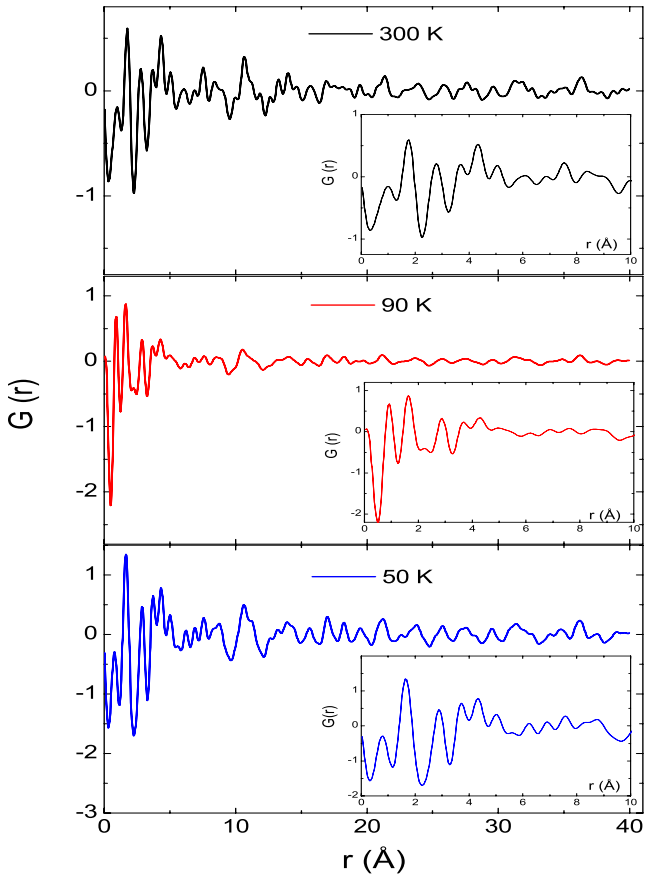
ID15B data: *f*(T)

G(*r*)



κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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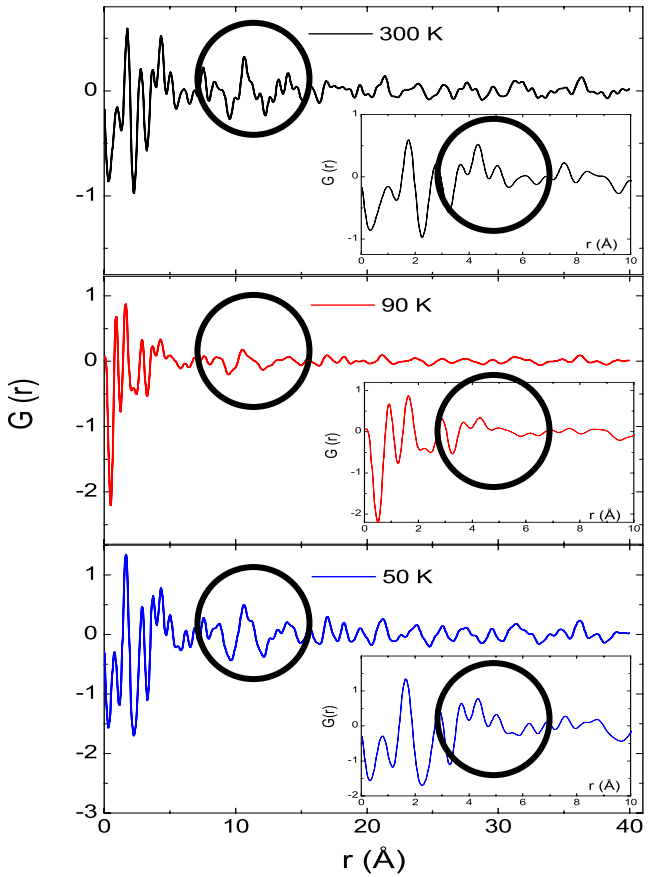
ID15B data: *f*(T)

G(*r*)



differences
at $r \approx 8..10$Å
–

where
do we expect
changes?

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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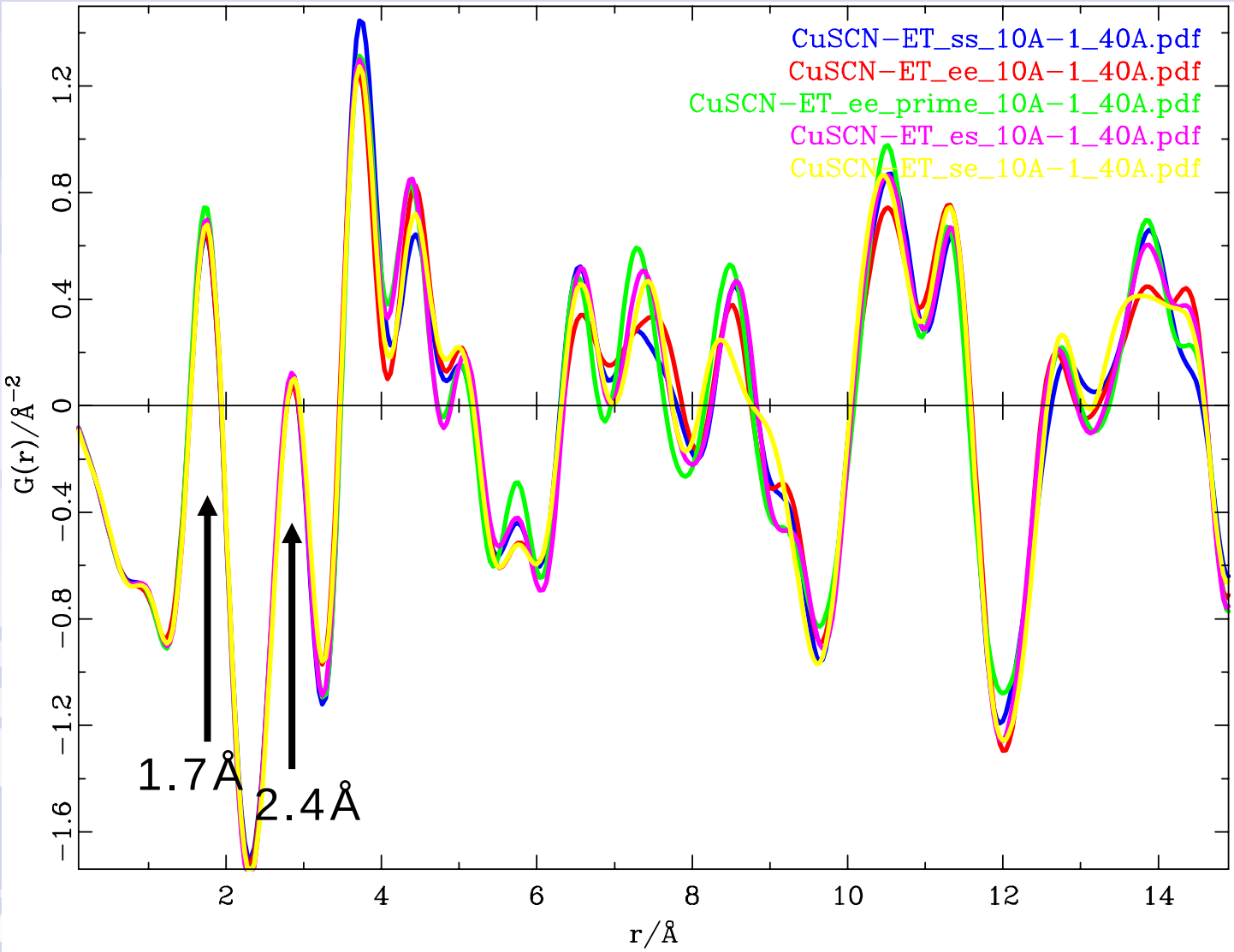
set up models with a local cell containing different eclipsed (e) and staggered (s) conformation combinations

ss
ee
ee'
es
se

N. Rademacher

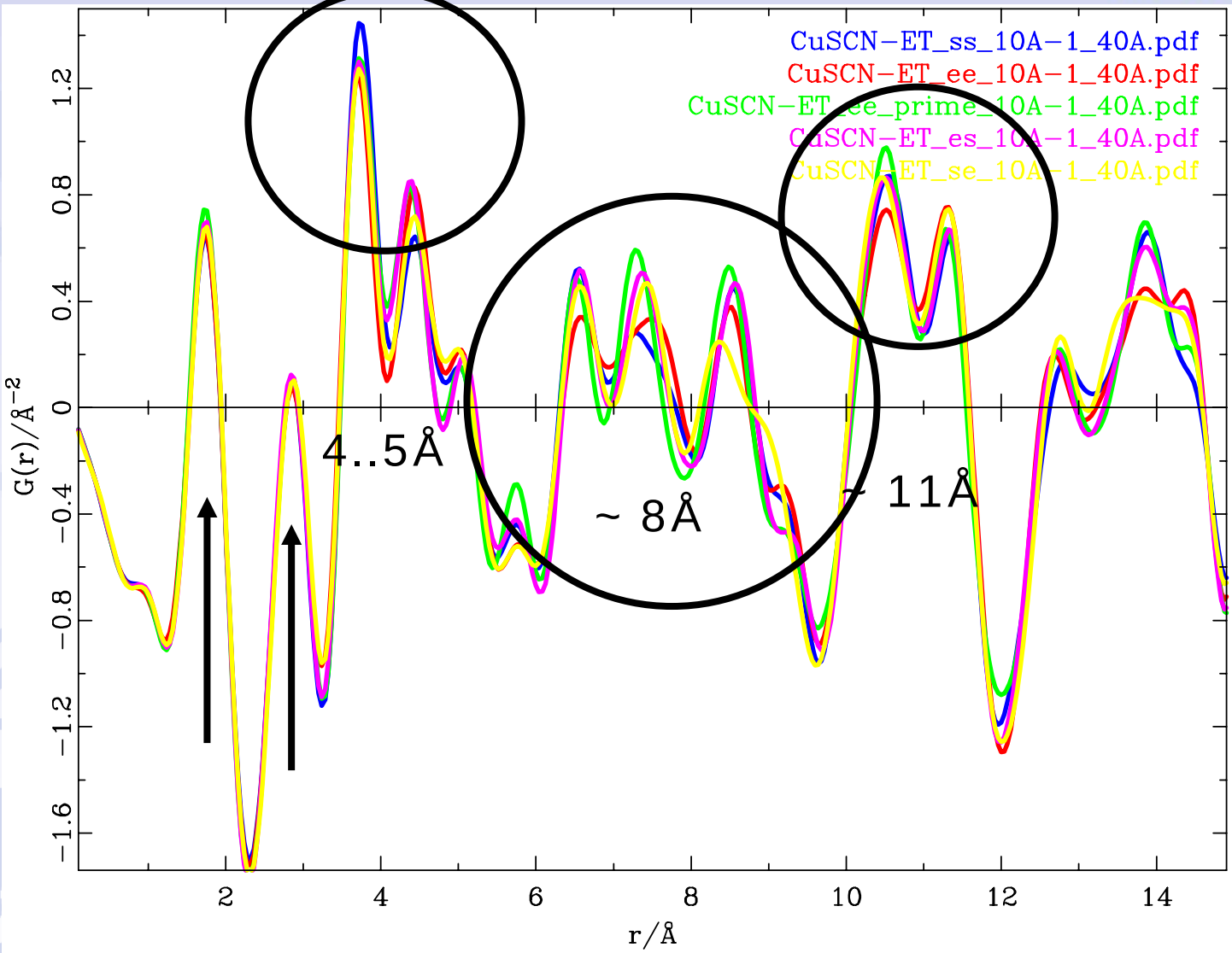
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

