

# V. 13.11.2007

## Gegenüberstellung

direkter (realer) Raum  
primitive Translationen  $a, b, c$

Ebenenschar

(hkl)

Abstand der Ebenen

$d$  in cm oder Å

Bedeutung Ortskoordinate

Zentriertes Gitter

Bragg-Gesetz

reziproker Raum

primitive Translationen  $a^*, b^*, c^*$

Punkt im reziproken Gitter

$G = ha^* + kb^* + lc^*$

Länge von  $G = 2\pi/d$

$G$  in  $\text{cm}^{-1}$  oder  $\text{Å}^{-1}$

Wellenvektor

Auslöschungsregeln

von Laue-Formulierung

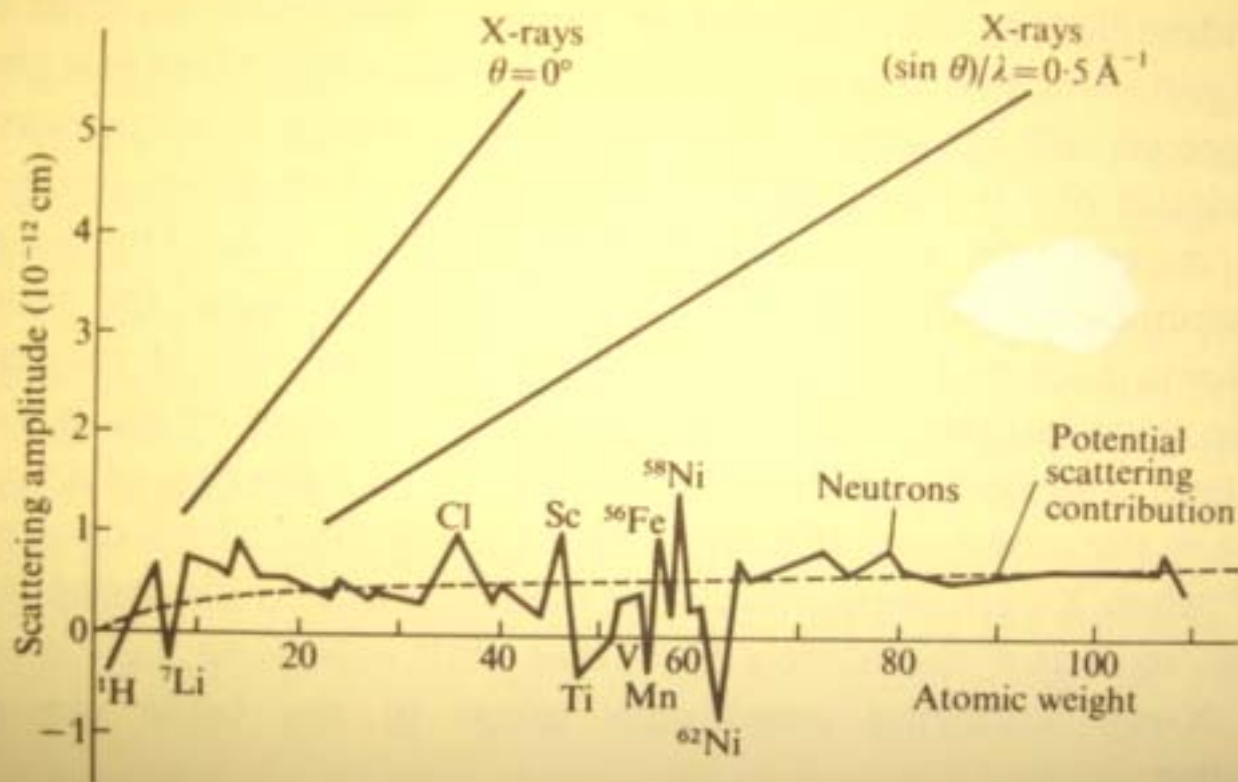


FIG. 22. Irregular variation of neutron scattering amplitude with atomic weight due to superposition of 'resonance scattering' on the slowly increasing 'potential scattering'; for comparison the regular increase for X-rays is shown. (From *Research (London)* 7, 257 (1954).)

# Besondere Atome

- **H** stark inkohärent
- **V** fast nur inkohärent (kein Struktur Beitrag)
- **Ti, Mn** negative Streulänge (Null-Legierung möglich)
- **Al** gesamter Querschnitt (koh.+ink.+abs.) sehr gering  
→ geringe Schwächung des Strahls
- **Cd, B, Gd, Eu, Sm** sehr hohe Absorption

Anwendungen : **H** Moderator, Abschwächer

**V** Eichsubstanz, Probenhalter

**Al** Konstruktion

**Cd, Gd, B, <sup>6</sup>Li ...** Beam-Stop, Blenden,  
Kollimatoren

# Nachweis von Neutronen

## **n nicht ionisierend – daher immer indirekter Nachweis**

(keine Energieanalyse bei Nachweis)

**schnelle Neutronen (MeV):** Stöße mit p-haltigen Substanzen

**thermische Neutronen (meV):**

1. **Aktivierung** durch n – Einfang (z.B. n- $\gamma$  Reaktionen in Au,In)
2. **Kernreaktionen und anschließender Nachweis der (geladenen) Reaktionsprodukte** – üblich in der Neutronenstreuung: Geiger Müller Zählrohr
  - a)  $\text{BF}_3$ :  $\text{B}^{10}(\text{n}, \alpha) \text{Li}^7 + 2.79\text{MeV}$
  - b)  $\text{He}^3$ :  $\text{He}^3(\text{n}, \text{p}) \text{H}^3 + 0.765\text{MeV}$Nachweiswahrscheinlichkeiten ca 95% (hängt von  $\lambda$  ab,  $\lambda^2 \propto 1/v$ )
3. **Szintillationszähler:**  $\text{n} \rightarrow \text{B} \rightarrow \alpha \rightarrow \text{ZnS}$  (Photomultiplier)
4. **Imageplates** : Gd-Schicht  $\rightarrow$  n- $\gamma$  Reaktionen  $\rightarrow$  Detektion wie in x-ray





# **II. Pulverdiffraktion**

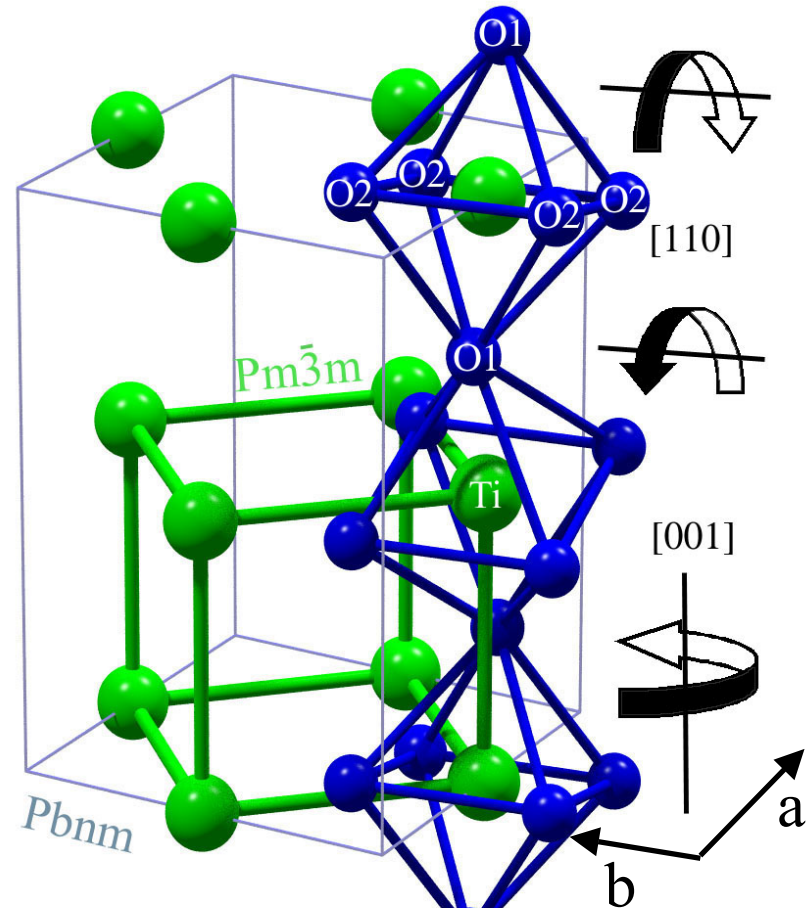
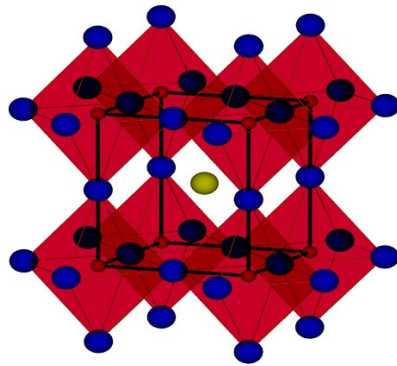
## **A) nukleare Strukturen**

- I. Prinzipien der Pulverdiffraktion**
- II. Rietveld-Methode**
- III. Diffraktometer-Typen**
- IV. „high impact“ Beispiele**



