Microstructure of Nitrocellulose and NC-based Gun Propellants investigated by means of X-ray Diffraction

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Content

- X-ray diffraction for explosive characterization
- From cellulose to gun propellant: Structural approaches to
  - Cellulose
  - Nitrocellulose
  - Blasting oils
  - Crystalline additives of gun propellants
- NC propellants
  systematic of single/double/triple base propellants
- Summary

X-ray Diffraction @ Fraunhofer ICT

- Non destructive method for…
- Crystal and real structure
  polymorphism, crystallite size, strain, defects, crystallinity, density…
- Crystalline explosives
  AN, HMX, RDX, FOX-7, FOX-12, CL-20…
  -> polymorphism & stabilization
  -> quality assessment
  -> co-crystals
  -> effects of mech. & shock loading
  -> reduced sensitivity, aging
- Amorphous and partial amorphous energetic materials
  PBX, LED, E-Binder, Block-Co-Polymers, NC & NC gun propellants

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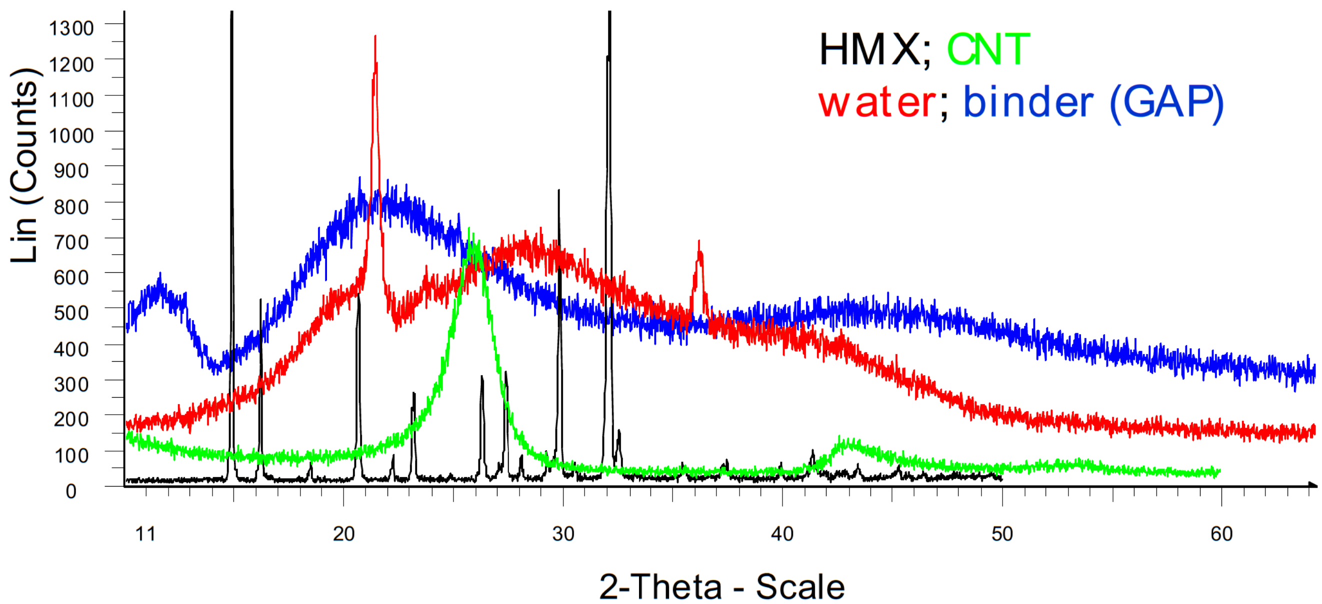
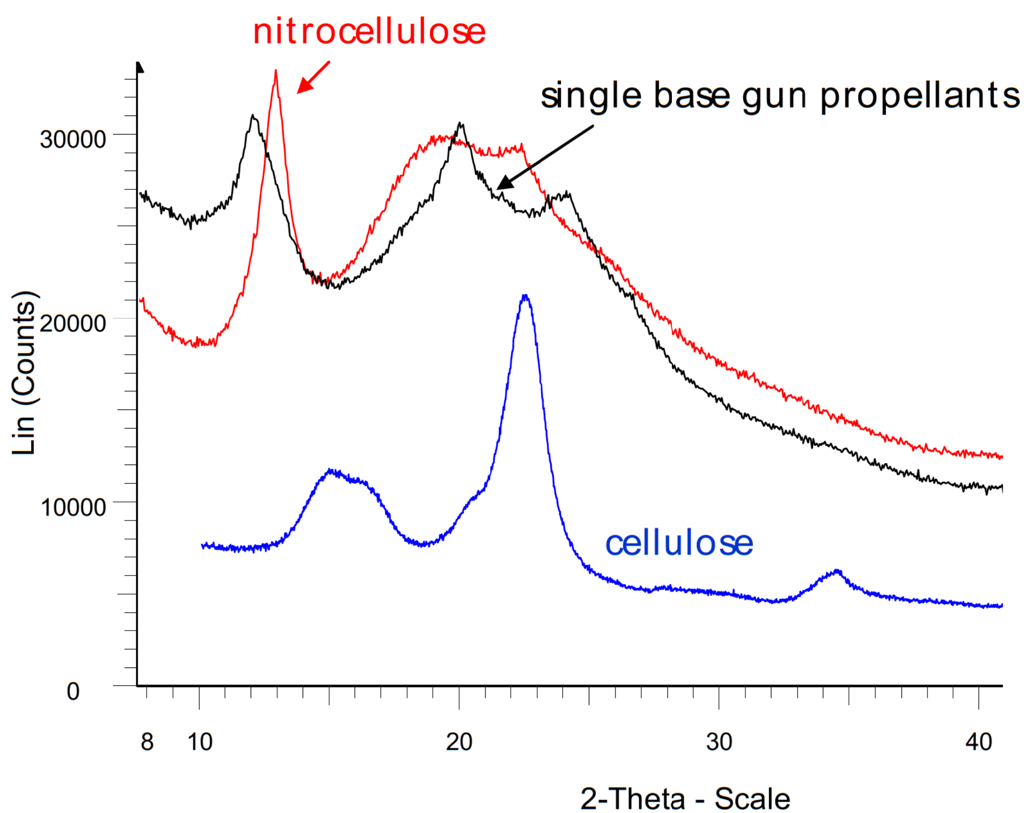
…from crystalline to amorphous energetic materials