N. Rademacher



κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

N. Rademacher

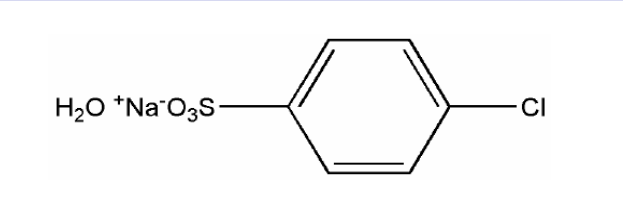


κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$

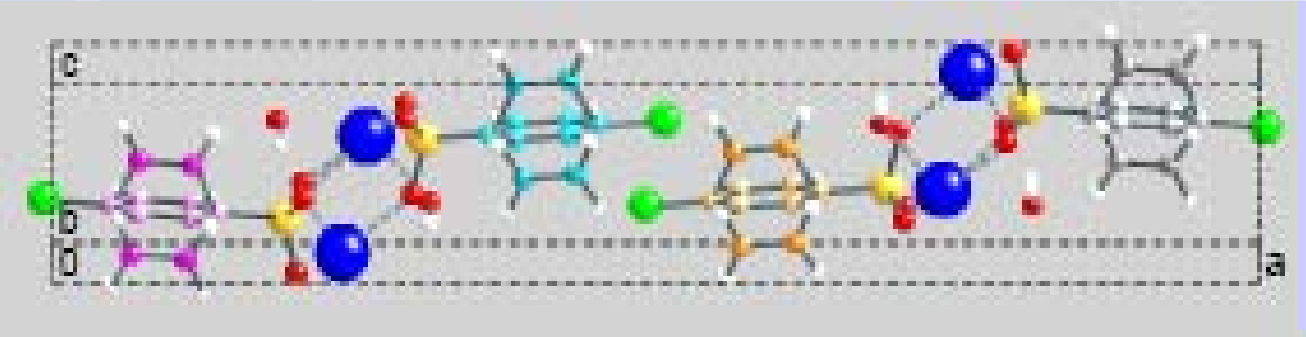
Conclusion:

- challenge: first peak in $G(r)$ at $r \sim 1.4$Å
- first organic PDF, $f(T)$ at ID15B
- features expected at higher r
- quantitative analysis has to follow!

Na-*p*-chlorosulfonate

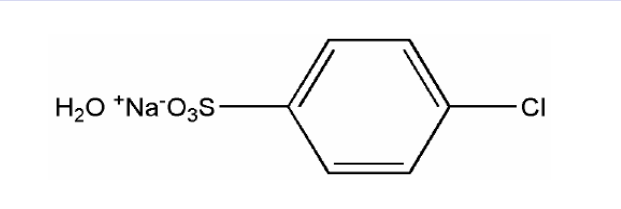


M.U. Schmidt,
A. Wolf



single crystal structure analysis: 50:50 disorder of ϕ-rings in *Pnma*

Na-*p*-chlorosulfonate



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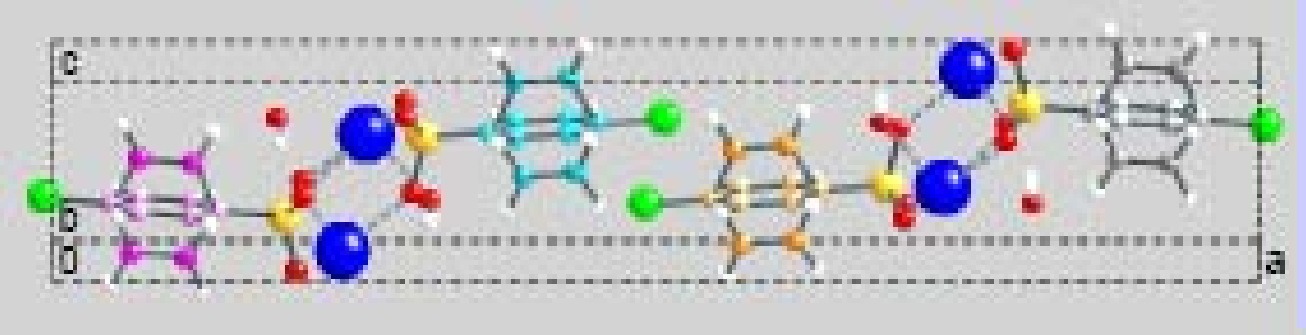
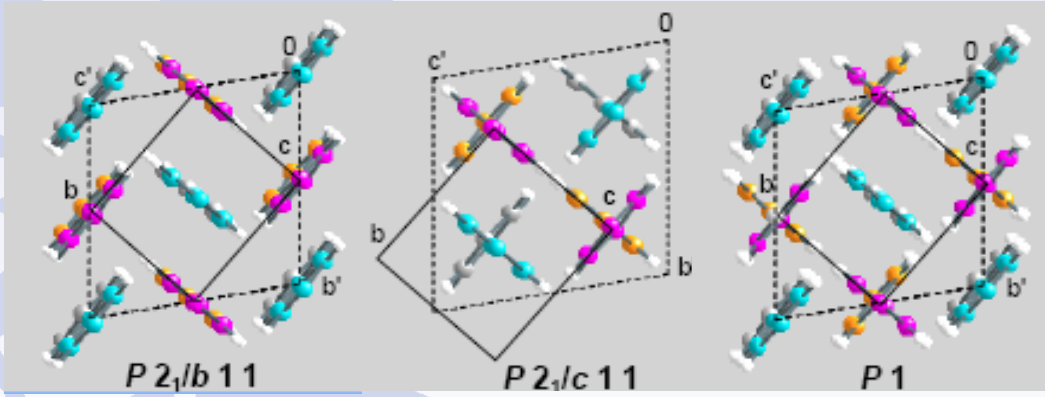


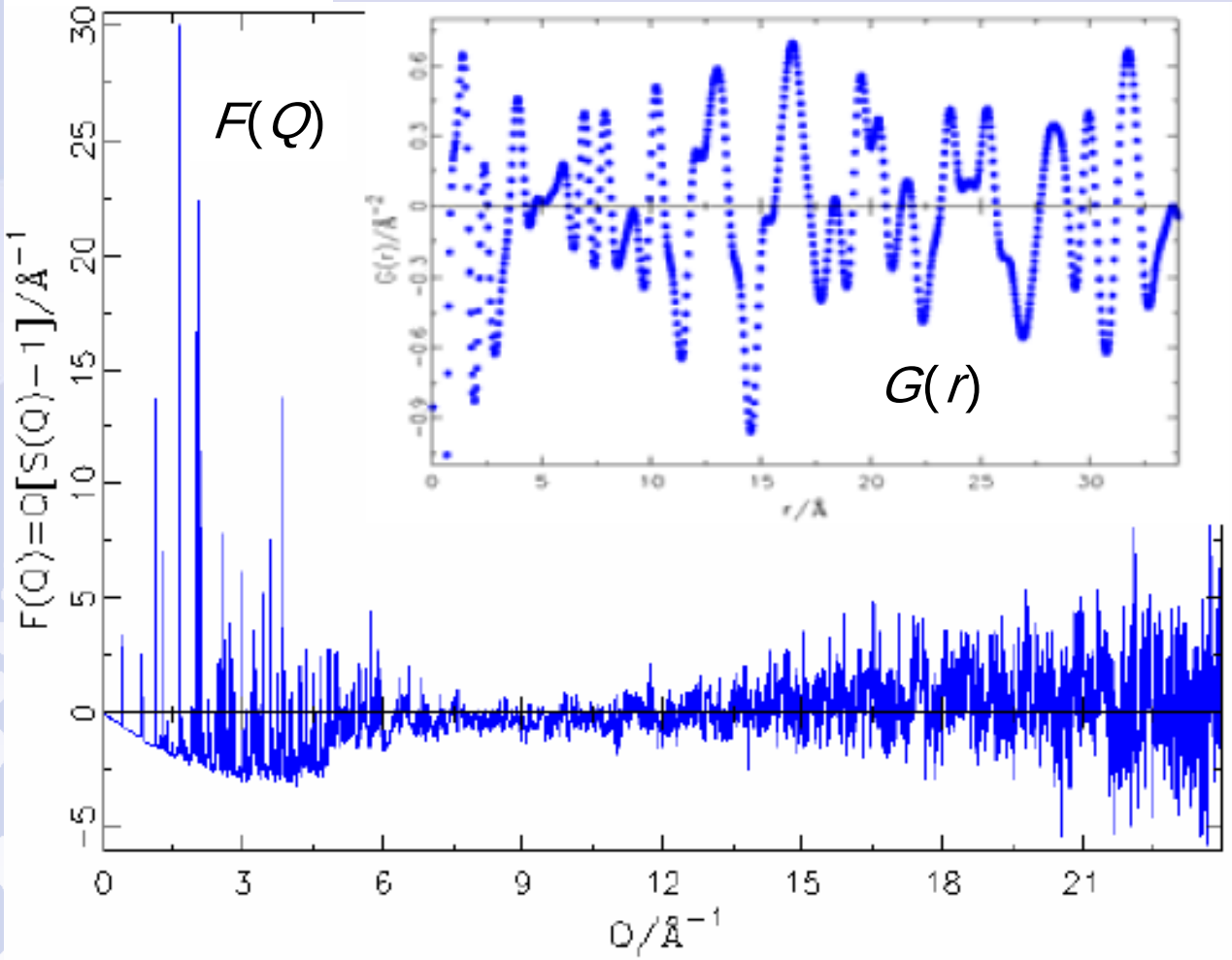


3 ordered variants
Possible
in $P2_1/b$, $P2_1/c$ *or* $P1$

H.B. Bürgi

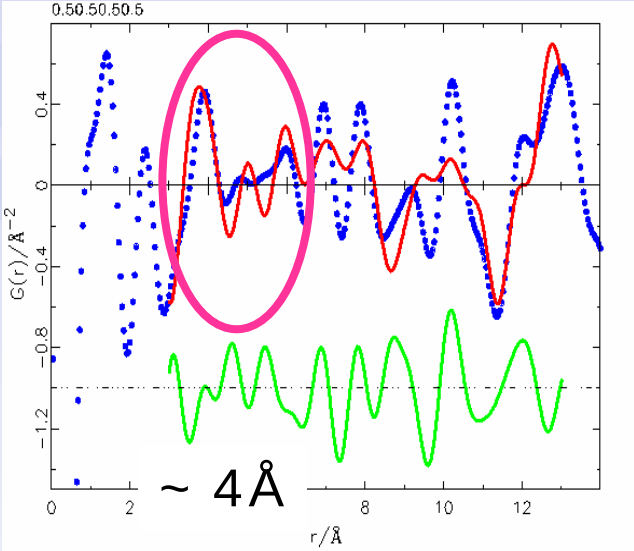
Na-*p*-chlorosulfonate

ID31 data:



Na-*p*-chlorosulfonate

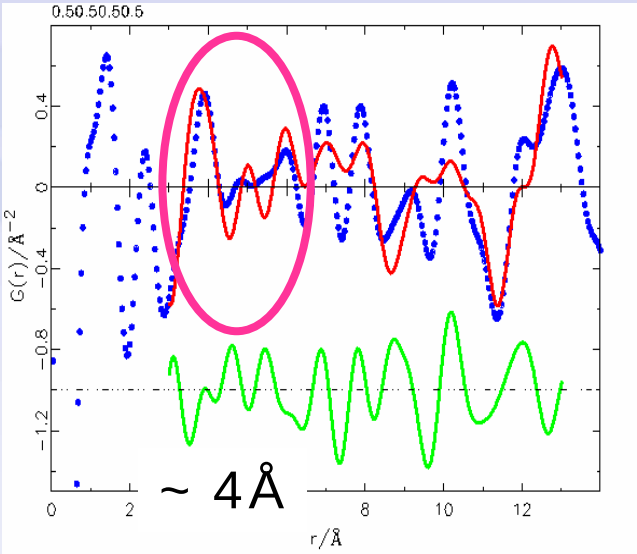
refinements

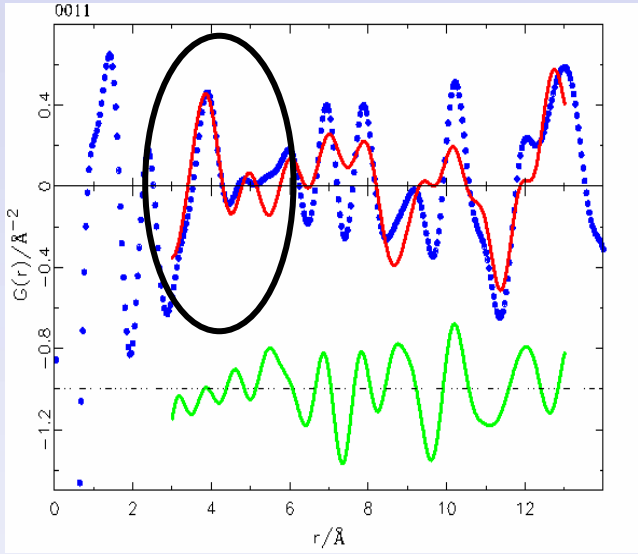


models	*E* [kJ/mol]	*R* [%] (PDFfit)
		r = 3-13 Å
P nma	–	62.1
P 2_1/*b* 11	-582,720	54.6
P 2_1/*c* 11	-582,855	54.6
P 1	-582,785	54.6

Na-*p*-chlorosulfonate

refinements





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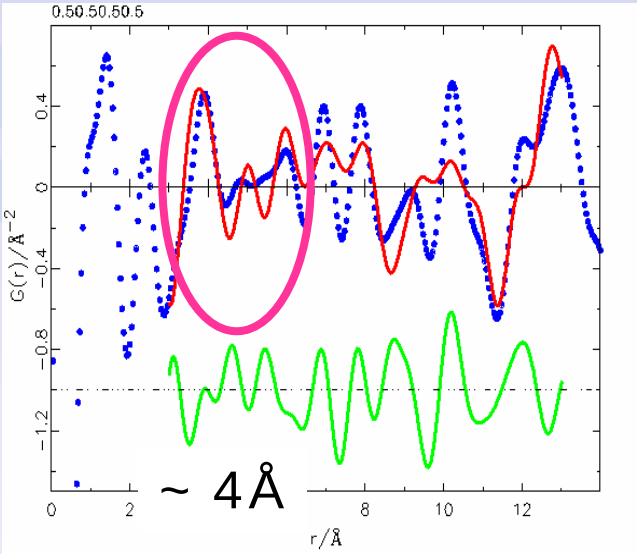
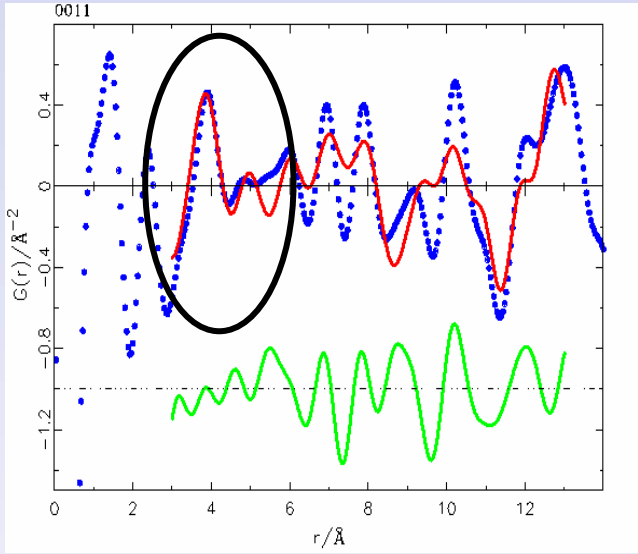
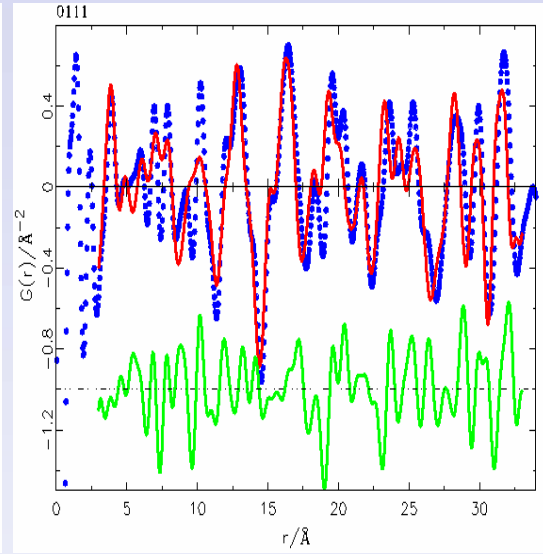
Na-*p*-chlorosulfonate

refinements







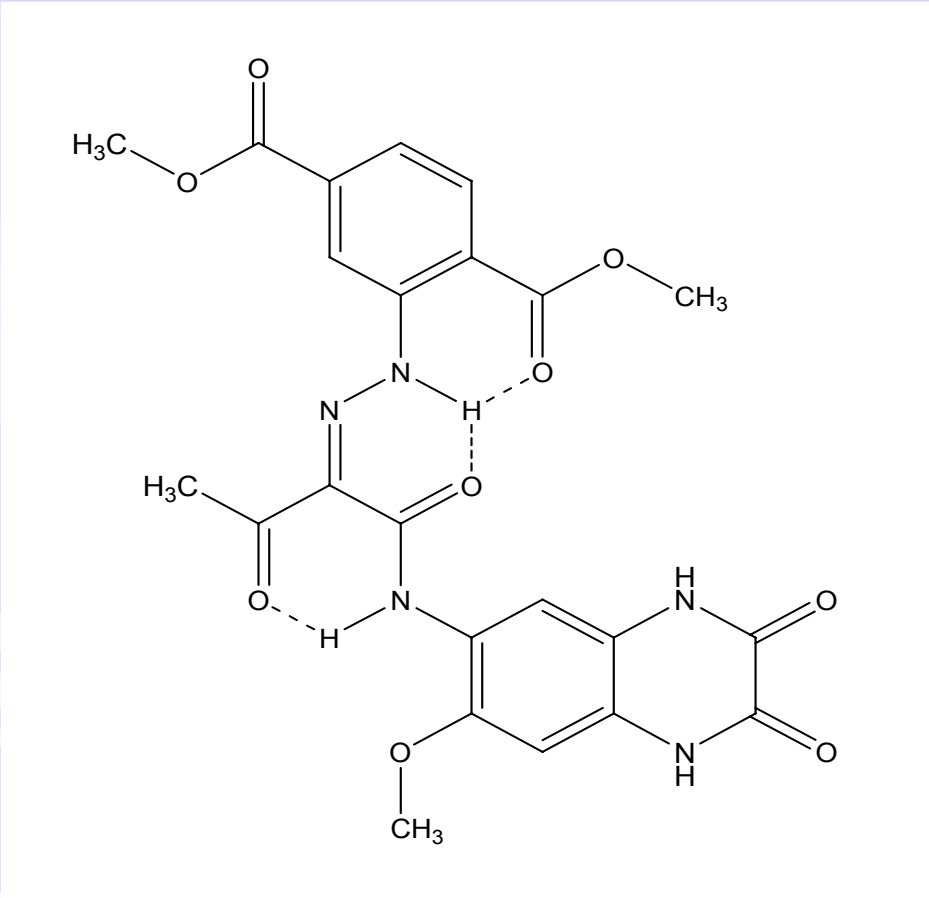
models	*E* [kJ/mol]	*R* [%] (PDFfit)		
		r = 3-13 Å	*r* = 3-23 Å	*r* = 3-33 Å
P nma	–	62.1	50.9	52.9
$P\,2_1/b\,11$	-582,720	54.6	54.0	52.6
$P\,2_1/c\,11$	-582,855	54.6	50.9	52.3
P 1	-582,785	54.6	47.4	52.6

Na-*p*-chlorosulfonate

Conclusion:

- PDF proves order for $r < 13$Å from diffraction data
- none of the models is favoured energtically
- ⇒ statistical disorder
- orthorhombic symmetry is mocked