# I. Prinzipien der Pulverdiffraktion

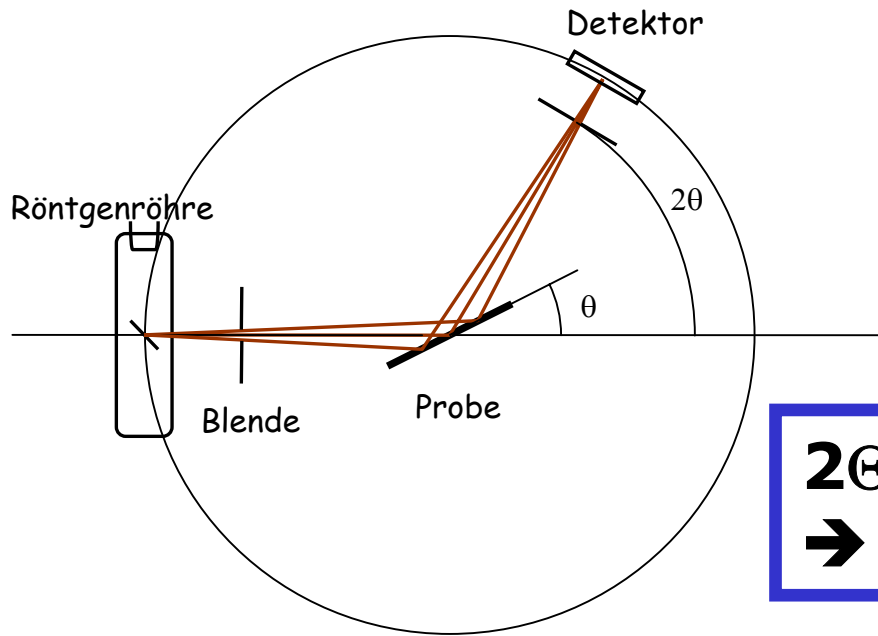
Beispiel :  $\text{LaTiO}_3$



Kristallstruktur :

- Metrik (Gitterkonstanten)
- Atompositionen und Temperaturfaktoren (ADP)  
( $x_i, y_i, z_i$ ) mit  $0 < x_i, y_i, z_i < 1$
- Raumgruppe → nur ein Teil der Zelle unabhängig

# Pulverdiffraktometrie



**2 $\theta$ -Positionen der Reflexe  
→ Gitterparameter**

Braggbedingung  $2d \sin \theta = n\lambda$

$$\sin^2 \theta = \frac{\lambda^2}{4} [h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2klb^* c^* \cos \alpha^* + 2lhc^* a^* \cos \beta^* + 2hka^* \cos \gamma^*]$$

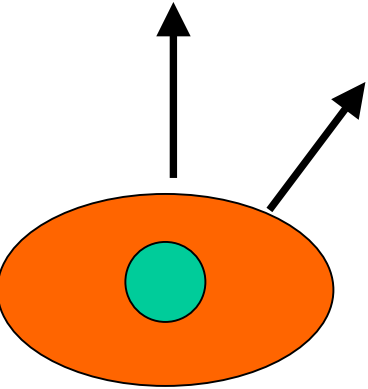
Orthorhombisches System:

$$\sin^2 \theta = \frac{\lambda^2}{4} \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)$$



# Analyse der Intensitäten

## Intensitäten der Reflexe → komplette Strukturinformation



$$\mathbf{F}_{\mathbf{G}} = \int_{\text{Zelle}} dV n(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) \quad n(\mathbf{r})\text{-Streudichte; Strukturfaktor}$$
$$= \sum_j \mathbf{f}_j \cdot \exp(-i\mathbf{G} \cdot \mathbf{r}_j)$$

$$\mathbf{f}_j = \int dV \cdot n_j(\rho) \exp(-i\mathbf{G} \cdot \rho) \quad \text{Atomformfaktor}$$

$$\mathbf{F}_{(hkl)} = \sum_j \mathbf{f}_j \exp[-i2\pi(x_j h + y_j k + z_j l)]$$

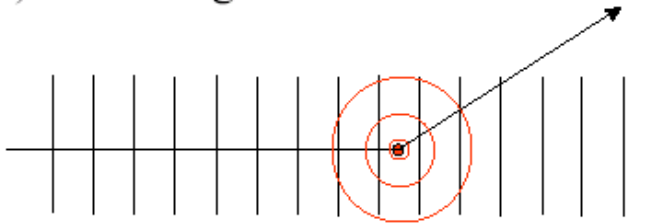
- weitere Verschmierung durch thermische Bewegung oder Unordnung

$$\mathbf{F}_{(hkl)} = \sum_j \mathbf{f}_j \exp[-i2\pi(x_j h + y_j k + z_j l)] * \exp\left(-\frac{1}{3}\langle \mathbf{u}^2 \rangle \mathbf{G}^2\right)$$

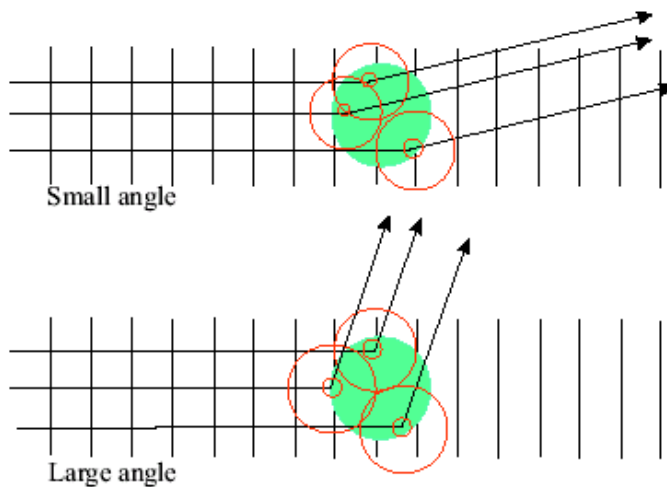
- aber : man misst  $F_{(hkl)}^2$  Verlust der Phaseninformation  
bei Zentrosymmetrie nur Vorzeichen !!