- …from narrow peaks to halos -> crystallite sizes decrease and/or defective areas increase approaching an amorphous state
- Diffraction patterns are still characteristic (even for water)
- Information rather bound to background of patterns than to diffraction peaks

Herrmann, M. et al., Proc. of the 14th NTREM, Pardubice, Czech Republic, April 13–15, **2011**, pp 681-686

From cellulose to NC-gun propellants: XRD patterns



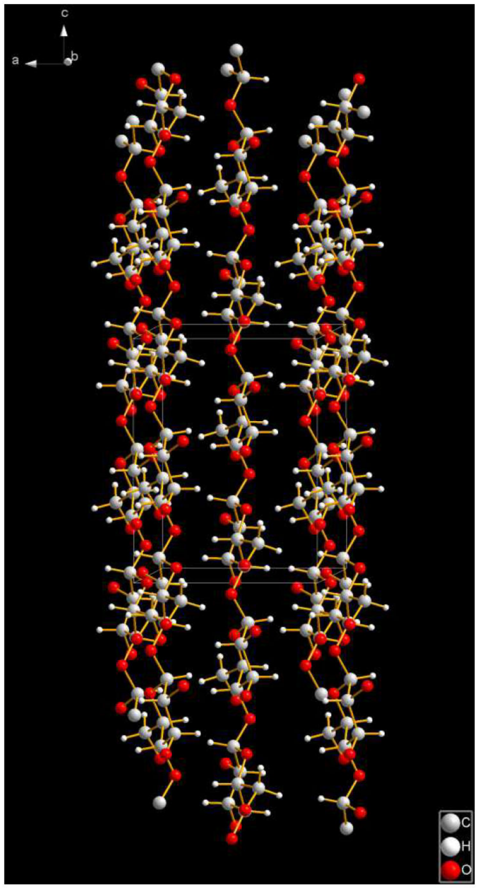
- Characteristic patterns with “spikes” and halos
- Typical for partial crystalline materials
- Differences between patterns represent changes of microstructure due to the nitration of the cellulose and the gelling of NC during the processing of the gun propellant
- Evaluation would gain from structure models

Gun propellants – ingredients and processing

base	Ingredients / processing
single	**Nitrocellulose (NC)**
	Mixture of guncotton (13.0–13.4 % N) and soluble guncotton (11-13% N) is gelatinized with the aid of solvents (alcohol, ether). -> process with solvent no plasticizer -> horny structure; poor mechanical properties
double	**NC + blasting oil** (25–50%); e.g. nitroglycerine (Ngl), diethyleneglycol dinitrate (DEGDN) or mixtures; Ngl plasticizes NC! NC is suspended in water and Ngl is slowly added. All Ngl is absorbed the NC. After separation from water the paste is ground, mixed with additives and gelatinized on hot rollers (1% residual water content) -> solventless process Ball powders: Suspension of NC-solution in Water + evaporation of solvent.
triple	**NC + blasting oil + energetic solid material**; e.g. Nitroguanidine (Nigu)

R. Meyer et al., Explosives, Wiley-VCH Verlag GmbH, Weinheim, 2007

Crystal structures of cellulose



- C is built up of crystalline microfibrils consisting of parallel, hydrogen-bonded molecules.
- Two native crystalline phases I_α and I_β , both can be found not only within the same cellulose sample, but also along a given microfibril.

  I_α-rich: cell wall of some algae and in bacterial cellulose
  I_β-rich: cotton, wood and ramie fibers
- Crystal structures solved by X-ray and Neutron Diffraction*

* Y. Nishivama et al., *J. Am. Chem. Soc.*, **2002**, *124* (31), pp 9074-9082 and *J. Am. Chem. Soc.* **2003**, 125, pp 14300–14406

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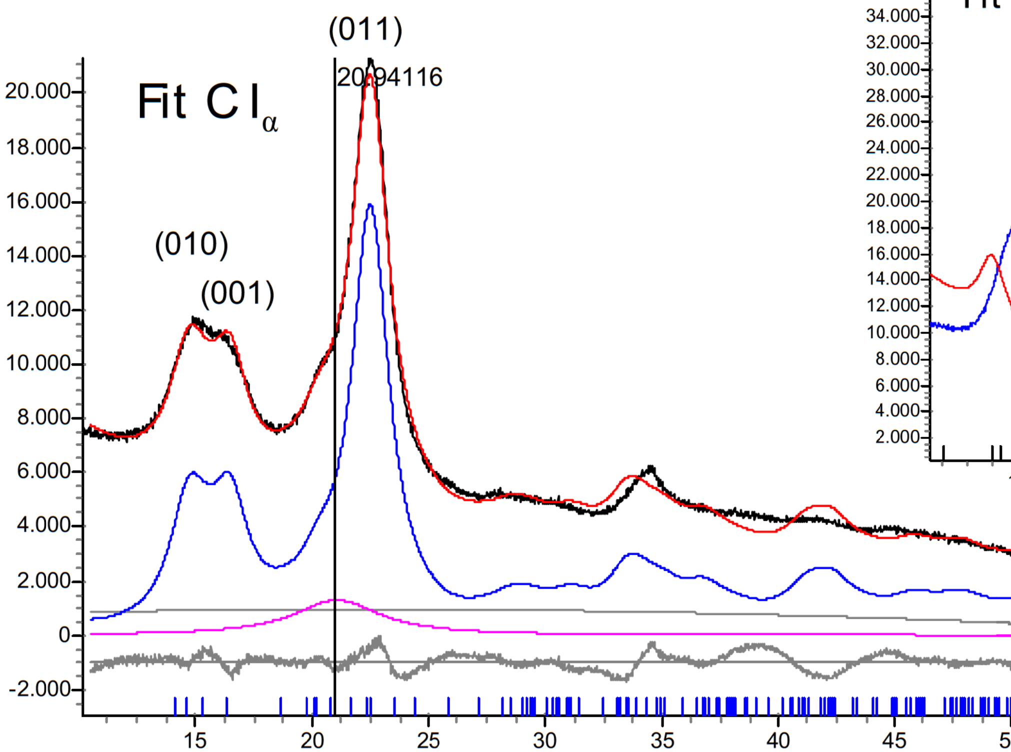
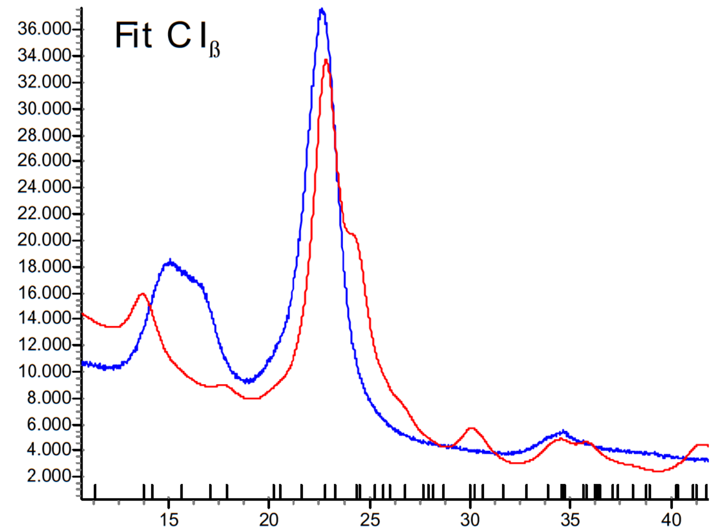
Evaluation of cellulose