Pigment Yellow 213

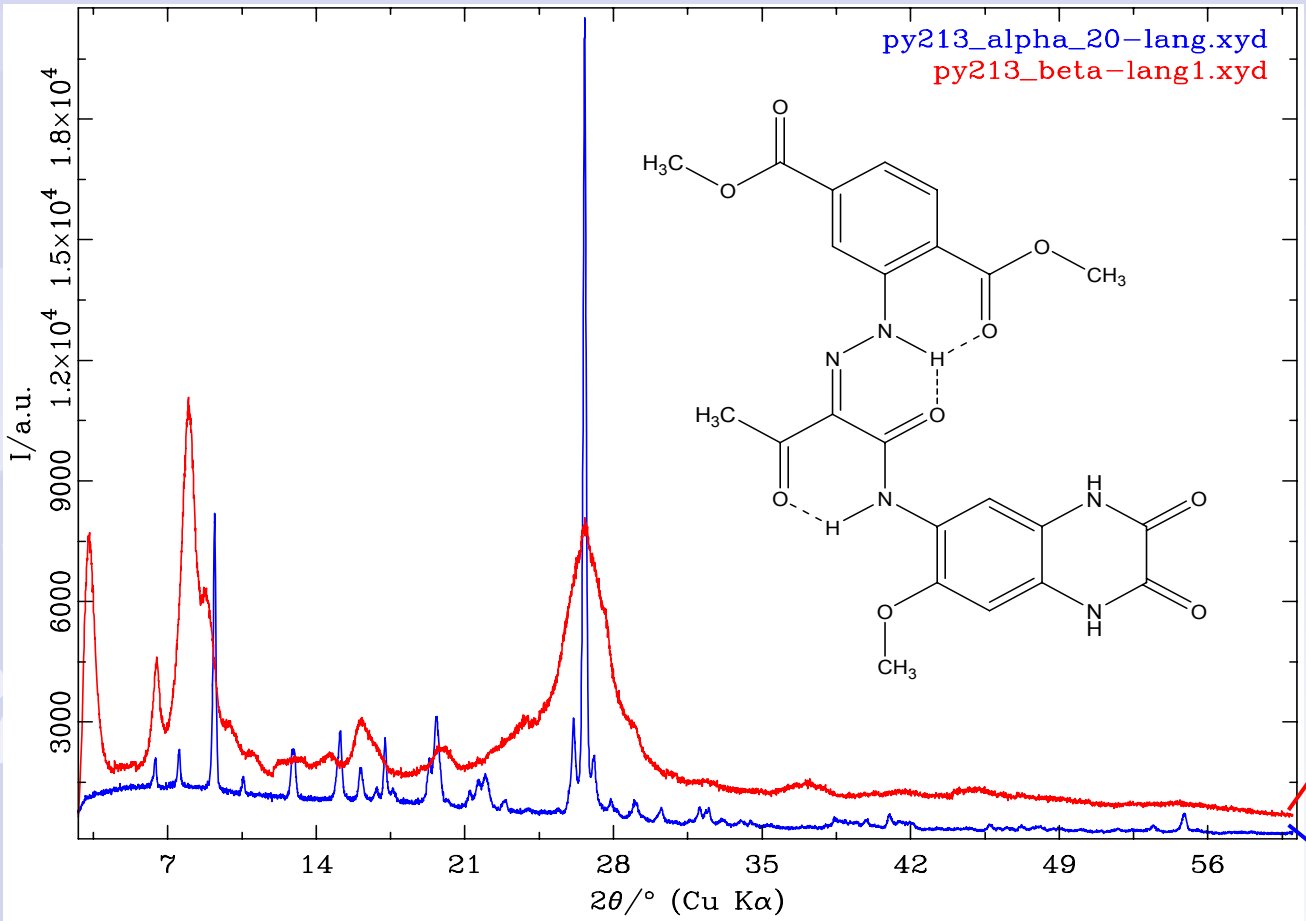


polymorphism:
2 phases

α-phase: yellow, β-phase: red

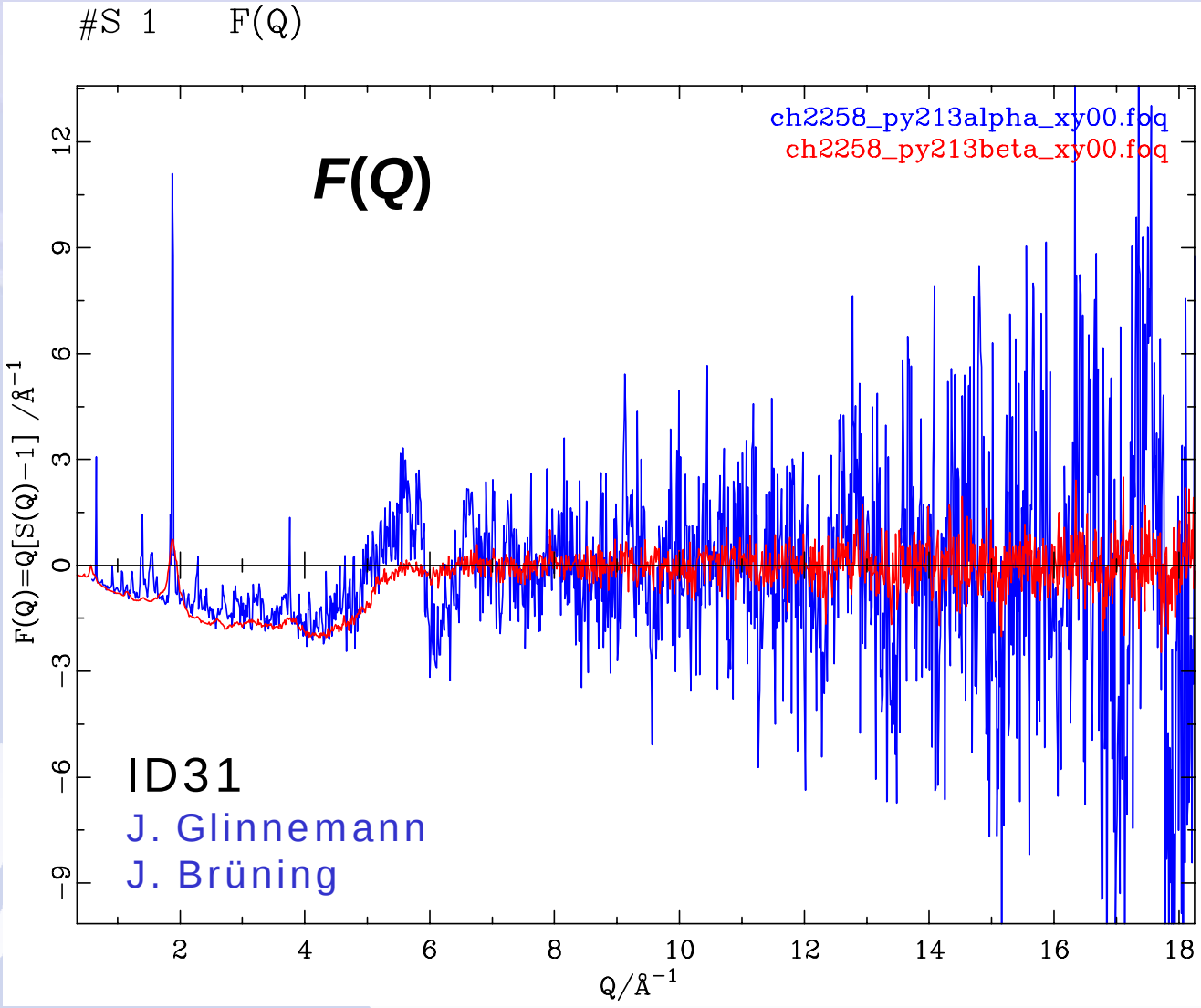
M.U. Schmidt

Pigment Yellow 213



"nice" and "bad" powder diffractograms

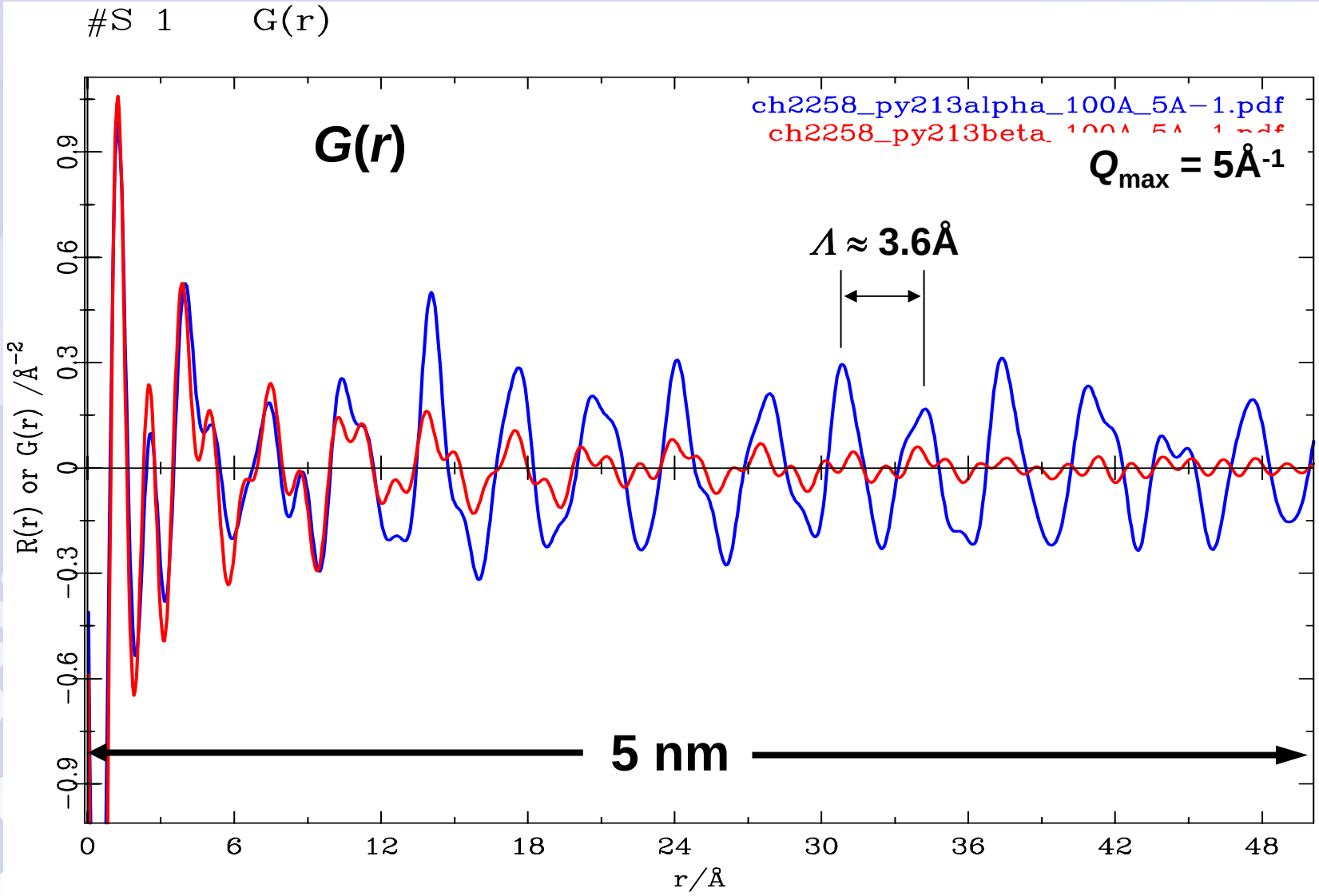
Pigment Yellow 213



β

α

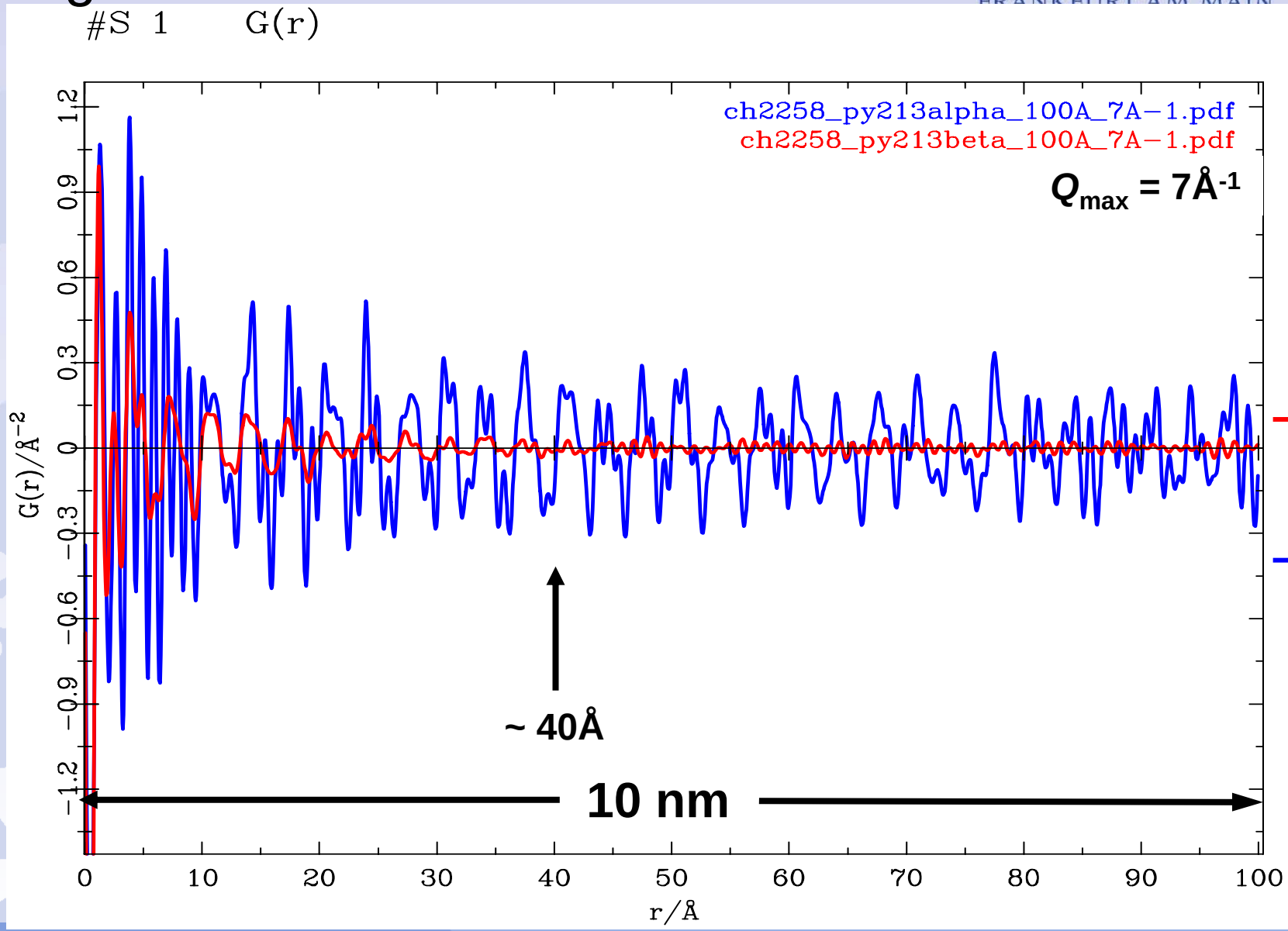
Pigment Yellow 213



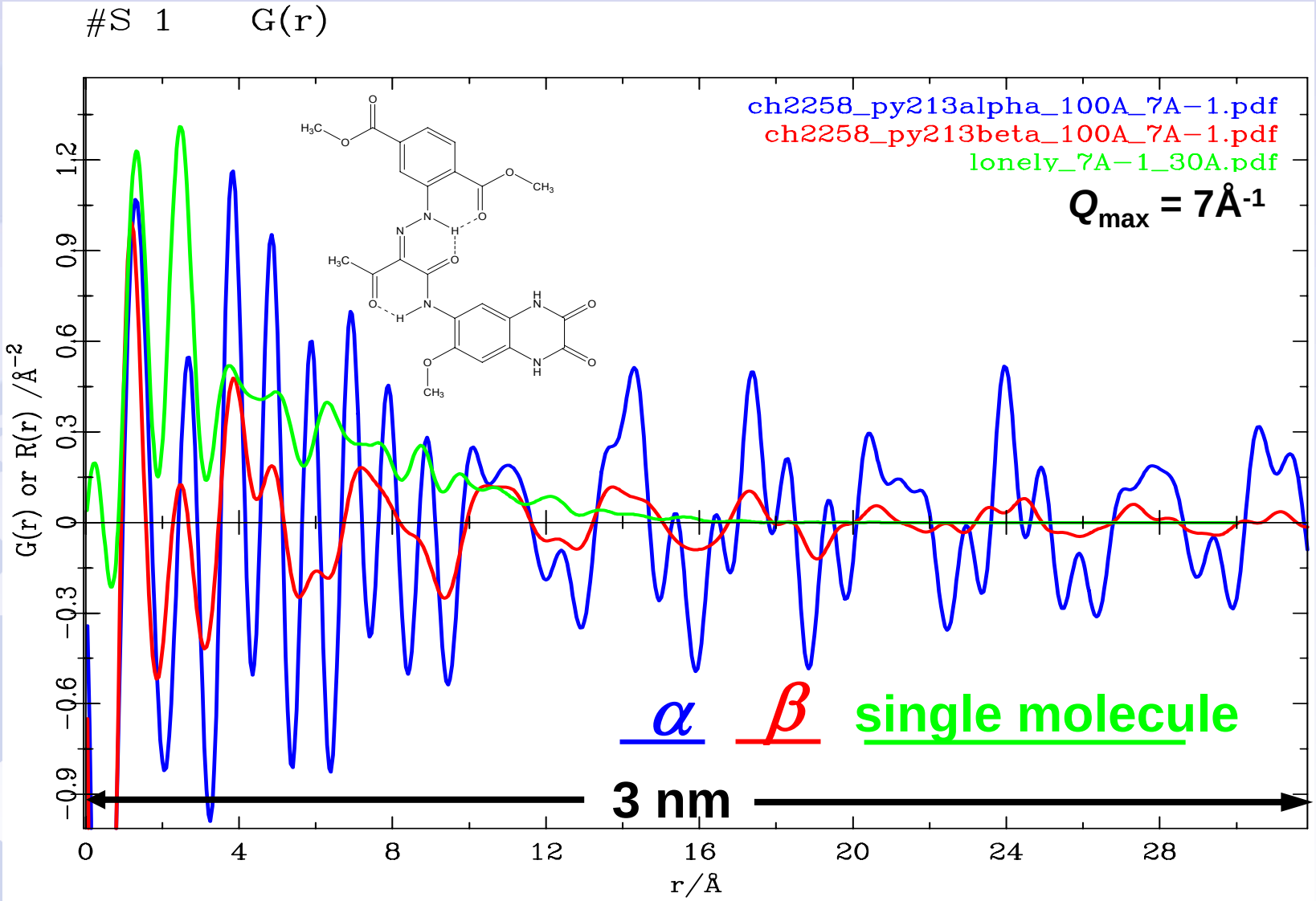
β

α

Pigment Yellow 213



Pigment Yellow 213



Pigment Yellow 213
Conclusion:

- for $r < 5$ Å one can „see“ the molecule