# Formfaktor

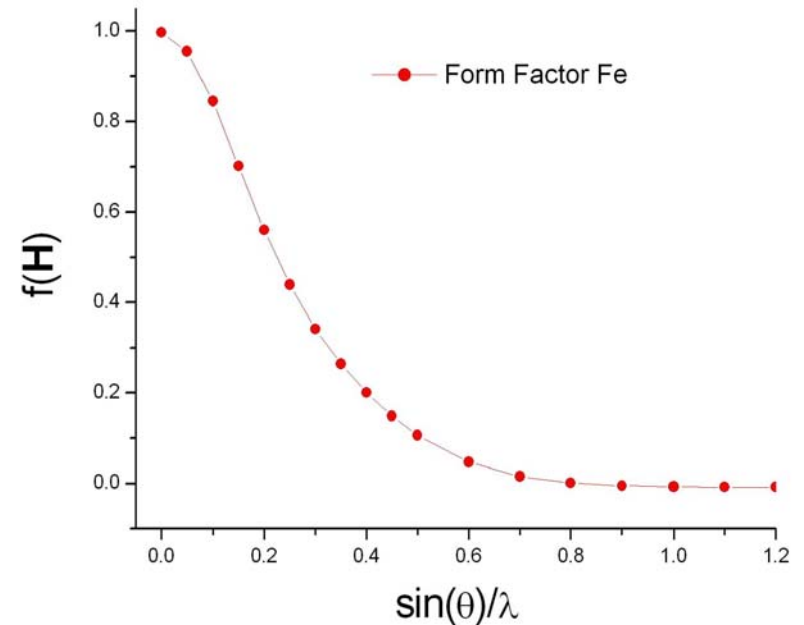
(a) scattering from nucleus



(b) scattering from electrons



Formfaktor : Fe äußere e<sup>-</sup>



-Vorwärtsstreuung : volle Streukraft

- Rückwärtsstreuung : Phasenunterschied der Elektronenhülle

# Wie geht man vor?

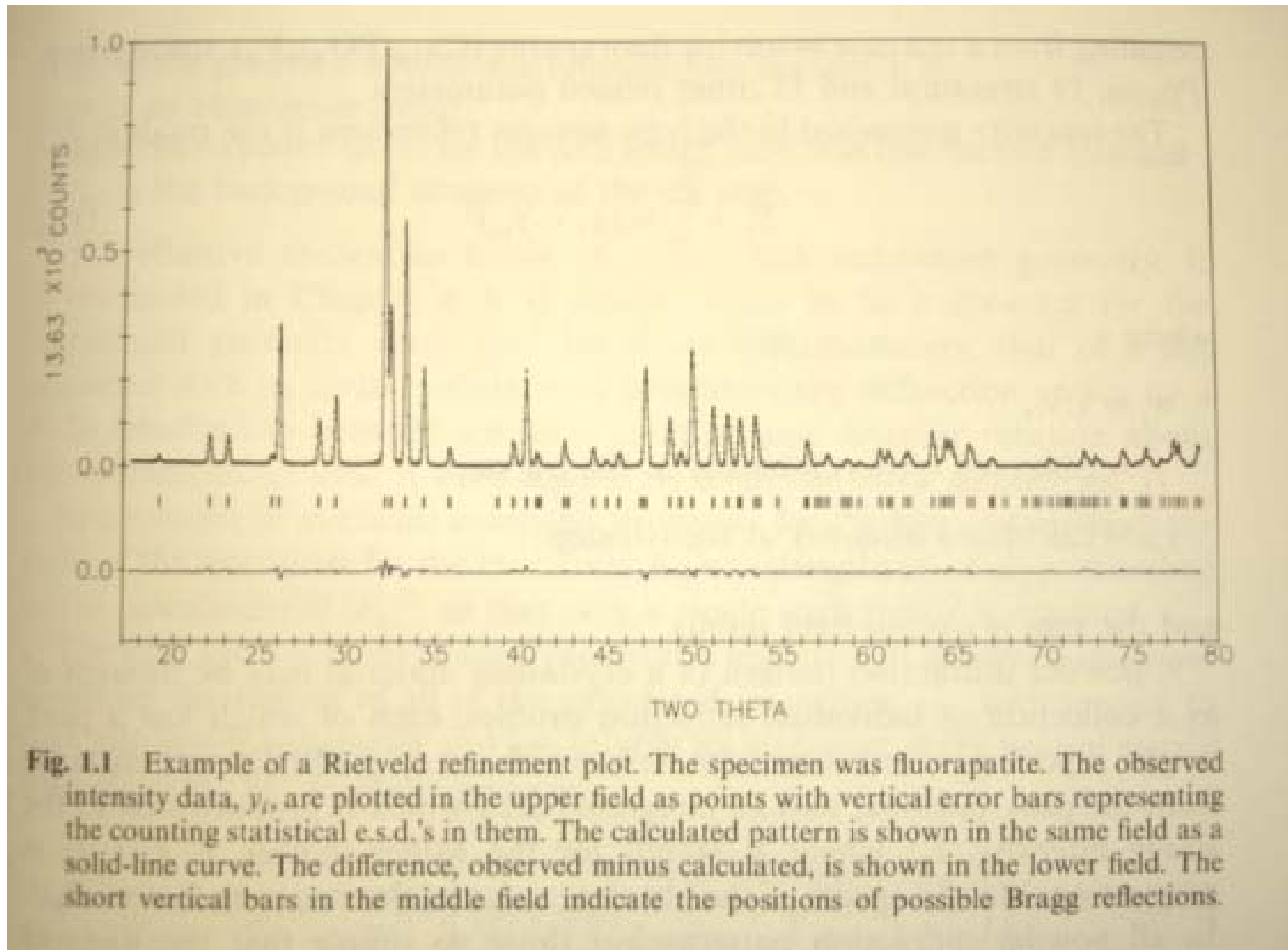


Fig. 1.1 Example of a Rietveld refinement plot. The specimen was fluorapatite. The observed intensity data,  $y_i$ , are plotted in the upper field as points with vertical error bars representing the counting statistical e.s.d.'s in them. The calculated pattern is shown in the same field as a solid-line curve. The difference, observed minus calculated, is shown in the lower field. The short vertical bars in the middle field indicate the positions of possible Bragg reflections.

## II.II. Rietveld-Verfahren

- einfaches Verfahren : Anfitten isolierter Peaks

→ Positionen der Bragg-Reflexe

→ Bestimmen der Metrik

→ Indizierung der Peak (hkl)

→ Bestimmung der  $F(hkl)^2$

aber Problem : Überlagerung durch

a) schlechte Auflösung

b) intrinsisch : kubisch (300) und (221)

c) ist viel Arbeit !!!

Rietveld-Verfahren : **direkte Beschreibung des gemessenen Pulverbeugungsbildes  $I(2\theta)$**

# -Original-Arbeit H.M. Rietveld 1966

## - heute Standardverfahren

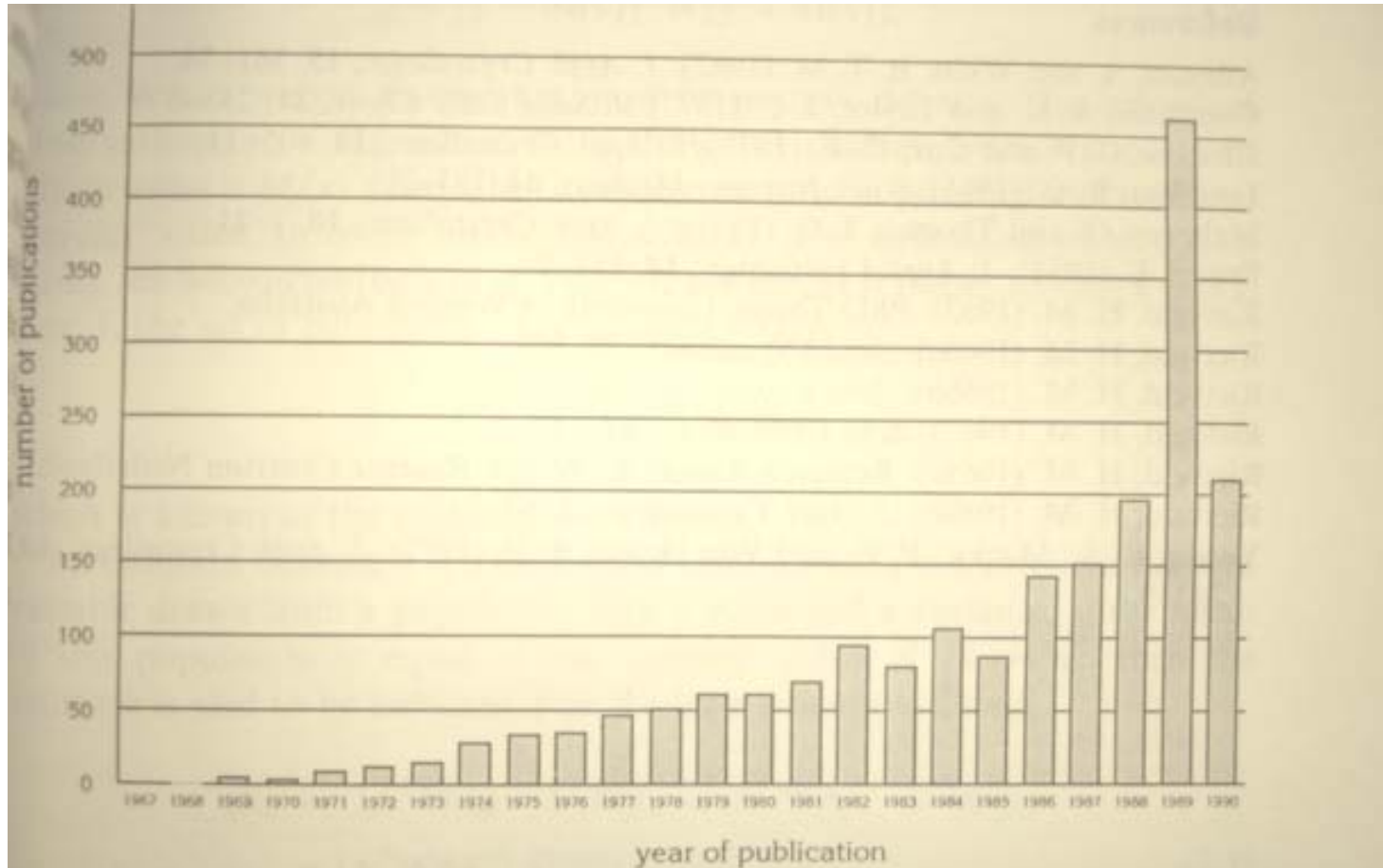
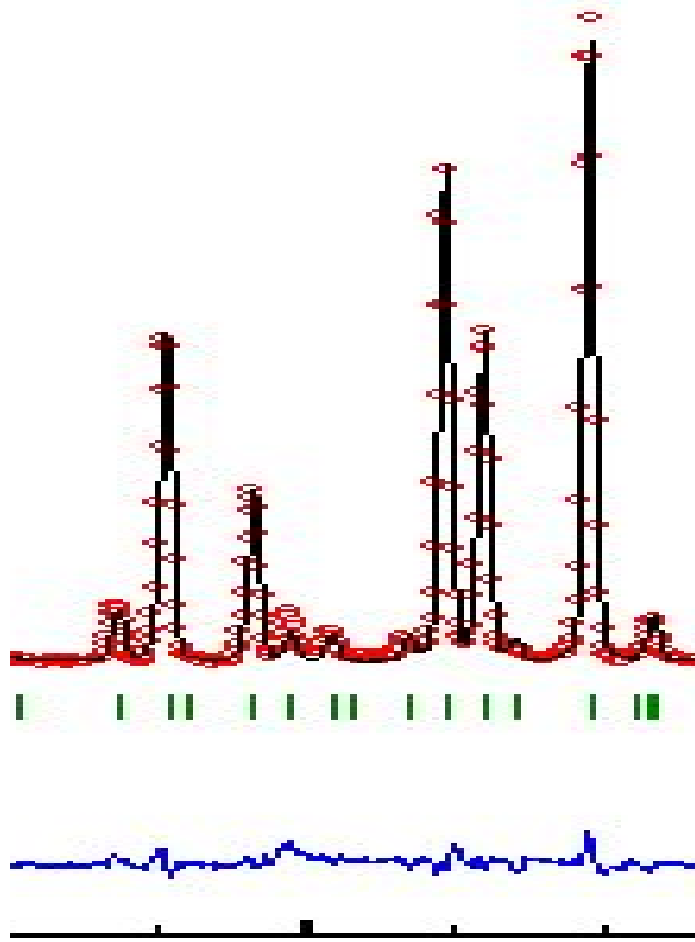


Fig. 2.1 Number of publications, in the Science Citation Index, citing as reference the original papers (Rietveld 1967, 1969a, 1969b) on the Rietveld method or having the name Rietveld in their title.