(hkl)	CrySize L [nm]
whole pattern	5.5
(010)*	3.5
(001)*	2.9
(011)*	5.1

* fundamental parameter fit

- C I_α fits well; C I_β and C II (Kolpak et al.) do not
- Crystallite sizes were determined from peak broadening (5.5 nm)
  -> crystallization perpendicular to the chains

Crystal structure of nitrocellulose

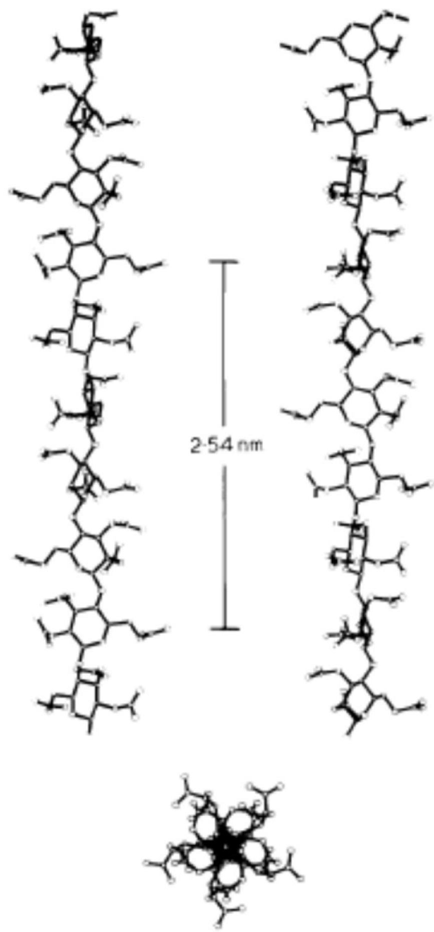
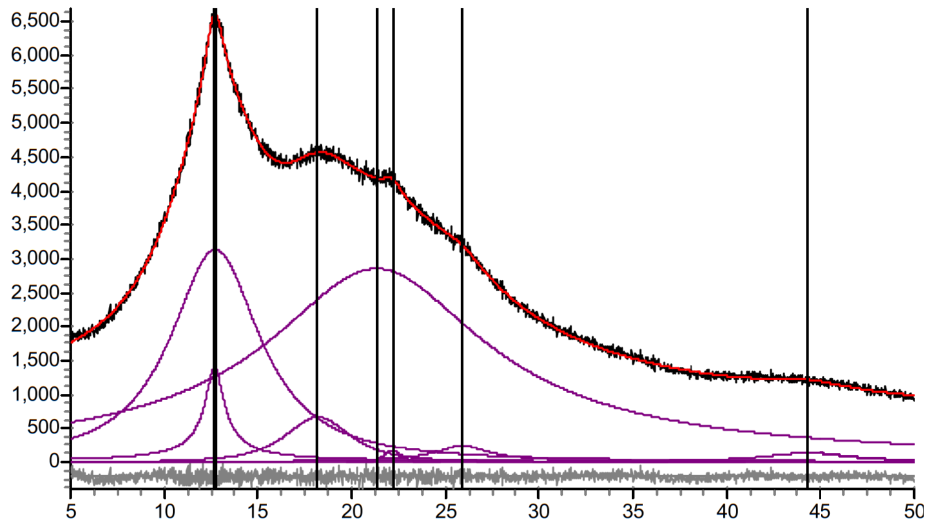


Fig.: Structure proposed by Maeder

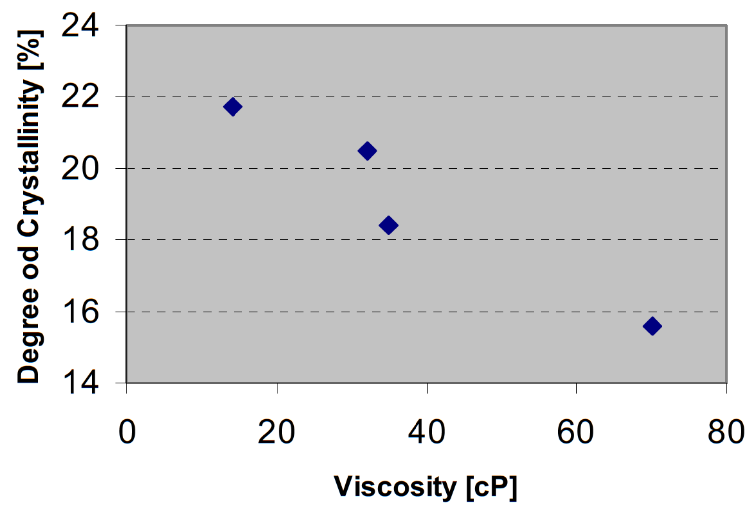
Meader, D. et al., Cellulose trinintrate: molecular conformation and packing considerations. Polymer, 1978, Vol. 19, 1371–1373.