- the β-phase looses correlation about $r > 40$ Å (it is a „*nano*-material“ !)
- in α and β we see the inter-layer distance of ~ 3.6 Å

quantitative analysis has to follow!

pharmaceuticals

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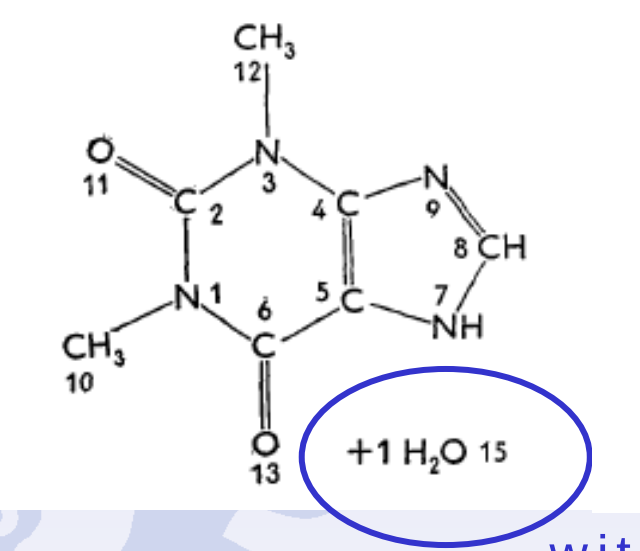
two main issues

- Polymorphism
- Amorphous formulations

can PDF help?

Theophylline

Polymorphism - Hydrate/Anhydride



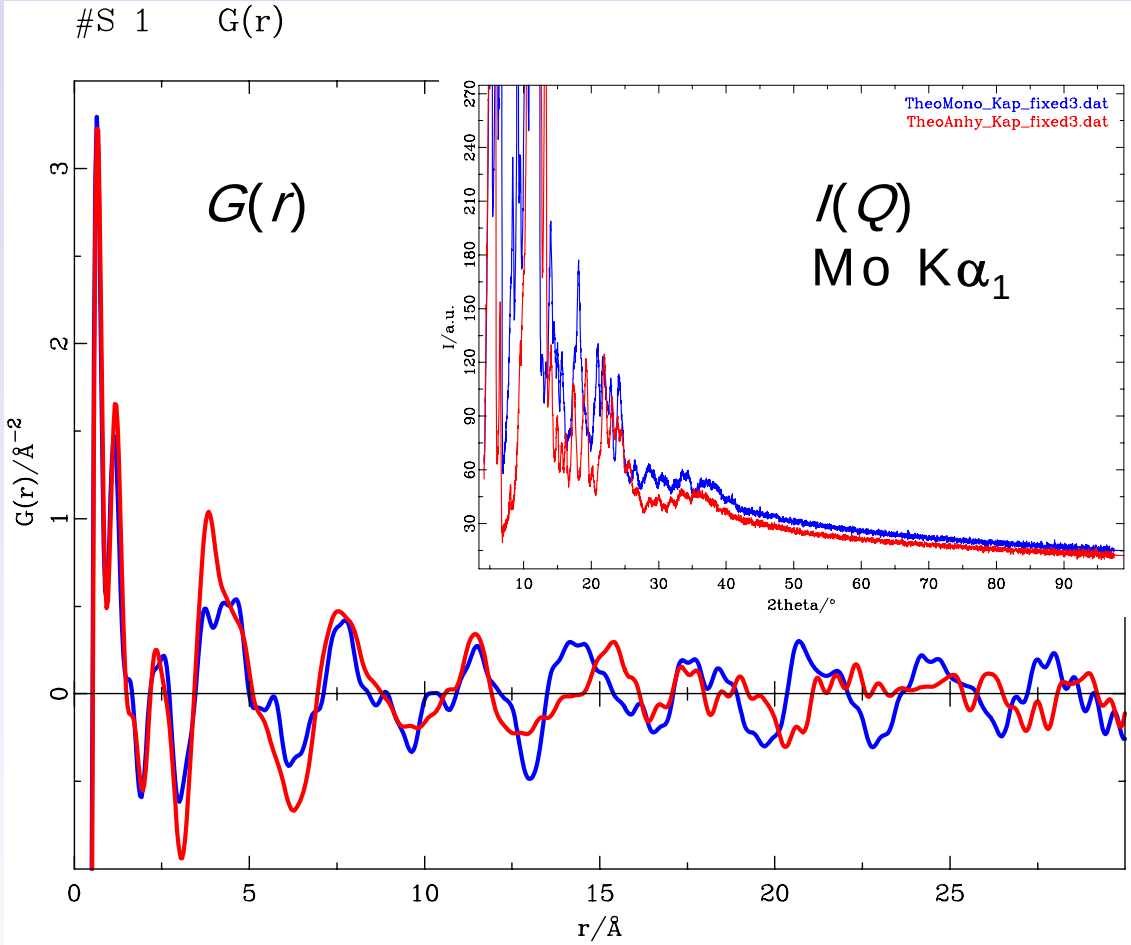
Sometimes,
solvates are subsumed
with the term "polymorphism".