30

## II.II. Rietveld-Verfahren

**Minimierung der quadratischen Abweichungen**

$$S_y = \sum_i w_i \cdot (y_i - y_{ci})^2$$

$y_i, y_{ci}$  beobachtete und berechnete Intensität an Position  $i$

$w_i = 1/y_i$  Gewicht des Punktes  $i$

$$y_{ci} = s \sum_{(hkl)} L_{(hkl)} |F(hkl)|^2 \Phi(2\Theta_i - 2\Theta(hkl)) \cdot P_{(hkl)} \cdot A + y_{bi}$$

$s$  - Skalierungsfaktor

$L_{(hkl)}$  - Lorentzfaktor (und Polarisationsfaktor)

$F(hkl)$  - Strukturfaktor von  $(hkl)$

$\Phi(2\theta)$  - Form der Peak-Profile

$P_{(hkl)}, A$  - Korrektur für Textur und Absorption

$y_{bi}$  - Untergrundbeitrag an der Position  $i$

# Minimierungsschritt

Standardverfahren : Nullstelle der Ableitung suchen

$$\mathbf{M}_{jk} = -\sum_i 2w_i [(y_i - y_{ci}) \frac{\partial^2 y_{ci}}{\partial x_j \partial x_k} - (\frac{\partial y_{ci}}{\partial x_j}) \cdot (\frac{\partial y_{ci}}{\partial x_k})]$$

$$\Delta \mathbf{x}_k = \sum_j \mathbf{M}_{j,k}^{-1} \cdot \frac{\partial S}{\partial x_k}$$

$\mathbf{M}_{jk}$  - Normal-Matrix (Dim.: Anzahl Param. \*\*2)

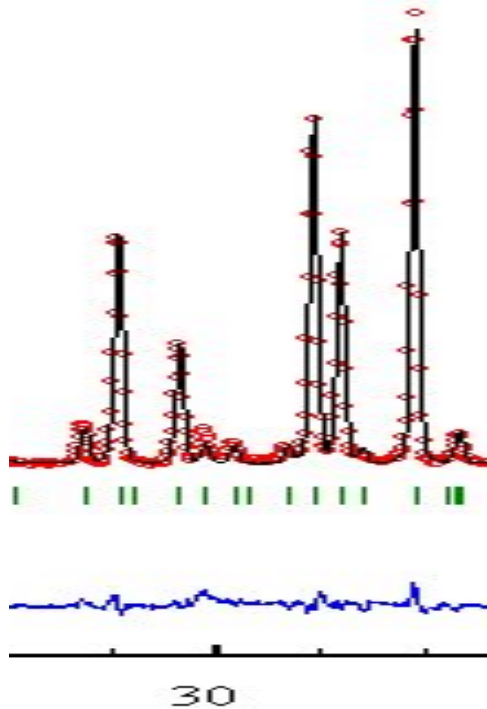
$\Delta \mathbf{x}_k$  - Verschiebung der Parameter

**nicht-lineares Problem !**

**im wesentlichen Invertierung einer Matrix**



# Peak-Profile



- experimentelle Auflösung
- Verschmierung der Bragg-Reflexe zu endlicher Breite
- ⇔ genaue Beschreibung notwendig

# Peak-Profile

Table 1.2 Some symmetric analytical profile functions that have been used\*

Function	Name
(a) $\frac{C_0^{1/2}}{H_k \pi^{1/2}} \exp(-C_0(2\theta_i - 2\theta_k)^2/H_k^2)$	Gaussian ('G')
(b) $\frac{C_1^{1/2}}{\pi H_k} \frac{1}{\left[1 + C_1 \frac{(2\theta_i - 2\theta_k)^2}{H_k^2}\right]}$	Lorentzian ('L')
(c) $\frac{2C_2^{1/2}}{\pi H_k} \frac{1}{\left[1 + C_2 \frac{(2\theta_i - 2\theta_k)^2}{H_k^2}\right]^2}$	Mod 1 Lorentzian
(d) $\frac{C_3^{1/2}}{2H_k} \frac{1}{\left[1 + C_3 \frac{(2\theta_i - 2\theta_k)^2}{H_k^2}\right]^{3/2}}$	Mod 2 Lorentzian
(e) $\eta L + (1 - \eta)G$	pseudo-Voigt ('pV')

The mixing parameter,  $\eta$ , can be refined as a linear function of  $2\theta$  wherein the refinable variables are  $NA$  and  $NB$ :

$$\eta = NA + NB*(2\theta)$$

$$(f) \frac{C_4}{H_k} \left[1 + 4*(2^{1/m} - 1) \frac{(2\theta_i - 2\theta_k)^2}{H_k^2}\right]^{-m} \quad \text{Pearson VII}$$

$m$  can be refined as a function of  $2\theta$ ,

$$m = NA + NB/2\theta + NC/(2\theta)^2,$$

where the refinable variables are  $NA$ ,  $NB$ , and  $NC$ .

$$(g) \text{Modified Thompson-Cox-Hastings pseudo-Voigt, ('TCHZ')} \quad \text{(Mod-TCH pV)}$$

$$\text{TCHZ} = \eta L + (1 - \eta)G$$

where

$$\eta = 1.36603q - 0.47719q^2 + 0.11116q^3$$

$$q = \Gamma_L/\Gamma$$

$$\Gamma = (\Gamma_0^4 + A\Gamma_0^3\Gamma_L + B\Gamma_0^2\Gamma_L^2 + C\Gamma_0\Gamma_L^3 + D\Gamma_0\Gamma_L^4 + \Gamma_L^5)^{0.2} = H_k$$

$$A = 2.69269 \quad B = 2.42843$$

$$C = 4.47163 \quad D = 0.07842$$

$$\Gamma_0 = (U \tan^2 \theta + V \tan \theta + W + Z/\cos^2 \theta)^{1/2}$$

$$\Gamma_L = X \tan \theta + Y/\cos \theta$$

[The modification consists of adding the term with the parameter  $Z$  to the original Thompson *et al.* (1987) pseudo-Voigt function ('TCH') in order to provide a component of the Gaussian FWHM which is constant in  $d^*$ , as is the  $Y$  component of the Lorentzian FWHM.]

**n : ~ Gauss**  
**x : komplizierter**

Table 1.2 (continued)

In the above profile functions,

$H_k$  is the full-width-at-half-maximum (FWHM) of the  $K$ th Bragg reflection, as is  $\Gamma$ , the refinable parameters are those in  $\eta$ ,  $m$ , and  $H$  or  $\Gamma$ ,

$$C_0 = 4 \ln 2,$$

$$C_1 = 4,$$

$$C_2 = 4(2^{1/2} - 1),$$

$$C_3 = 4(2^{2/3} - 1), \text{ and}$$

$$C_4 = \frac{2\sqrt{m}(2^{1/m} - 1)^{1/2}}{(m - 0.5)\pi^{1/2}}.$$

\* The origins and performances of most of these functions are discussed in Young and Wiles (1982). The TCHZ function is discussed in Young and Desai (1989).

**Young The Rietveld method**  
**Oxford (1993)**

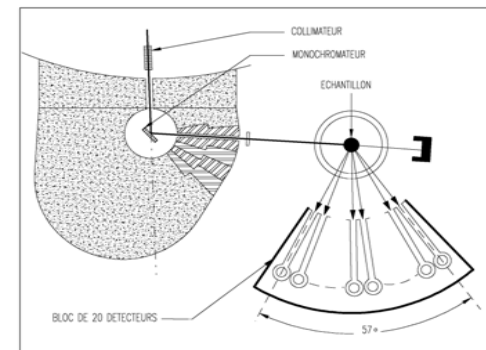
# Abhängigkeit der Auflösung von $2\theta$

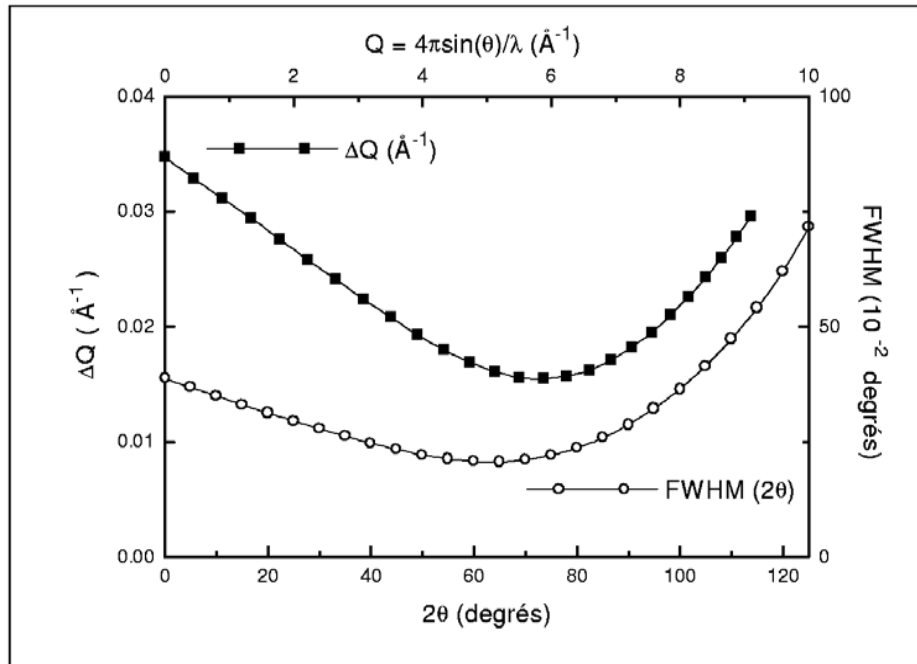
Caglioti et al. 1958

$$\text{FWHM}^2 = U \tan^2(\theta) + V \tan(\theta) + W$$

$V$  in der Regel negativ !