- Diffraction experiments & molecular model building
- 2.54 nm layer line spacing and five-fold helical symmetry, (native cellulose showing a layer line spacing of 1.04 nm)
- Proposed lattice parameters
  a=0.9, b=1.39, c=2.56 nm (Mathieu),
  a=0.9, b=1.224, c=2.54 nm (Happey),
  a=0.9, b=1.46, c=2.54 nm (Maeder),
  (c: fibre axis; α=ß=γ=90°; no space group specified)
- Complete model may be constructed from symmetry, lattice parameters, Cartesian coordinates of the asymmetric unit, the proposed side group orientations
- Data not yet conclusive!

Evaluation of nitrocellulose pattern



- Literature data do not fit patterns
  -> Evaluation by pattern decomposition
- Crystalline domains: larger in dry samples
- Degree of crystallinity:
  correlates to viscosity and fineness
  (DoC = $A_{cryst}/(A_{cryst} + A_{amorph})$)



Herrmann, M. et al.; Proc. 42nd Int Annu Conf of ICT, **2011**, 53.1-7

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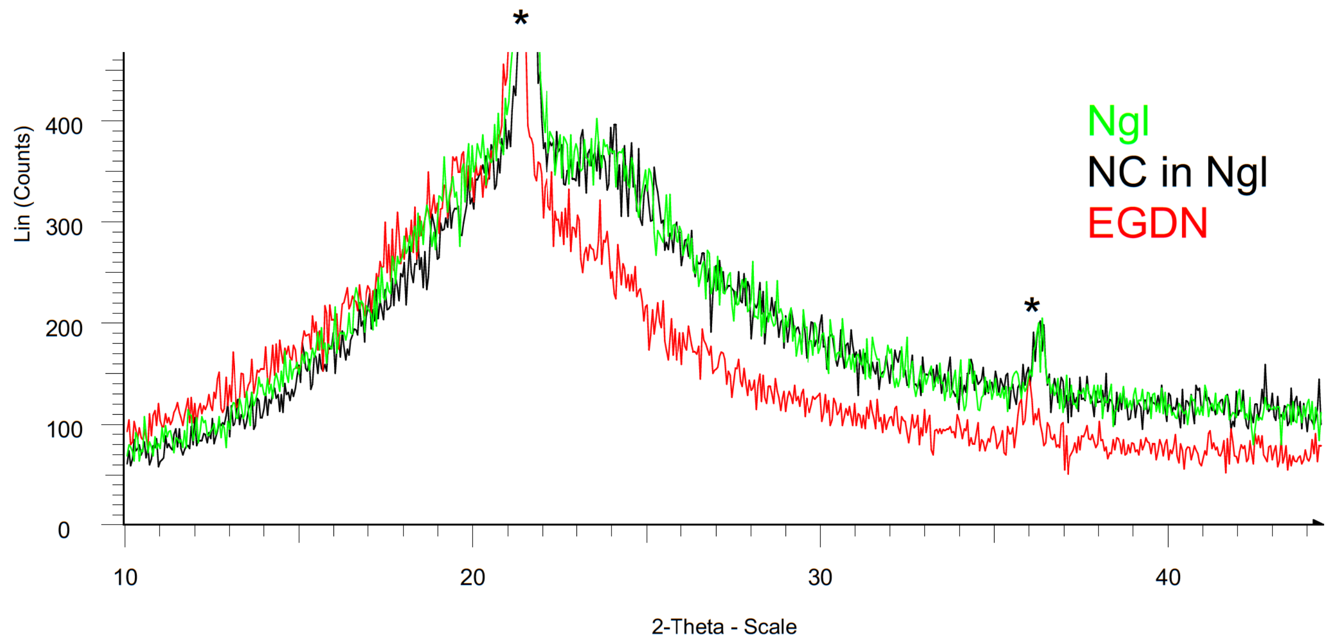
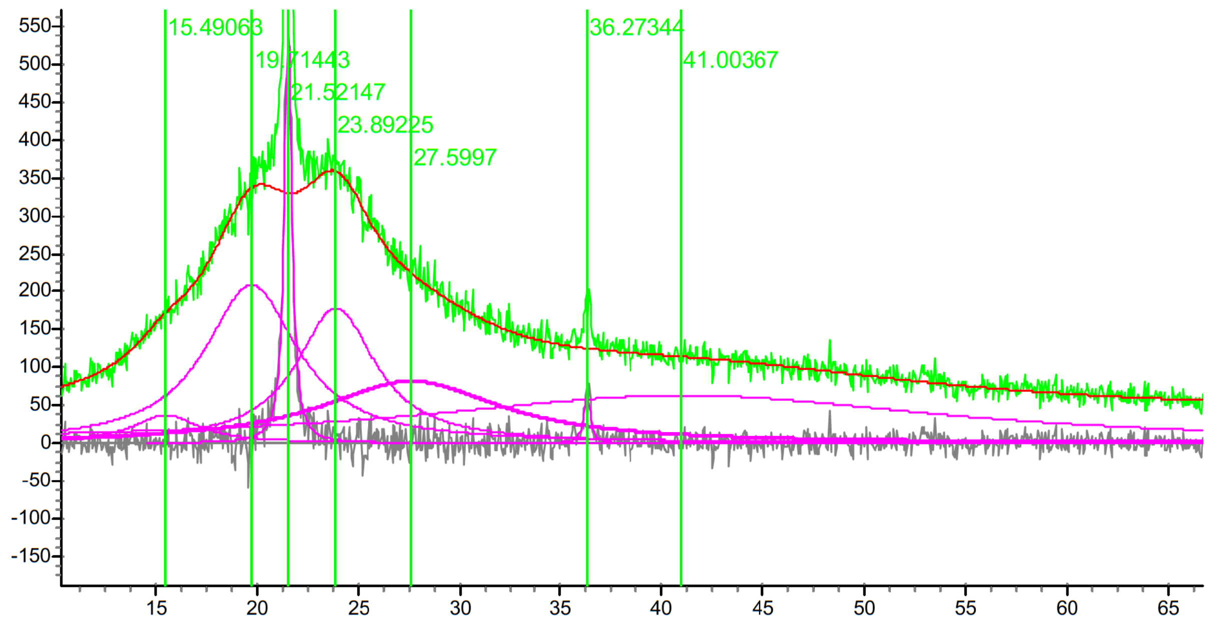
Blasting oil: Nitroglycerin (Ngl)