Is there local resemblence
in hydrates/anhydirides ???

with or without H_2O

Sutor, *Acta Cryst.* **11** (1958) 83

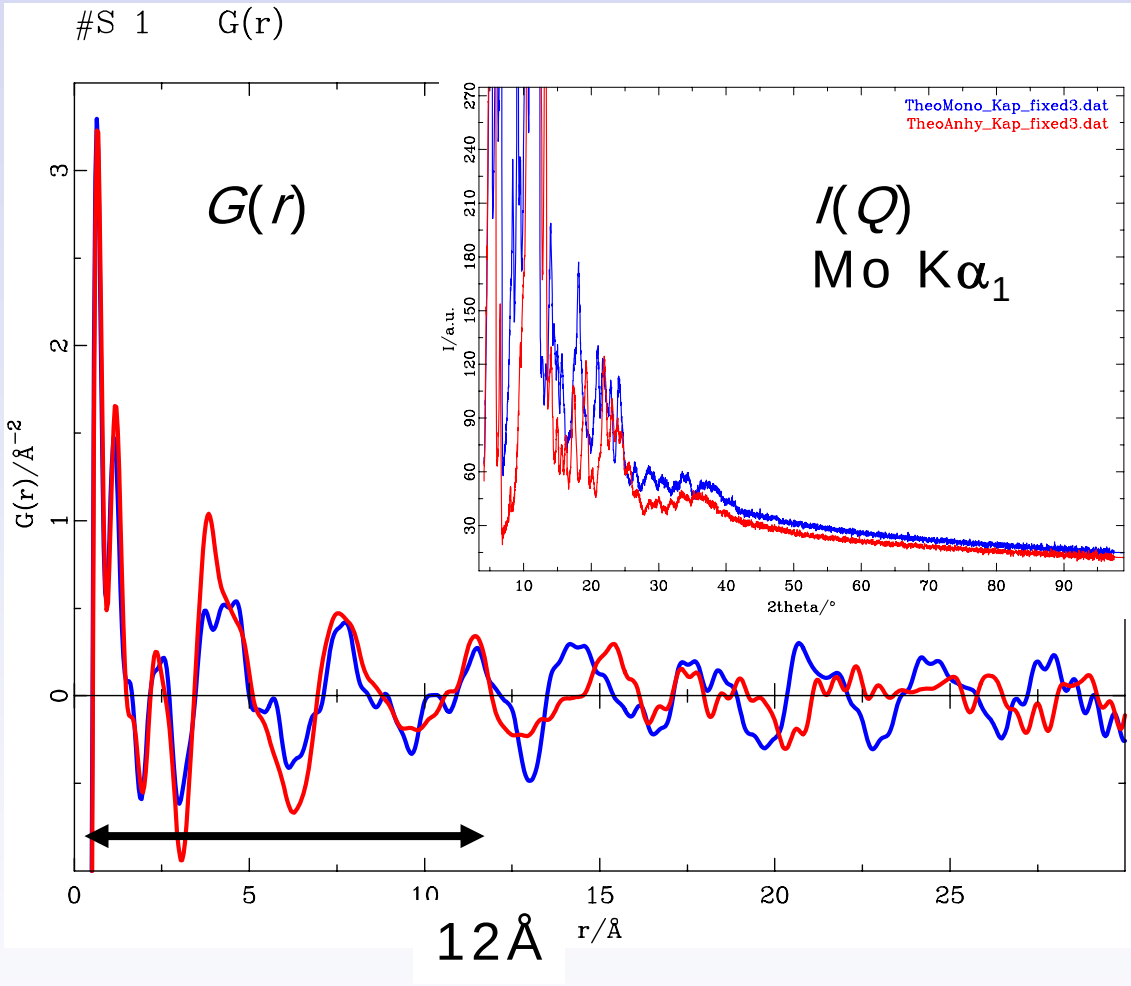
Theophylline



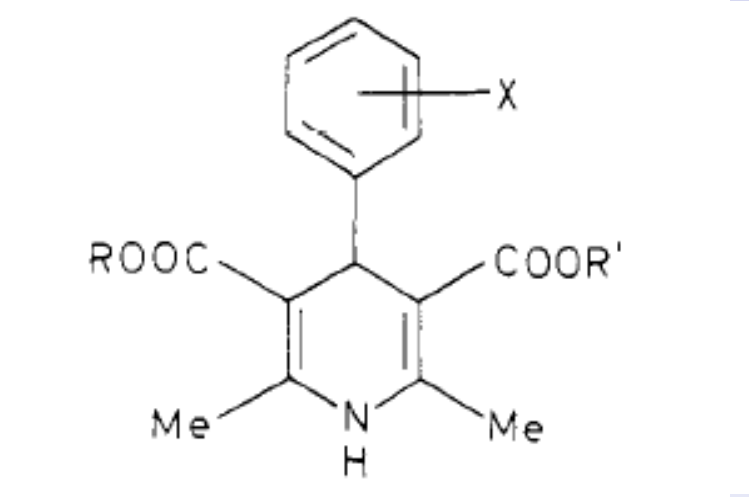
Theophylline

- Q_{max} = 13Å^{-1} reveals already:

- identical local structure finger-print for r < 12Å



Felodipine

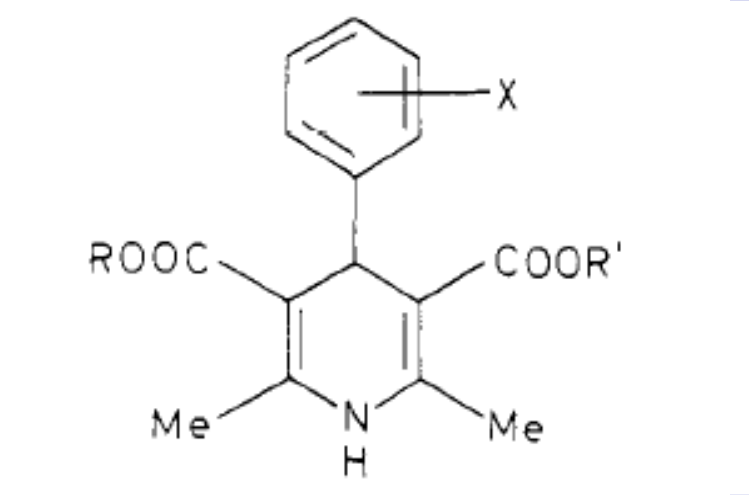


K. Nollenberger,
J. Dressman,
M.U. Schmidt,

a Ca-antagonist with
low water solubility

X = 2 Cl (*o* and *m*)
R = C_2H_5
R' = CH_3

Felodipine



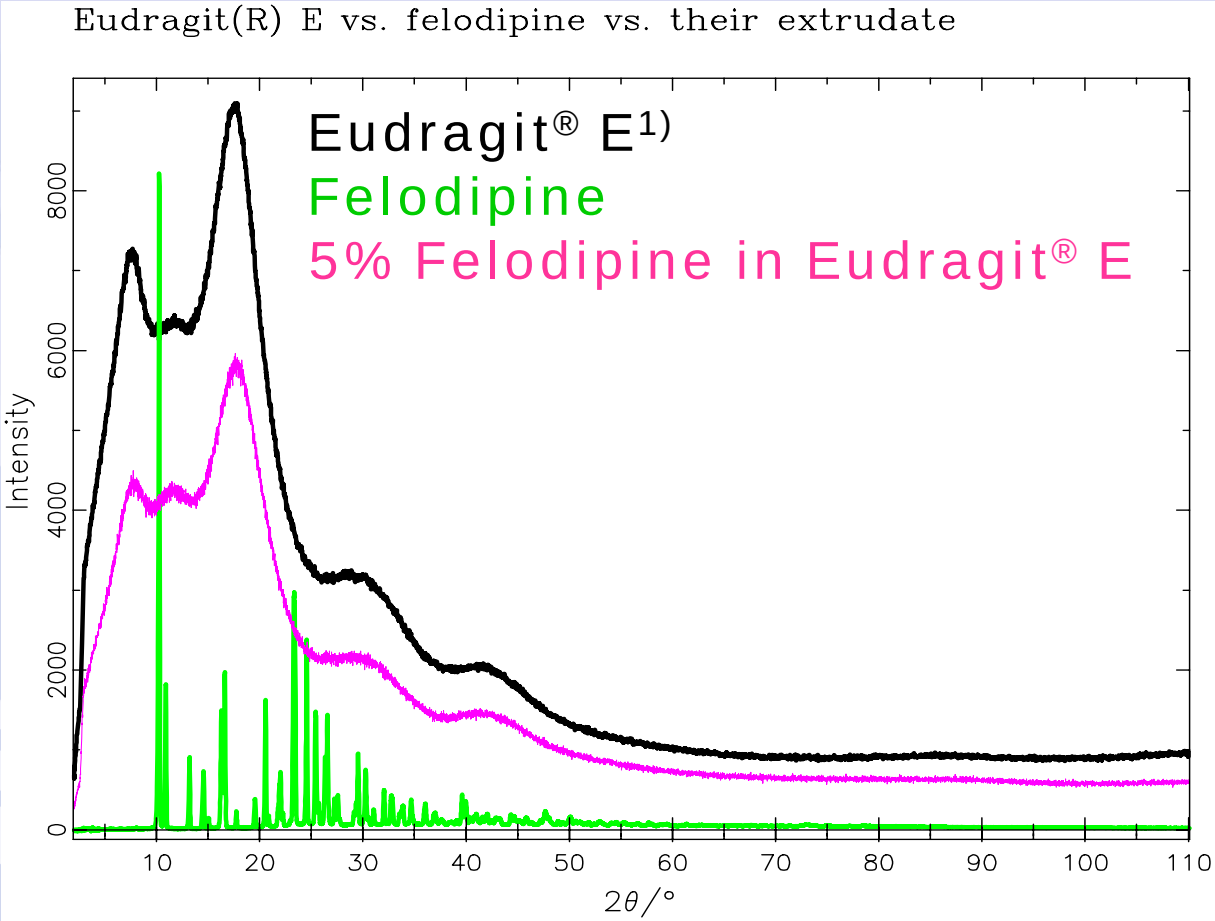
K. Nollenberger,
J. Dressman,
M.U. Schmidt,

a Ca-antagonist with
low water solubility

to enhance solubility:
co-extrudate with polymers[1)]!

or polymer mixtures...