→ es gibt ein Minimum in der Nähe von dem Monochromator-Take-Off





**Courbes de résolution :** (○) largeur à mi-hauteur (FWHM) en fonction de  $2\theta$ ;  
 (■)  $\Delta Q$  en fonction de  $Q$  ( $\lambda_0 = 1.225 \text{ \AA}$ )

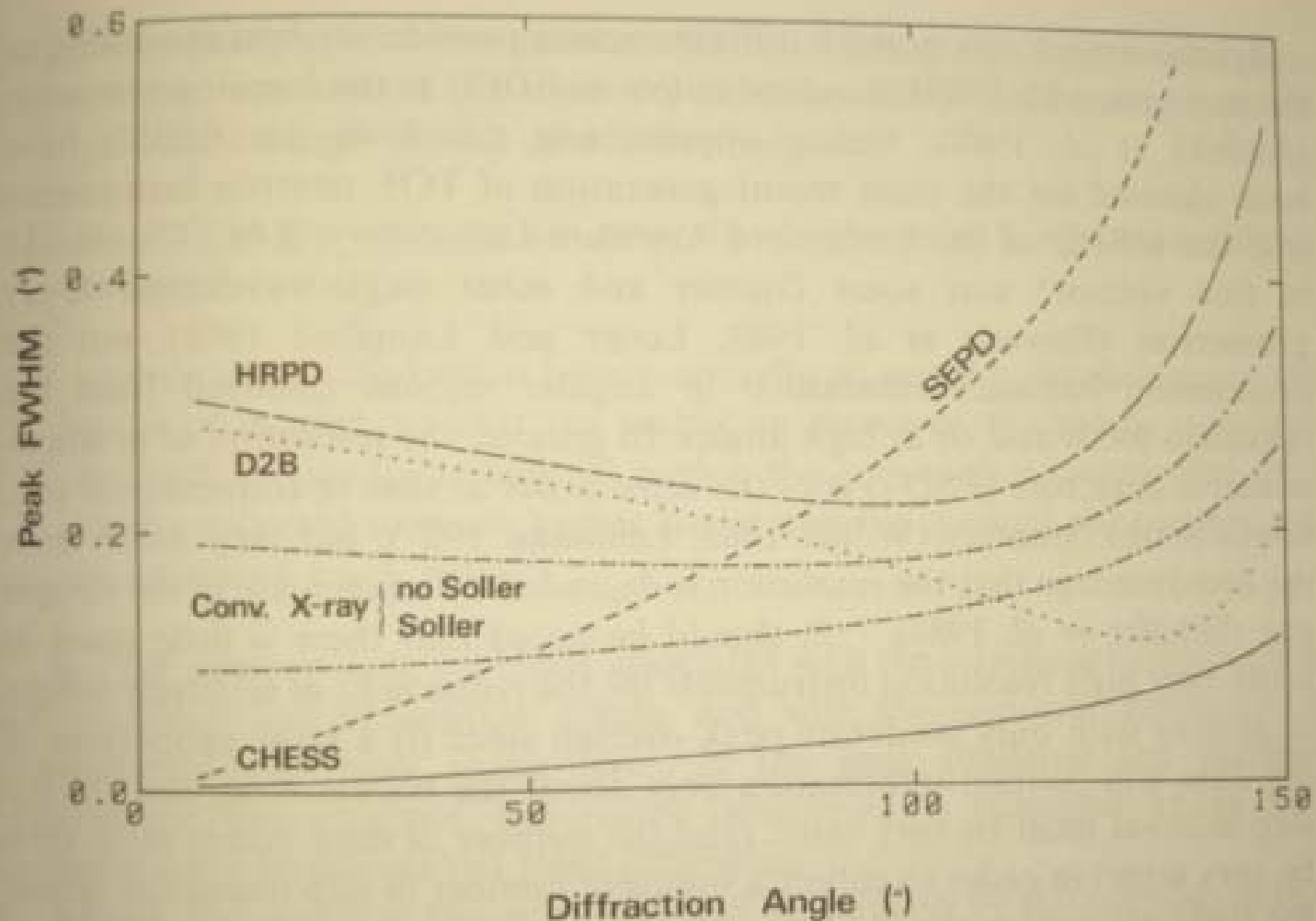


Fig. 5.1 Variation in the instrumental-only peak FWHM as a function of diffraction angle ( $2\theta$ ) for several neutron and X-ray diffractometers. The curves represent the following instruments: long — HRPD (CW neutron) at Lucas Heights; ··· D2B (CW neutron) at the ILL; short - - - SEPD (TOF neutron) at the ANL; - · - · conventional (X-ray) Bragg-Brentano with (lower) and without (upper) diffracted-beam Soller slits; — synchrotron (X-ray) Bragg-Brentano at CHES. Modified from Hill and Madsen (1987).

# Parameter

**Unterscheide : globale und Phasen-Parameter :**

**global** : Nullpunkt,

Peak-Profil-Parameter

Untergrund

Wellenlänge

Probenverschiebung

Absorption

**Phasen** : (x,y,z) U's und Besetzungen für jedes Atom

Skalierungsfaktor

Gitterparameter

Textur-Parameter

Mikrostrain- und Kristallitgröße

Extinction

# Verfeinerungsschritte

**Nichtlineares Problem → gute Startwerte nötig**

**Verfeinerung in Schritten :**

**A) scale**

**B) Untergrund + Gitterparameter**

**C) Positionen**

**D) thermische Parameter (anisotrop???)**

**E) Besetzungen**

**F) Profil-Parameter**

# Resumé : Rietveld Technik

- simultanes Anfitten des ganzen Spektrums (mehrere)
- Auflösung u,v,w-Formel
- gute Beschreibung der Peak-Profile essentiell
  
- Strukturmodell (nuklear oder magnetisch) PLUS  
Kenntnis der Diffraktometer-Funktion  
→ Beschreibung
  
- nicht-linearer Fit : a) gute Startwerte  
b) nach und nach Parameter freigeben
  
- Beurteilung : R-Werte ( $R_{WP}$  ist am wichtigsten)



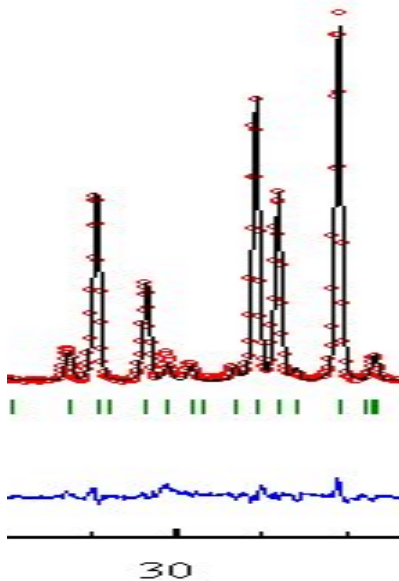
# VI. 20.11.2007

## Rietveld-Verfahren

R.A. Young: *The Rietveld Method*, Oxford University Press,  
[ISBN 0-19-855577-6](#)

Rudolf Allmann: *Röntgen-Pulver-Diffraktometrie*, Verlag Sven von Loga,  
[ISBN 3-87361-029-9](#)

C. Giacovazzo: *Fundamentals of Crystallography*, Oxford University Press,  
[ISBN 0-19-855578-4](#)



Petten, The Netherlands. (1987)

# Resume : Rietveld Technik

- simultanes Anfitten des ganzen Spektrums (mehrere)
- Auflösung u,v,w-Formel
- gute Beschreibung der Peak-Profile essentiell
  
- Strukturmodel (nuklear oder magnetisch) PLUS  
Kenntnis der Diffraktometer-Funktion  
→ Beschreibung
  
- nicht-linearer Fit : a) gute Startwerte  
b) nach und nach Parameter freigeben
  
- Beurteilung : R-Werte ( $R_{WP}$  ist am wichtigsten)

# Parameter

**Unterscheide : globale und Phasen-Parameter :**

**global** : Nullpunkt,

Peak-Profil-Parameter

Untergrund

Wellenlänge

Probenverschiebung

Absorption

**Phasen** : (x,y,z) U's und Besetzungen für jedes Atom

Skalierungsfaktor

Gitterparameter

Textur-Parameter

Mikrostrain- und Kristallitgröße

Extinction

# Verfeinerungsschritte

**Nichtlineares Problem → gute Startwerte nötig**

**Verfeinerung in Schritten :**

**A) scale**

**B) Untergrund + Gitterparameter**

**C) Positionen**

**D) thermische Parameter (anisotrop???)**

**E) Besetzungen**

**F) Profil-Parameter**

# R-Werte

## reliability - Fit-Kriterien

$$R_f = \frac{\sum |(I_k(\text{obs}'))^{1/2} - (I_k(\text{calc}))^{1/2}|}{\sum (I_k(\text{obs}'))^{1/2}} \quad (\text{'R-structure factor'})$$

$$R_B = \frac{\sum |I_k(\text{obs}') - I_k(\text{calc})|}{\sum I_k(\text{obs}')} \quad (\text{'R-Bragg factor'})$$

$$R_p = \frac{\sum |y_i(\text{obs}) - y_i(\text{calc})|}{\sum y_i(\text{obs})} \quad (\text{'R-pattern'})$$

$$R_{wp} = \left\{ \frac{\sum w_i (y_i(\text{obs}) - y_i(\text{calc}))^2}{\sum w_i (y_i(\text{obs}))^2} \right\}^{1/2} \quad (\text{'R-weighted pattern'})$$

zusätzlich erwarteter R-Wert und Goodnes of Fit

**WICHTIG**  $R_{wp}$  |

# Fehler-Quellen

## - **Quellen für „Ärger“**

**Textur (keine ideale Verteilung der Orientierungen)**

**hoher Untergrund**

**Profile (insbesondere anisotrope Verbreiterungen)**

**Extinktion**

**zu große Kristallite**

**Stabilität der Strahlung**

**Absorption**

**Phasengemische**

...