- Ngl & EGDN show only amorphous halos but distinguishable
- NC in Ngl ≅ Ngl
  no crystalline shares of NC -> solves in Ngl

* Peaks at 21 and 36 °2θ are from cover foil of the sample holder

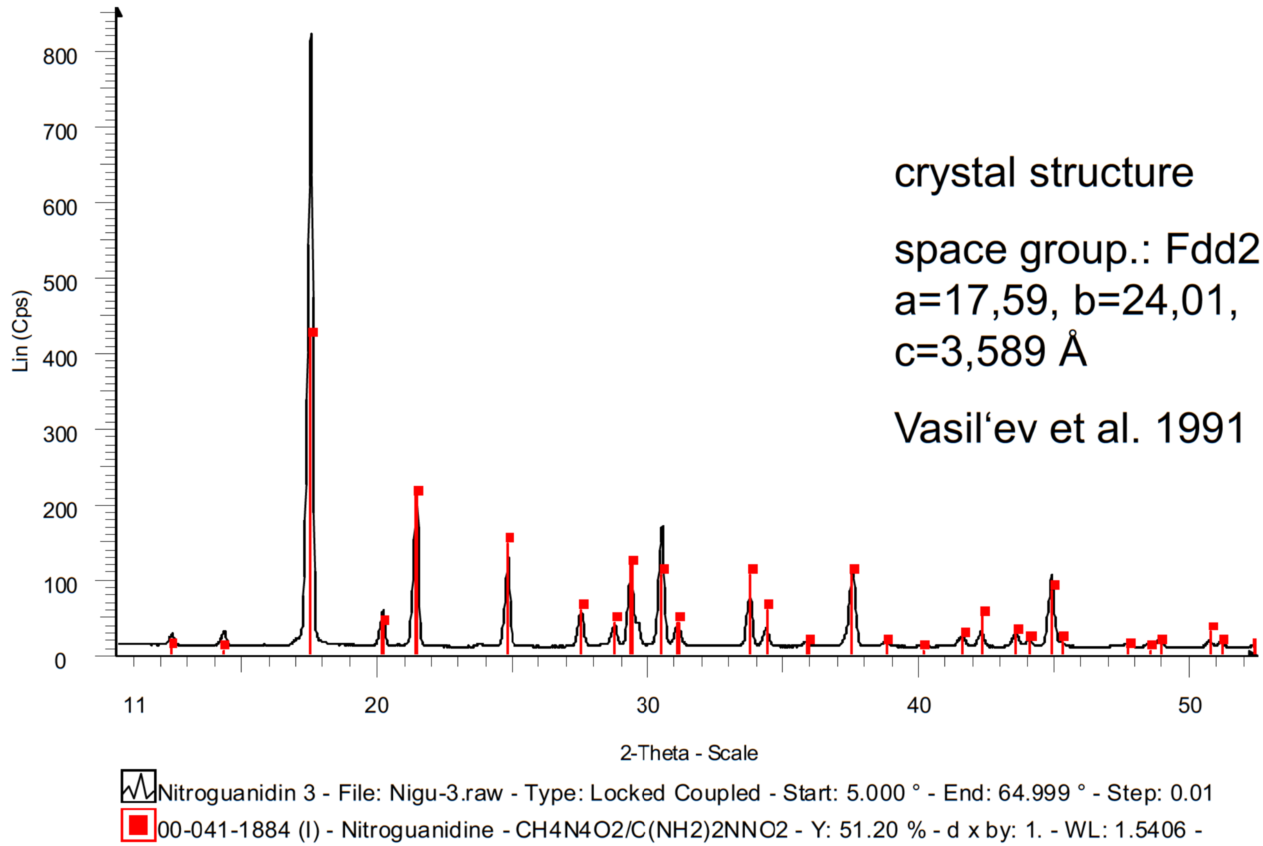
Evaluation of Nitroglycerin pattern



- Decomposition of the diffraction pattern: Fixed peak positions and widths, but constrained intensities
  -> scalable partial NG-pattern

- Relatively narrow intensity shares may relate to near order such as in gel structures (solidification temp. at 13 °C)

Additive Nitroguanidine



crystal structure

space group.: Fdd2
a=17,59, b=24,01,
c=3,589 Å

Vasil'ev et al. 1991

- Crystalline powder -> narrow peaks
- Identification through ICDD-PDF 41-1884 (red markers)

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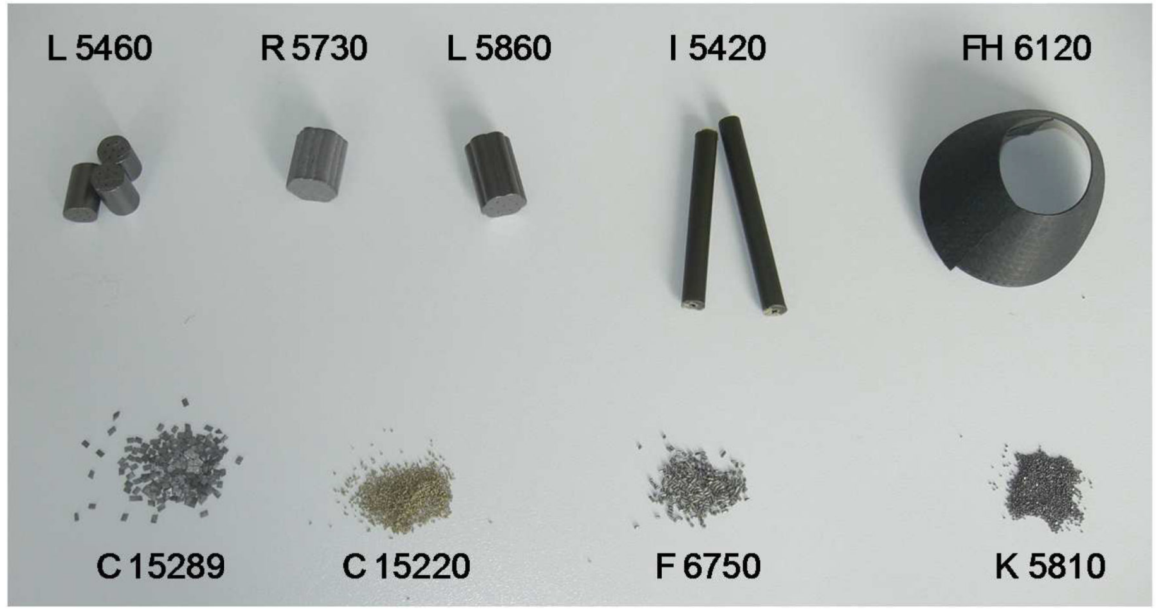
Gun propellants