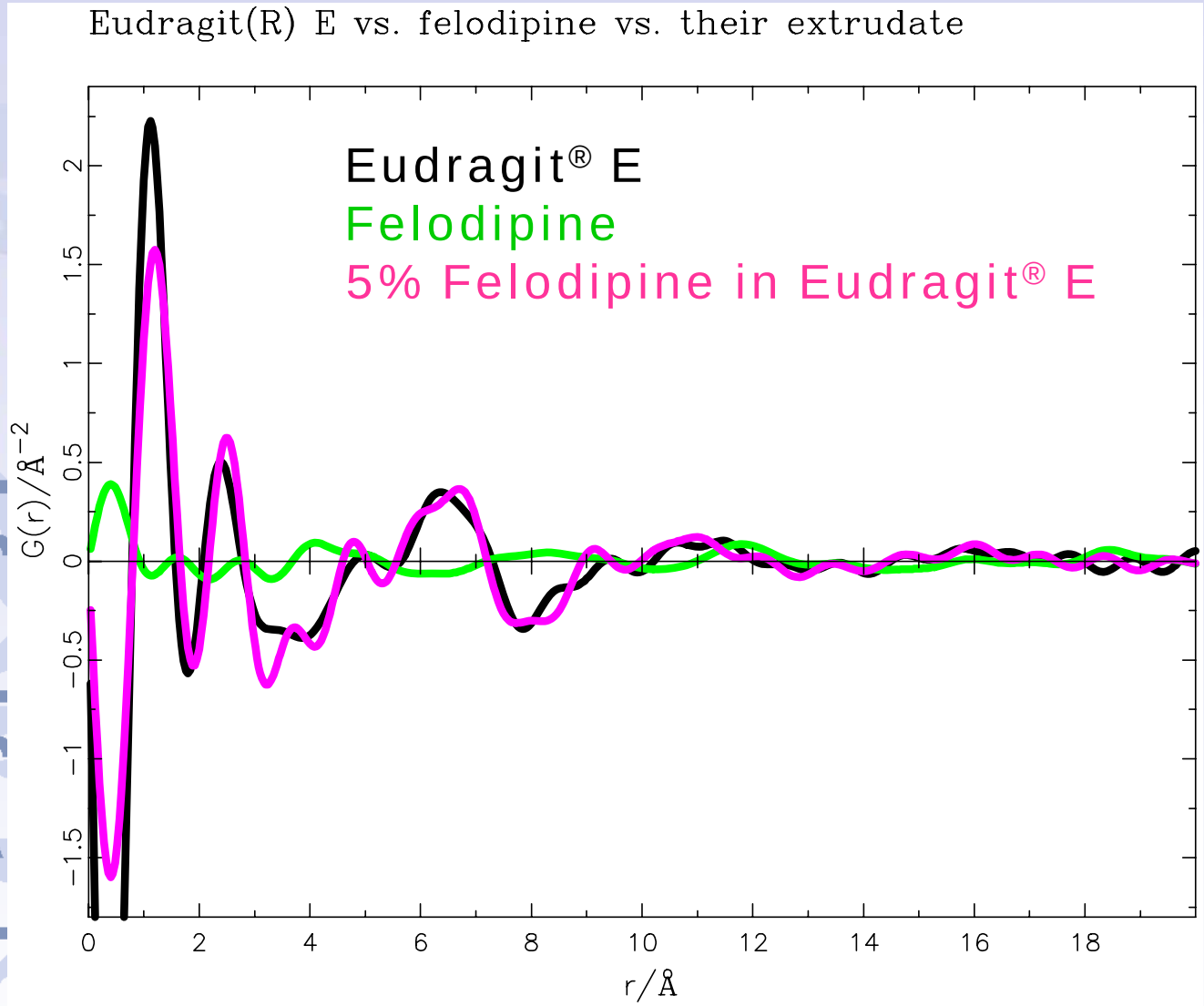
Felodipine



I(*Q*)
Cu Kα_1

[1)]Eudragit®: methacrylate copolymers (degussa Röhm)