**→ berechnete Fehler sind Anhaltspunkte !!!**

# Absorption

-Nachschlagen  $\sigma_{ai}$  für die Atome in der Zelle

-  $I=I_0\exp(-\mu d)$

-  $\mu[\text{cm}^{-1}]=(\sum\sigma_{ai} [\text{barn}])/Vol. [\text{\AA}^3]$

# Rietveld-Programme

- **GSAS General Structure Analysis System**  
van Dreele, ...

- **Wiles and Young DBWS**  
verschiedene Fortentwicklungen



- **Fullprof (Juan Rodriguez-Carvajal)**



- **Rietan** von Izumi (praktisch nur in Japan)

- **PREMOS** modulierte Strukturen (Yamamoto)

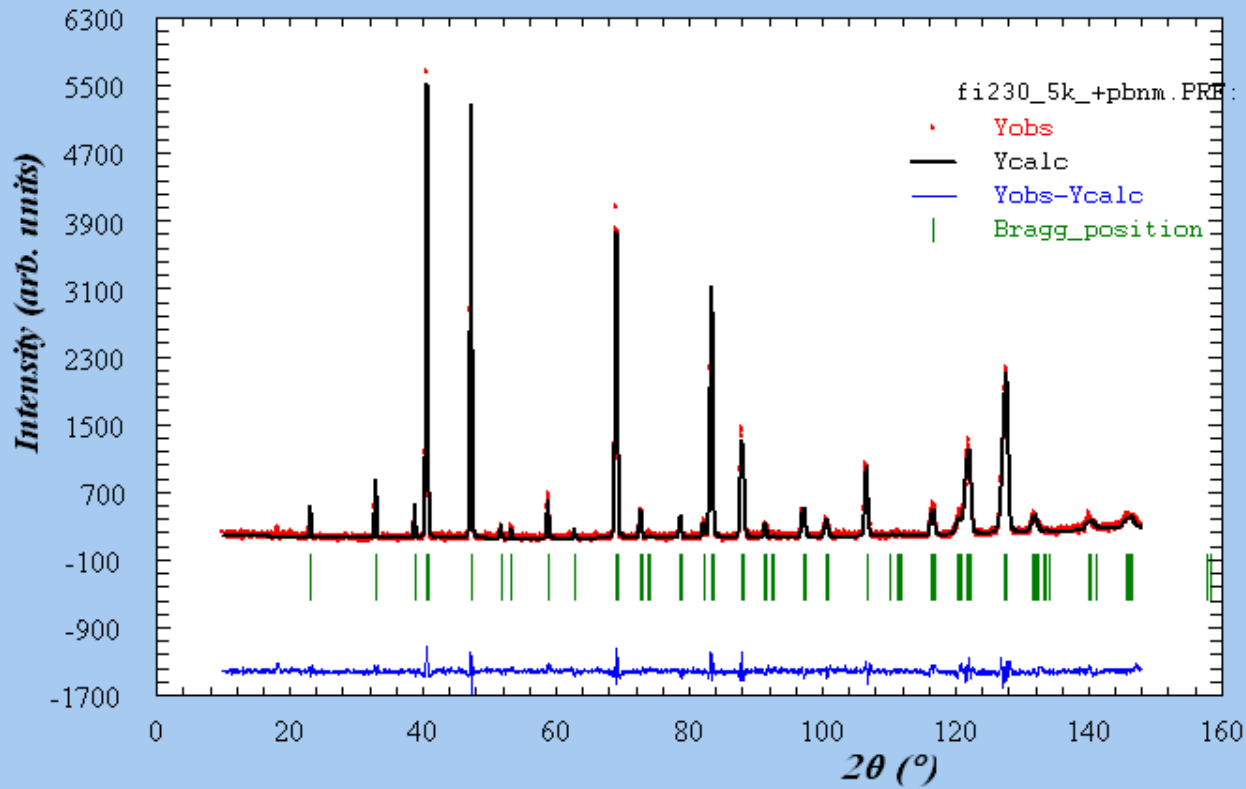


FullProf Suite ToolBar

File Programs Settings Help

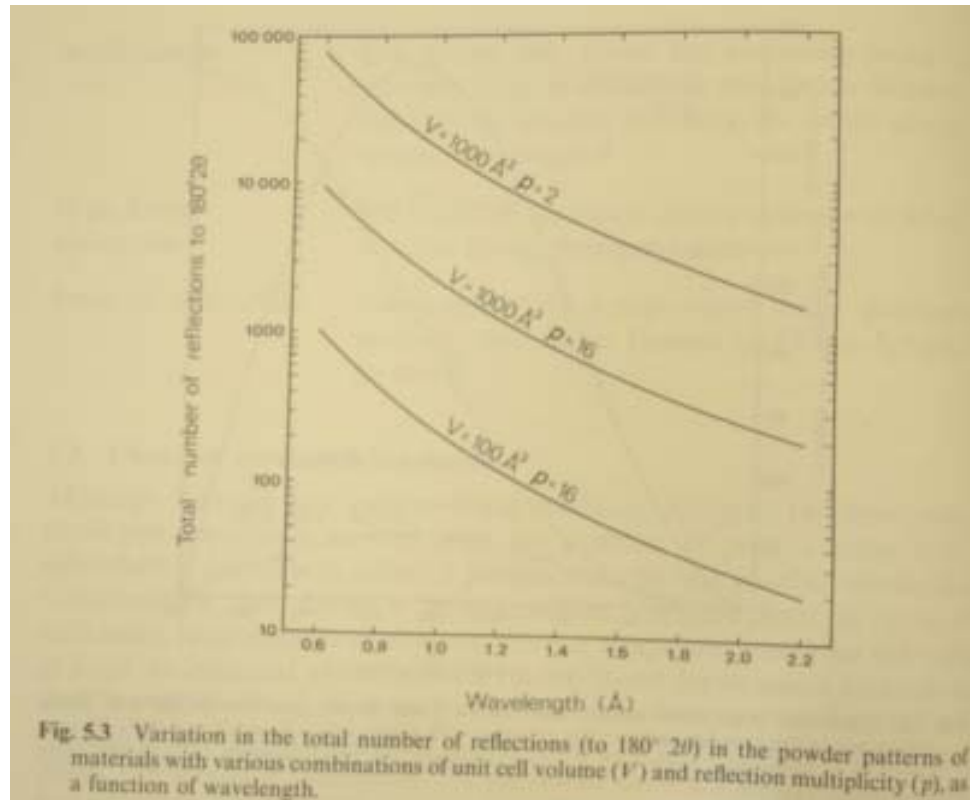
Working Directory: C:\braden\Lokal\materials\titanate\latio(mc27neutronen) Code File: mc27a020 Type: PCR Date: 12/11/2007