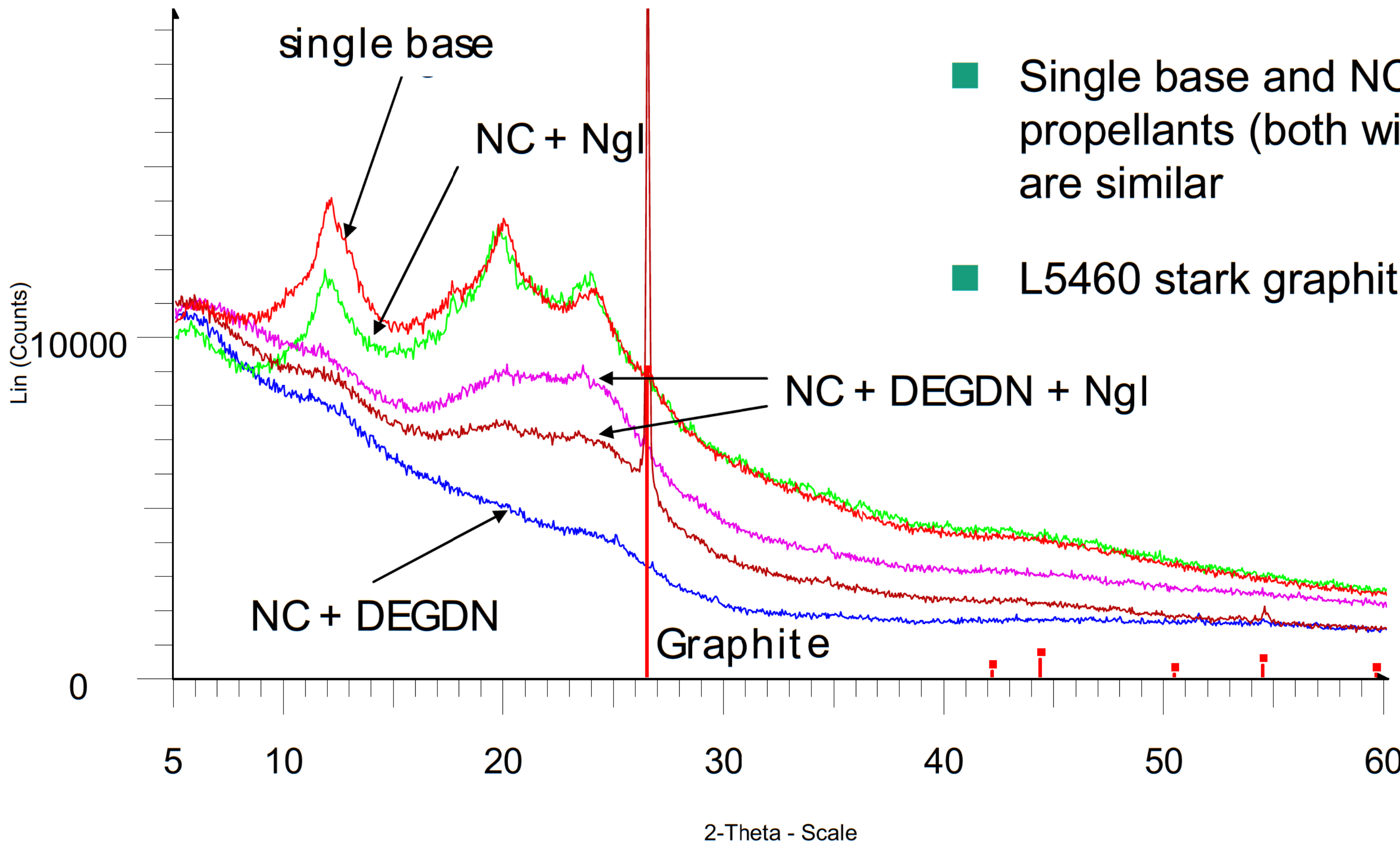


propellant	base	blasting oil	solvent	habit
C 15289	single		yes	fine square platelets
C 15220	single		yes	fine grey rods
F 6750	double	Ngl	yes	fine grey rods
K 5810	double	Ngl	yes	fine black balls
FH 6120	double	Ngl	no	black foil
L 5860	double	DEGDN + Ngl	no	big 7-hole grain
L 5460	double	DEGDN + Ngl	no	big 7-hole-grain
I 5420	double	DEGDN	no	black tubes
R 5730	triple*	DEGDN	no	big 19-hole grain

* + Nigu, RDX, plasticizer, Centralit

Herrmann, M.; Förter-Barth, U.; Kaiser, M.; Kupzik, K.; Scheibel, R.: Microstructure of NC-Propellants Investigated by X-ray Diffraction (Part I). Proc. 44th Int Annu Conf of ICT 2013, 43.1-9