Felodipine

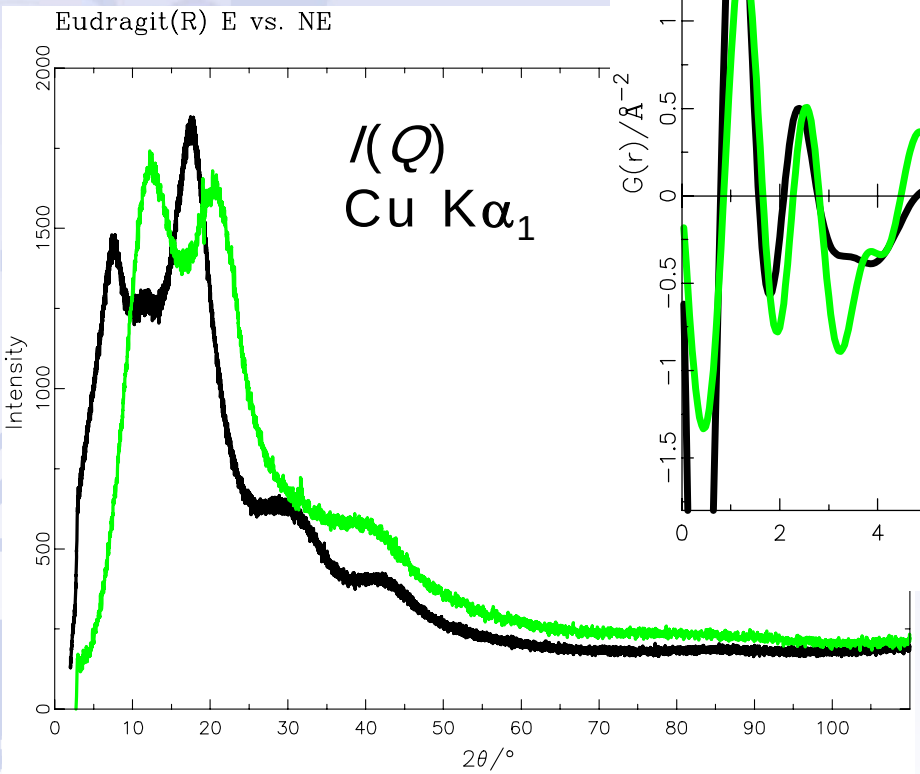


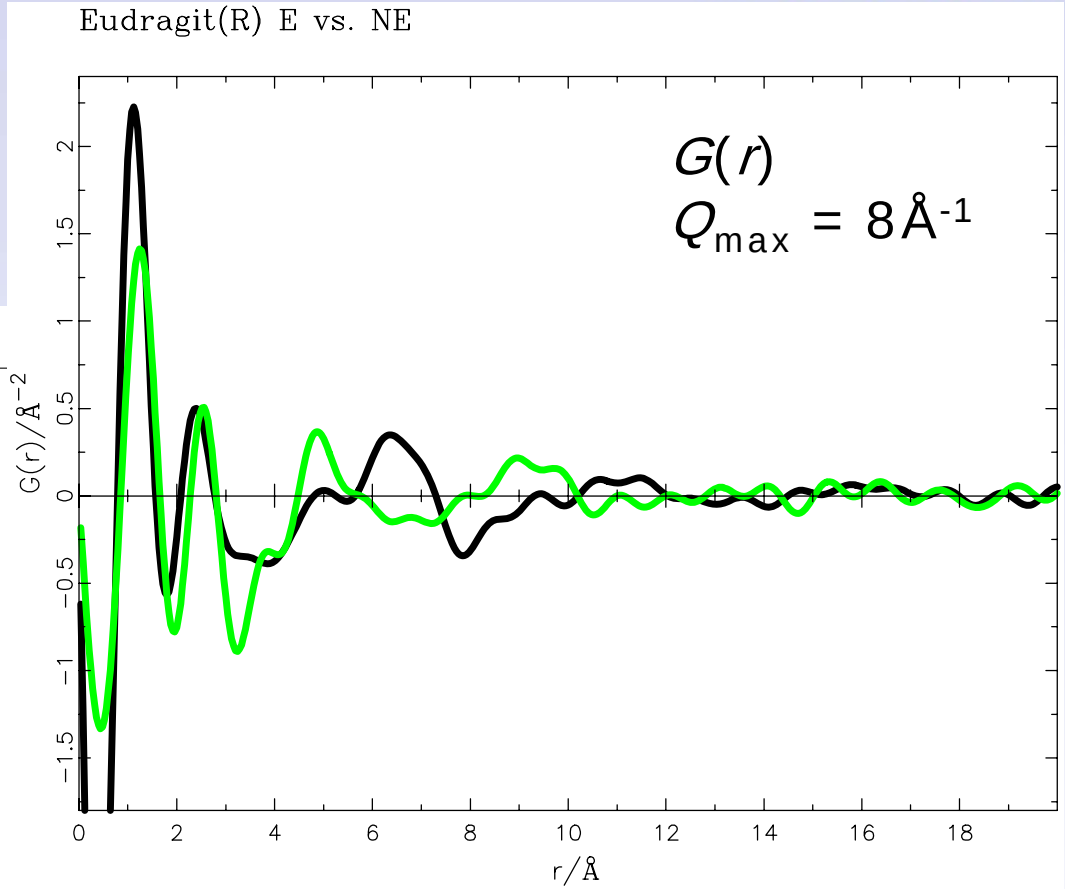
$G(r)$

Q_{max} = 8 Å^{-1}

Felodipine

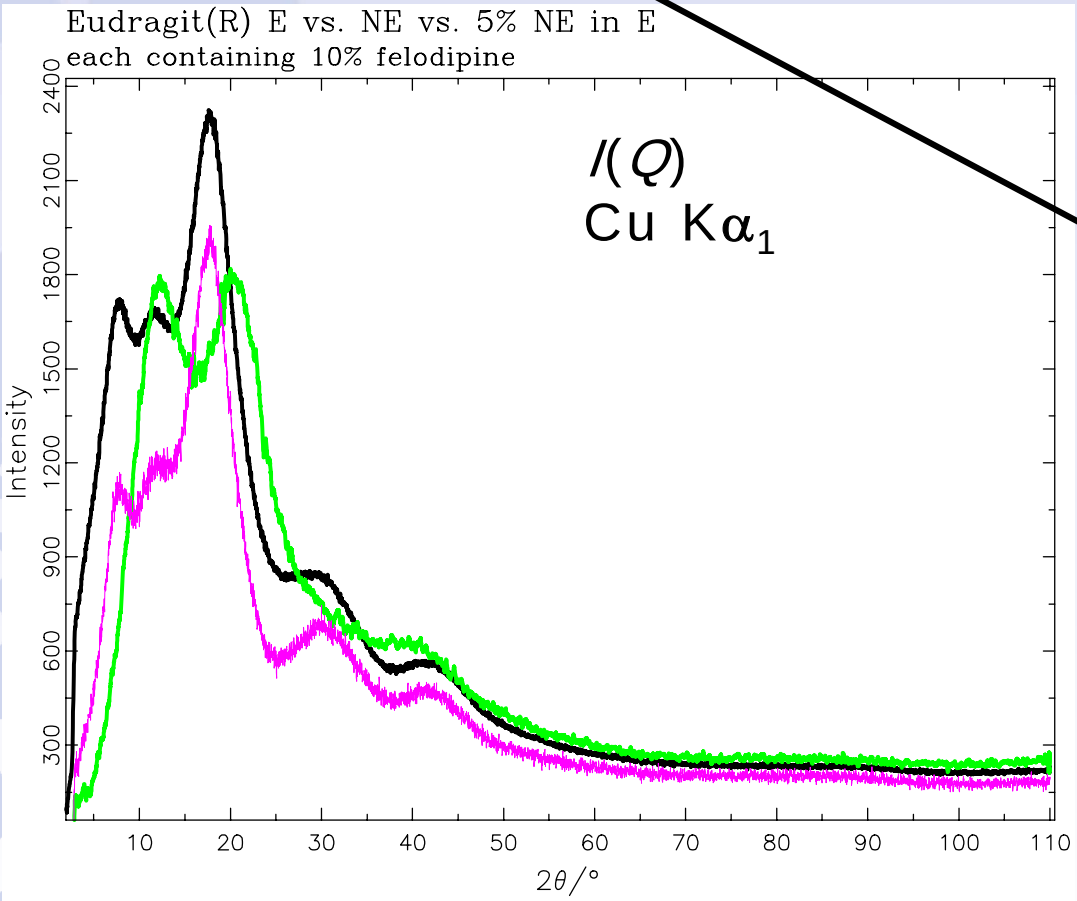
Eudragit® E
Eudragit® NE





Felodipine

Eudragit® E - 10% Felodipine
Eudragit® NE - 10% Felodipine
Eudragit® 85%E, 5%E - 10% Felodipine

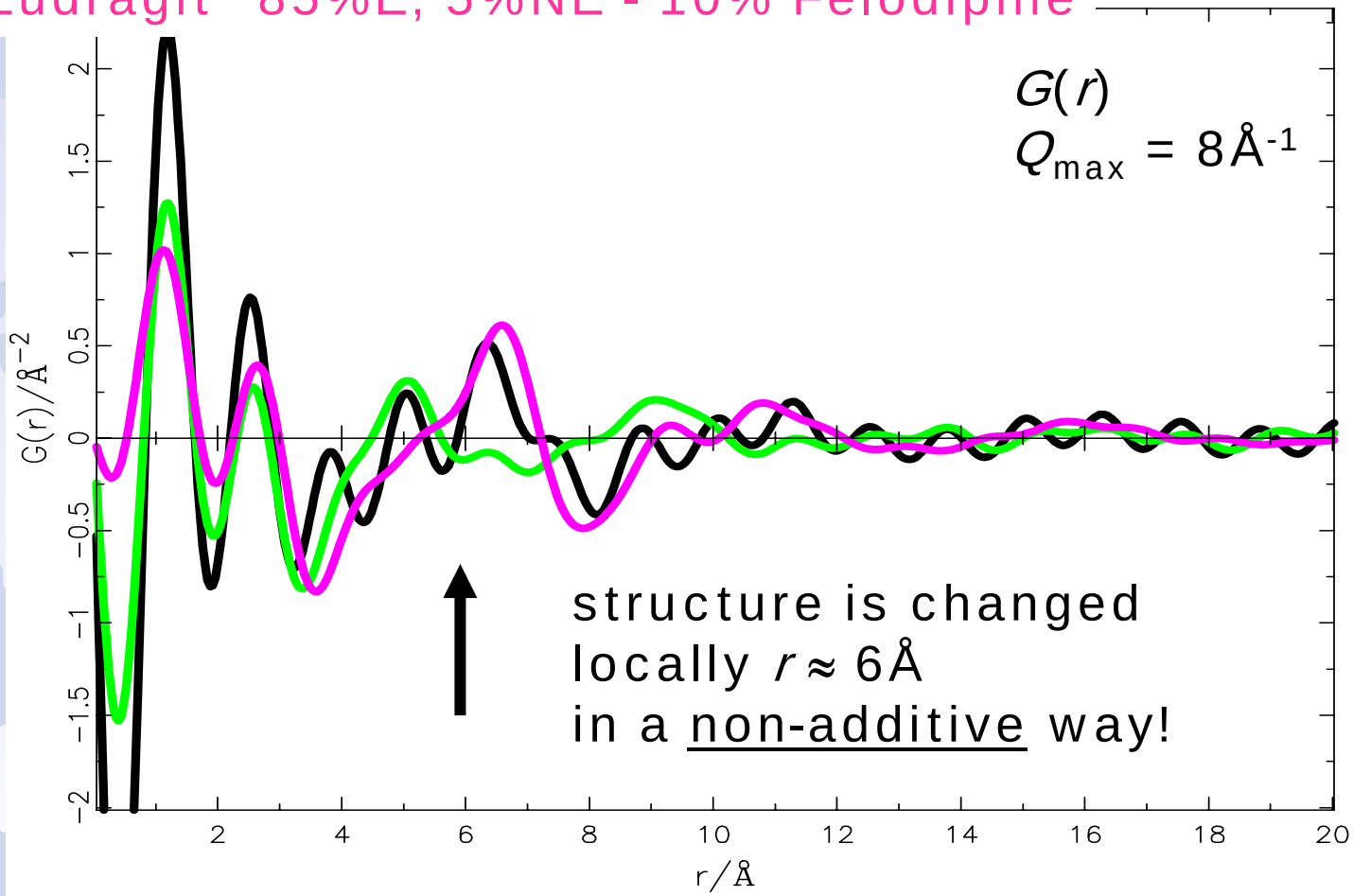


optimized solution characteristics!

but: why?

Felodipine

Eudragit® E - 10% Felodipine
Eudragit® NE - 10% Felodipine
Eudragit® 85%E, 5%NE - 10% Felodipine



Felodipine

Conclusion:

- when spectroscopy results are limited, PDF will help

- in this case, Cu Kα_1 data do well

- for the fist time, PDF has been applied successfully to understand a pharma melt extrusion problem

Nollenberger *et al.*, *J. Pharm. Sci.* (2007) in preparation

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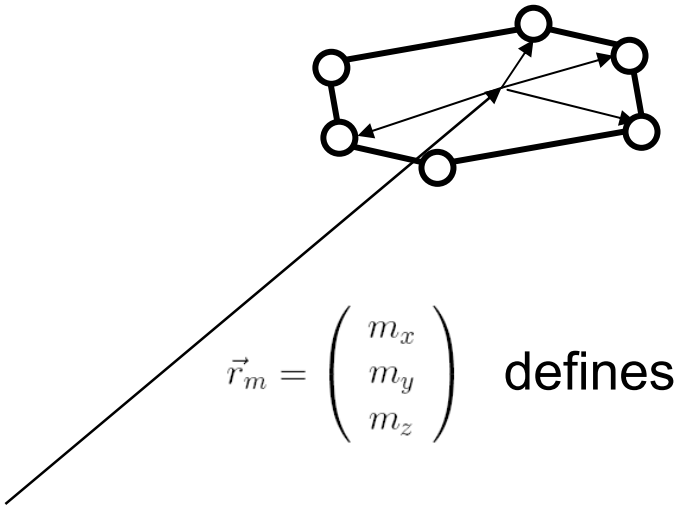
before I finish...

What is needed most ?



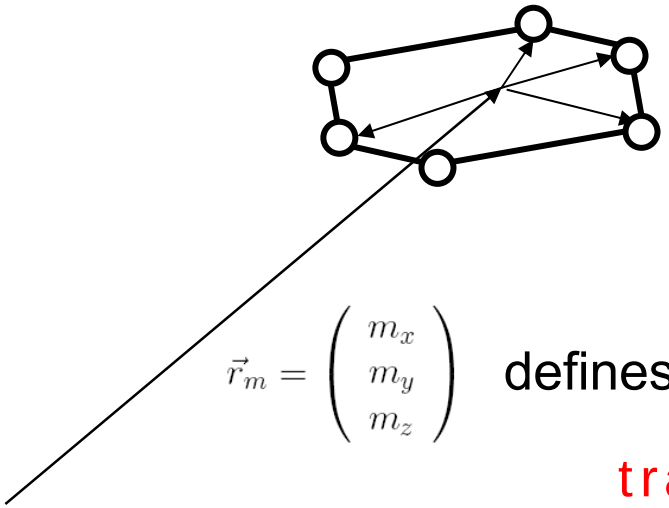
$$\vec{d}_i = \begin{pmatrix} d_{ix} \\ d_{iy} \\ d_{iz} \end{pmatrix} = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}_{cart} - \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_{cart}$$

$\left\{\vec{d}_i\right\}$ defines rigid geometry

$$\vec{r}_m = \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}$$ defines center of molecule

to do proper refinements
in the future...

Refinement constraints



$$\vec{d}_i = \begin{pmatrix} d_{ix} \\ d_{iy} \\ d_{iz} \end{pmatrix} = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}_{cart} - \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_{cart}$$

$\left\{\vec{d}_i\right\}$ defines rigid geometry

$$\vec{r}_m = \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}$$ defines center of molecule

translation of $\vec{r}_m$

rotation about χ, ϕ and θ

$$\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}_{frac} = \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix} + \begin{pmatrix} \frac{1}{a} & 0 & -\frac{\cot\beta}{a} \\ 0 & \frac{1}{b} & 0 \\ 0 & 0 & \frac{1}{c\sqrt{1-\cos^2\beta}} \end{pmatrix} \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\phi & 0 & \sin\phi \\ 0 & 1 & 0 \\ -\sin\phi & 0 & \cos\phi \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\chi & -\sin\chi \\ 0 & \sin\chi & \cos\chi \end{pmatrix} \begin{pmatrix} d_{ix} \\ d_{iy} \\ d_{iz} \end{pmatrix}$$

plus internal degrees of freedom ... !

Conclusion

it is all the same – but:

molecular solids,
they are different!

Conclusion

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it is all the same – but:

molecular solids,
they are different!

- challenging in terms of low *r* peaks
- qualitatively promising
- interesting applications
- but quantitative tools are needed !

Thank U

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to all those names mentioned...

in the order of appearence...

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G.G. Aviles
V. Honkimäki
Nadine Rademacher
Martin U. Schmidt
Alexandra Wolf
Hans-Beat Bürgi
Kathrin Nollenberger
Jennifer Dressman

(maybe someone else...)

... and the audience !

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