### La.70Ba0.30CoO3



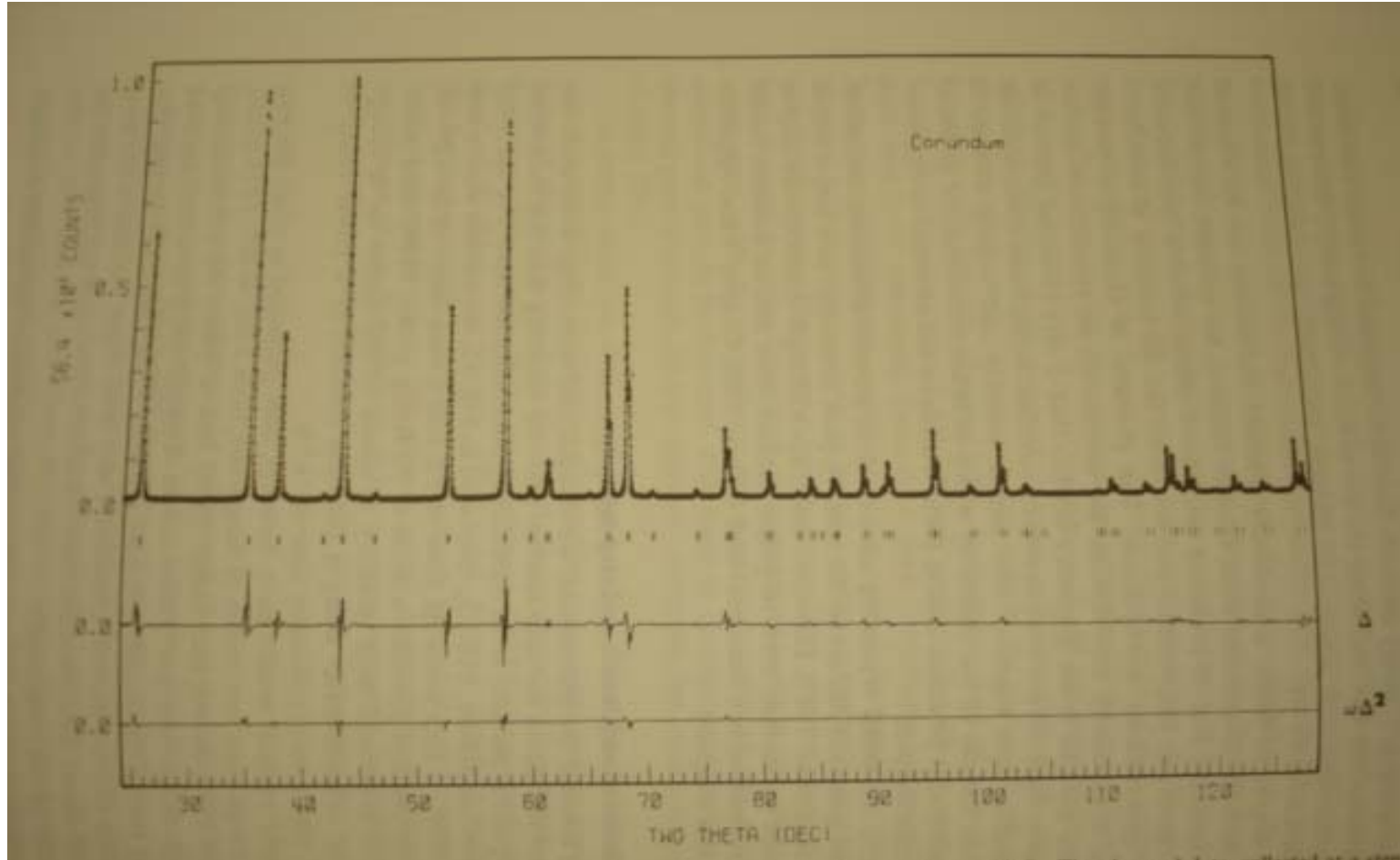
11-12-2007 21:30 X = Y =

# Wahlmöglichkeiten : a) Diffraktometer



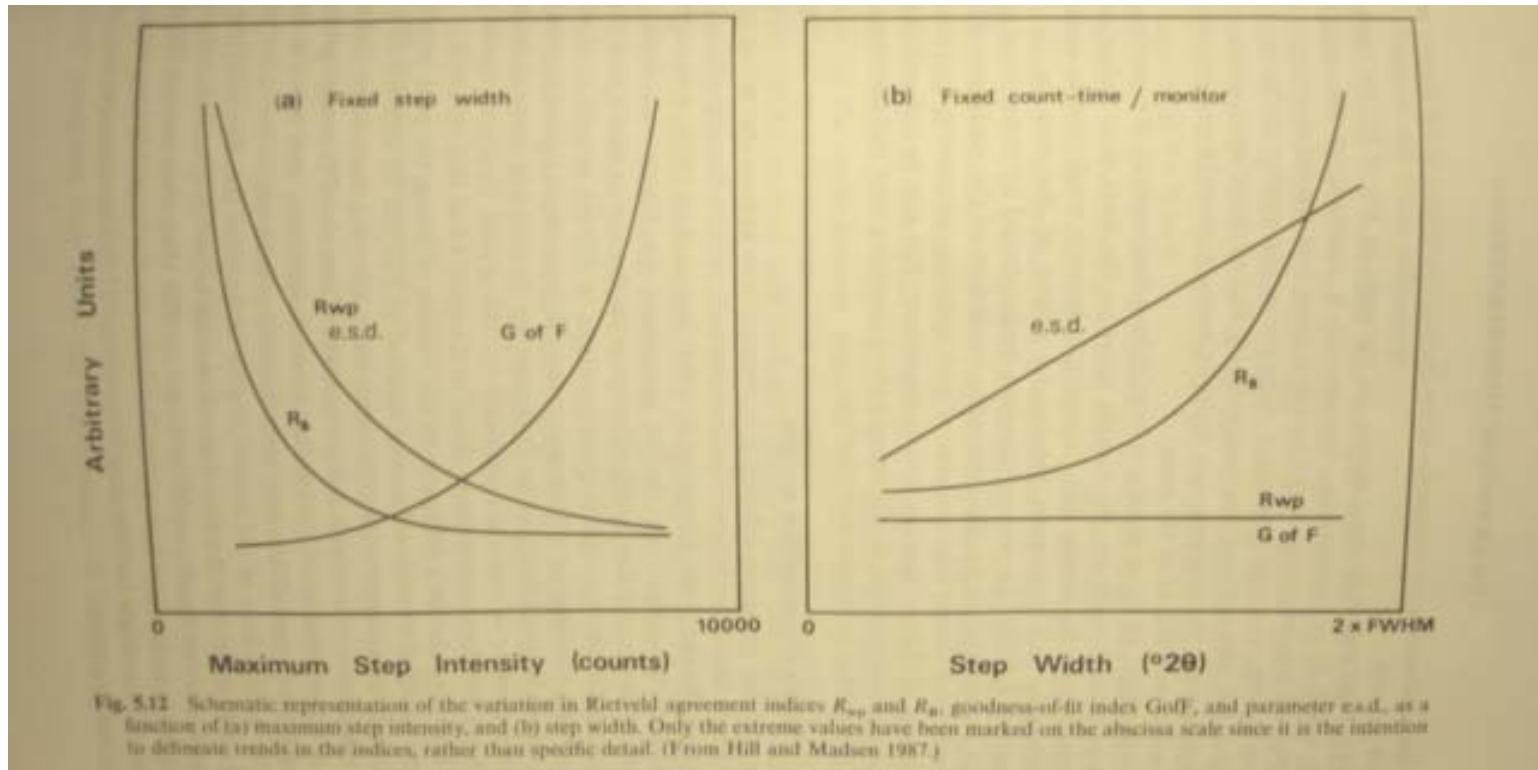
- man braucht kurze Wellenlänge, um genügend Bragg-Reflexe ausmessen zu können
- ideal Anzahl (Reflexe) > 10 Anzahl (Parameter)

# Wahlmöglichkeiten : Steps und Messzeit



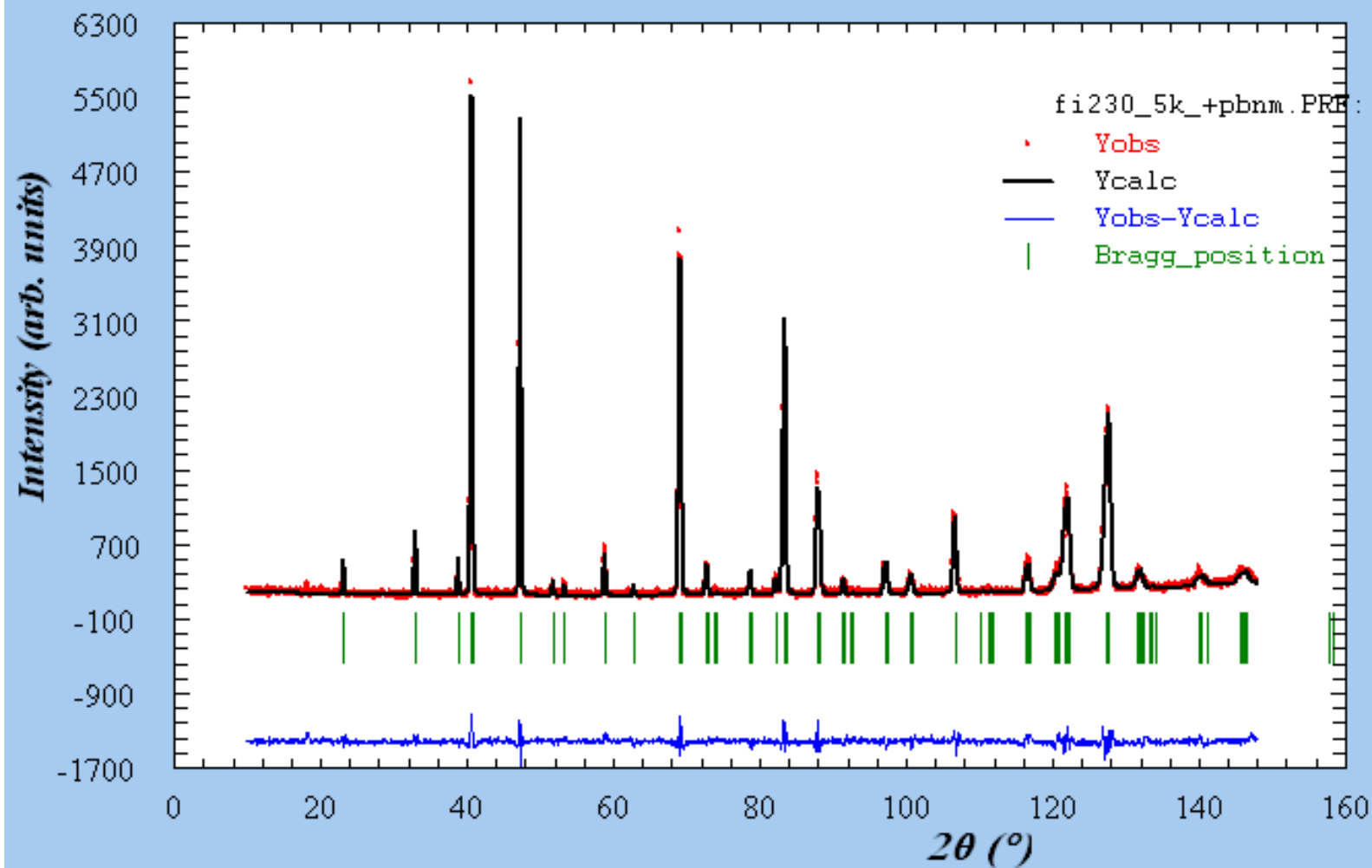
- Beispiel Al<sub>2</sub>O<sub>3</sub> mit Cu-Kα
- Frage wie lange Messen und wie viele Punkte?