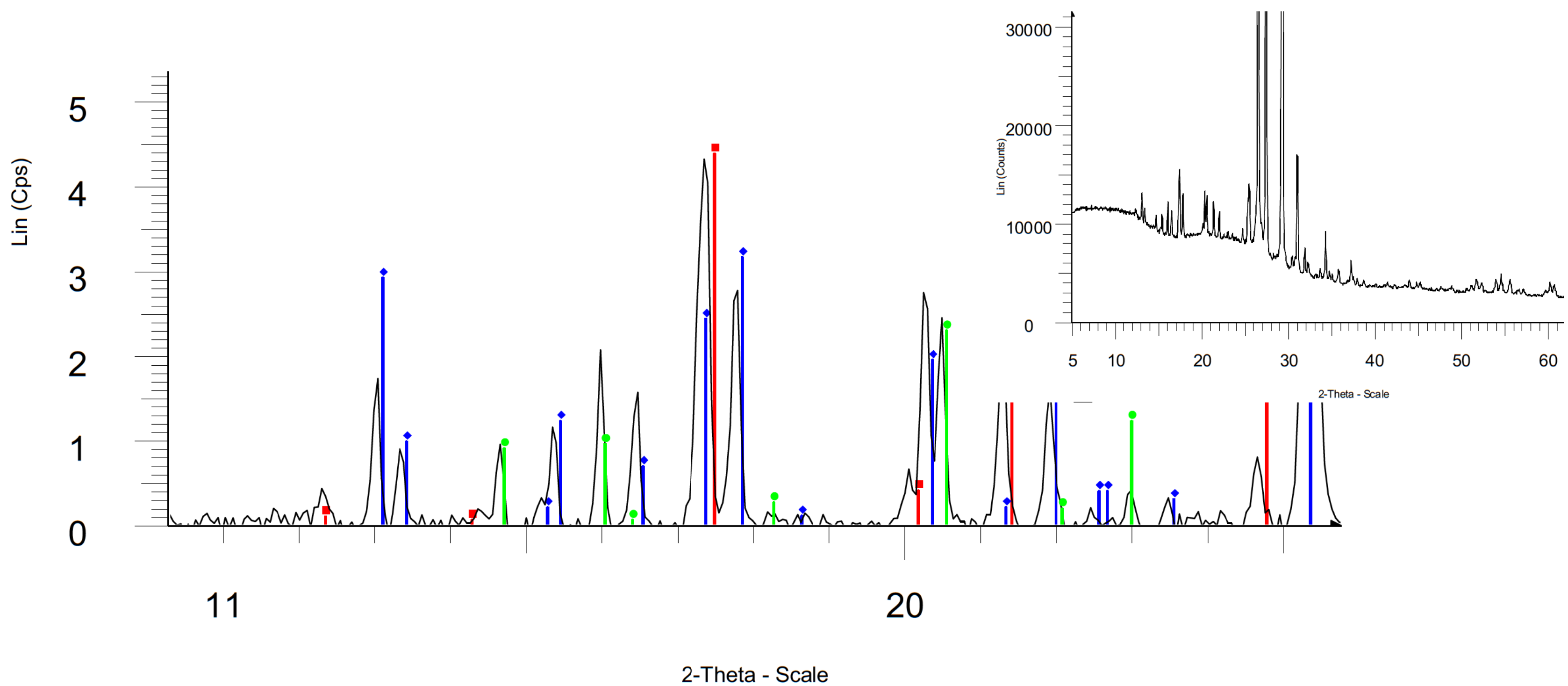
Systematic of blasting oils in the propellants



- No crystalline domains with DEGDN
- Single base and NC + NgI propellants (both with solvent) are similar
- L5460 stark graphitized

Herrmann, M.; Förter-Barth, U.; Kaiser, M.; Kupzik, K.; Scheibel, R.: Microstructure of NC-Propellants Investigated by X-ray Diffraction (Part II). Proc. 45th Int Annu Conf of ICT 2014

Crystalline ingredients of the triple base R 5730



- Reflections after halo and background subtraction
- Identification of RDX, HMX and nitroguanidine

Herrmann, M.; Förter-Barth, U.; Kaiser, M.; Kupzik, K.; Scheibel, R.: Microstructure of NC-Propellants Investigated by X-ray Diffraction (Part II). Proc. 45th Int Annu Conf of ICT 2014

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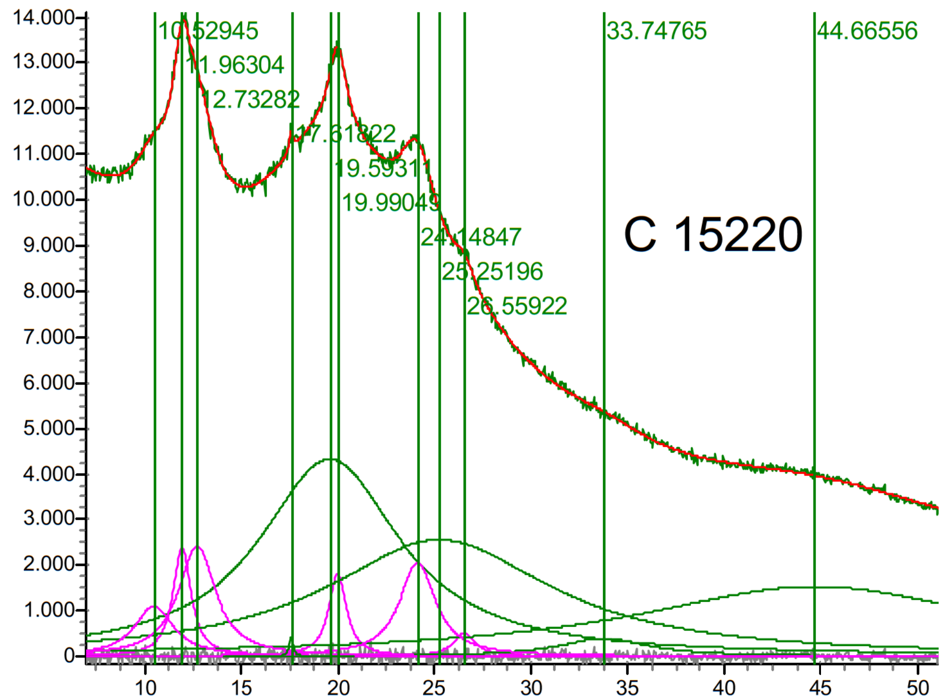
Pattern decomposition: single base propellant



- Partial patterns of crystalline and amorphous shares
- Fixed/constrained peak positions, widths and intensities -> scalable partial patterns (NC-propellant)

-> Evaluation with scalable patterns of crystalline NC-propellant, amorphous NC-propellant, nitroglycerin and crystalline additives

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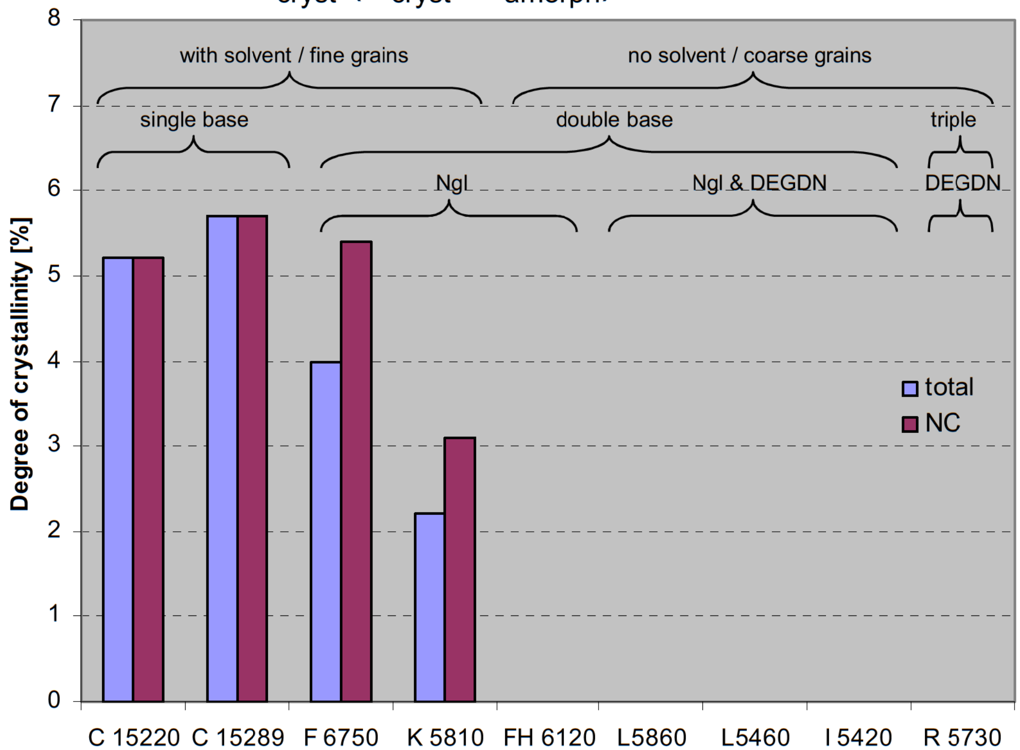
Degree of crystallinity and domain size

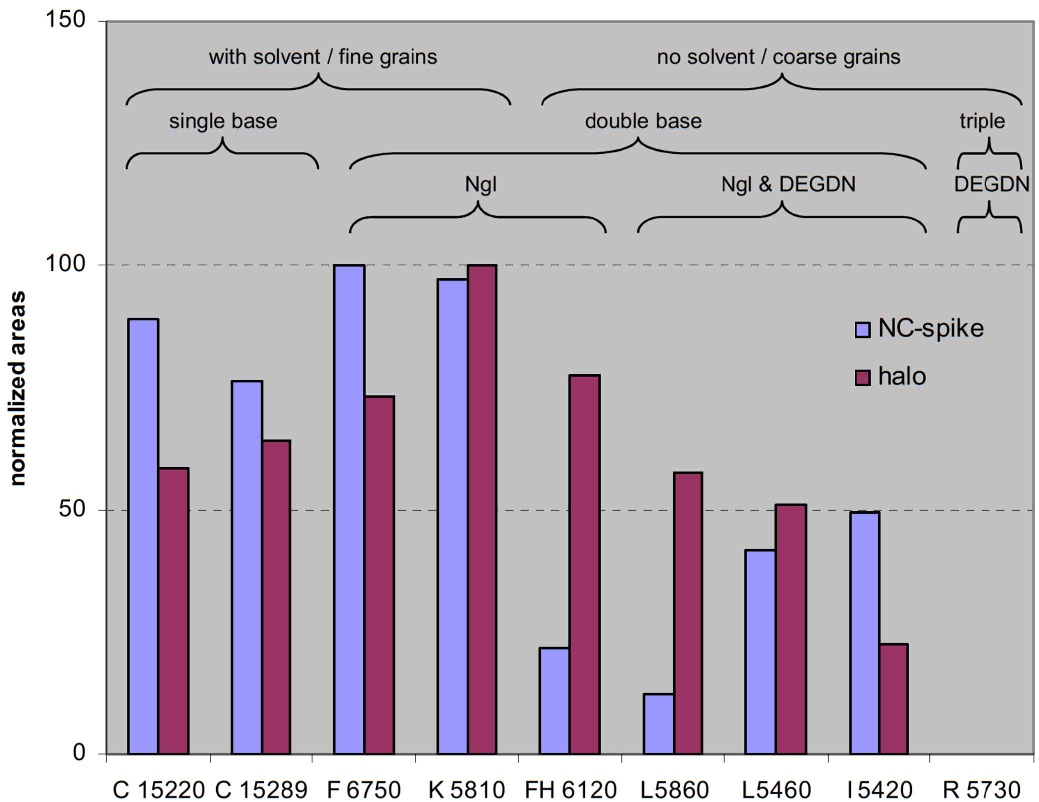
$DoC = A_{cryst}/(A_{cryst}+A_{amorph})$



- DoC correlates with use of solvents
- high DoC in sb-prop. & NC-share in db F6750
- rel. poor DoC in db-ball powder K 5810
- no crystalline domains detected w/o solvents
- large crystal domains in sb-propellants reduced in K 8510

  (7.4-9nm -> 5.8nm)

Areas of spike and halo



- NC-spike (blue bars) drops down w/o solvent, but increases with DEGDN (NC-gelling)
- Halo (red bars) correlates to Ngl content & replacement by DEGDN
- Ngl content
  25.1% F 6750
  29.3% K 5810
  by pattern decomposition

Conclusions and outlook

- X-ray diffraction reveals a variety of micro structural details

  -> different structures in cellulose, NC and NC propellants
  -> Process with solvents promotes crystal growth
  -> DEGDN enhances NC gelling

- In Future

  -> Reference data of DEGDN, high/low nitrated NC, further additives……
  -> Molecular models and simulation
  -> Evaluation using atomic pair distribution function (for amorphous materials)

Acknowledgement

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- Dr. Manfred Kaiser, Dr. Klaus Kupzik, Dr. Rudolf Scheibl, WTD 91 for samples, specifications, and discussions

Questions ?