# Wahlmöglichkeiten : Steps und Messzeit



- **Daumen-Regel** : 5000 ... 10000 maximale Intensität/Step
- Schrittweite  $\sim 1/5$  von FWHM bei bester Auflösung

# La<sub>0.70</sub>Ba<sub>0.30</sub>CoO<sub>3</sub>



# Vergleich : Neutronen – X-ray

- **Vorteile Neutronen :** dominieren Oxid-Literatur !!!
  - Profile leichter
  - keine oder wenig Extinktion
  - nicht Beugung an einzelnen Kristalliten
  - wenig Absorption
  - Kühlen + Heizen + Magnetfeld : alles leicht
  - Strahlstabilität
- **Vorteile x-ray bzw. Synchrotron :**
  - Verfügbarkeit
  - Auflösung
  - Intensitäten
  - nur kleine Probenmengen

## II.III. Diffraktometer-Typen

- wie meistens bei Neutronen-Streuung

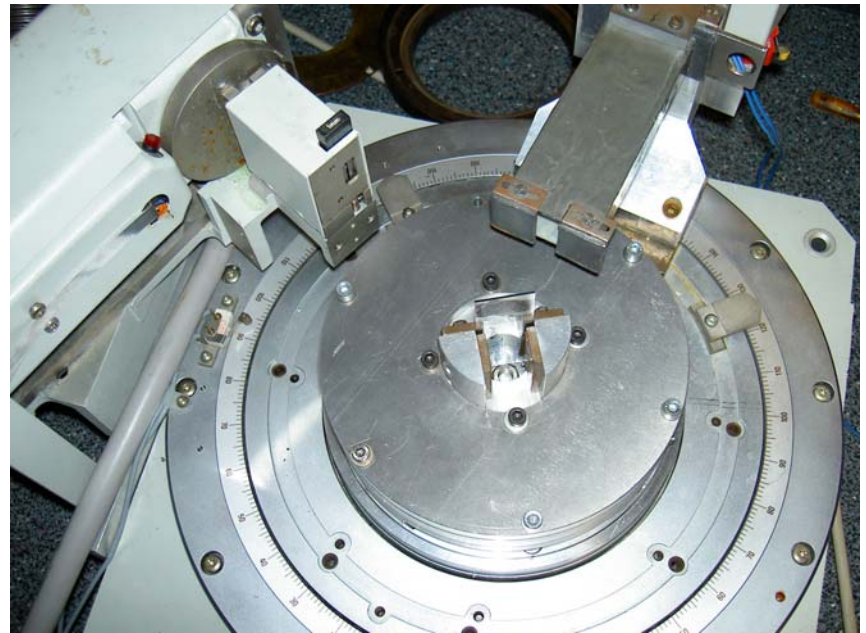
Abwägung von **hohem Fluss**  
und **hoher Auflösung**

- Strukturbestimmung mit Rietveld
  - ➔ hohe Anzahl von Reflexen erforderlich
    - ➔ relativ hohe Anforderungen an Auflösung und Wellenlänge nicht zu lang

# Röntgendiffraktometrie Pulver



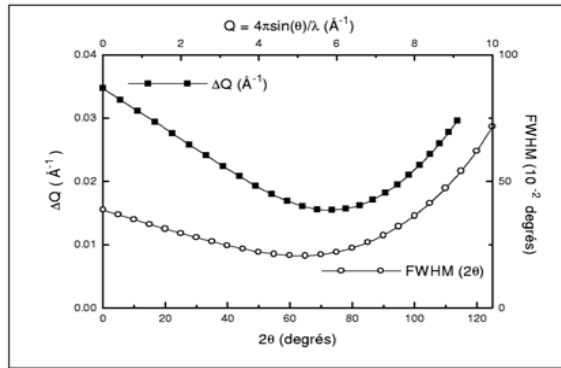
- Winkelbereich  $10^\circ \leq 2\Theta \leq 145^\circ$
- Maximale Auflösung  $0.01^\circ$
- Kryostat- und Hochtemperaturaufsatz:  
Messungen von 10K bis 1000K



**-D5000 Pulverdiffraktometer an Cu-Drehanode :  
T : 300-1200K automatisch**



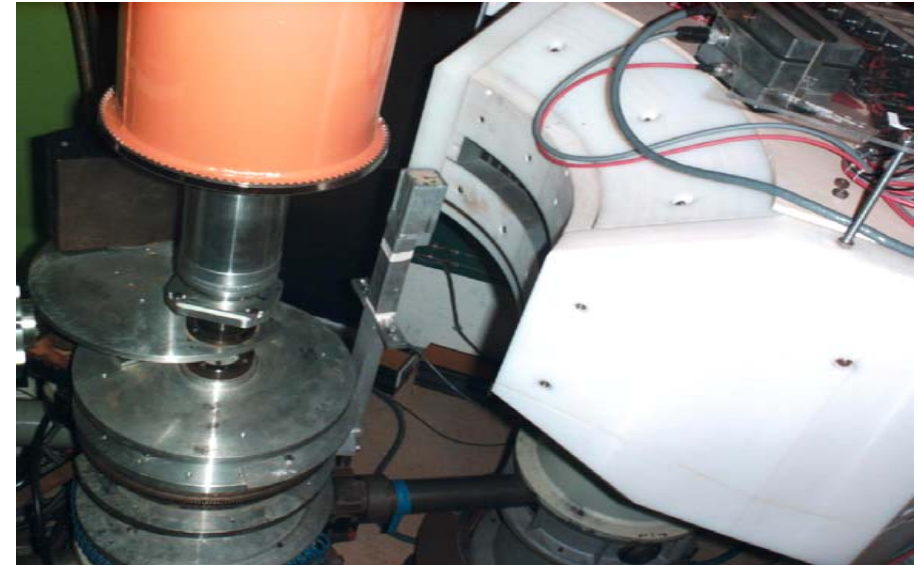
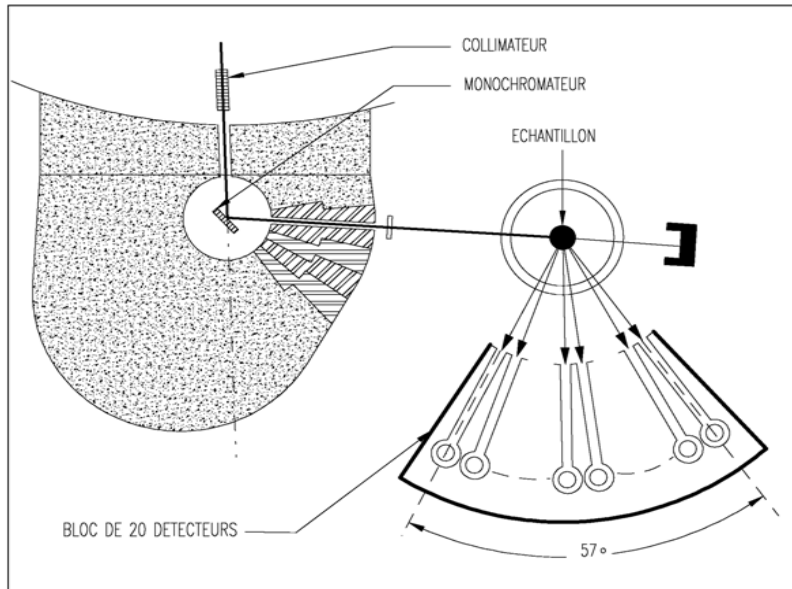
# Hochauflösung 3T2



Courbes de résolution : (○) largeur à mi-hauteur (FWHM) en fonction de  $2\theta$ ;  
(■)  $\Delta Q$  en fonction de  $Q$  ( $\lambda_0 = 1.225 \text{ \AA}$ )

Diffractomètre Poudres Haute Résolution

**3 T 2**



Wellenlänge  $\sim 1.2 \text{ \AA}$   
20 Detektoren mit Kollimation

Langsam  $\sim 24 \text{ h/Spektrum}$

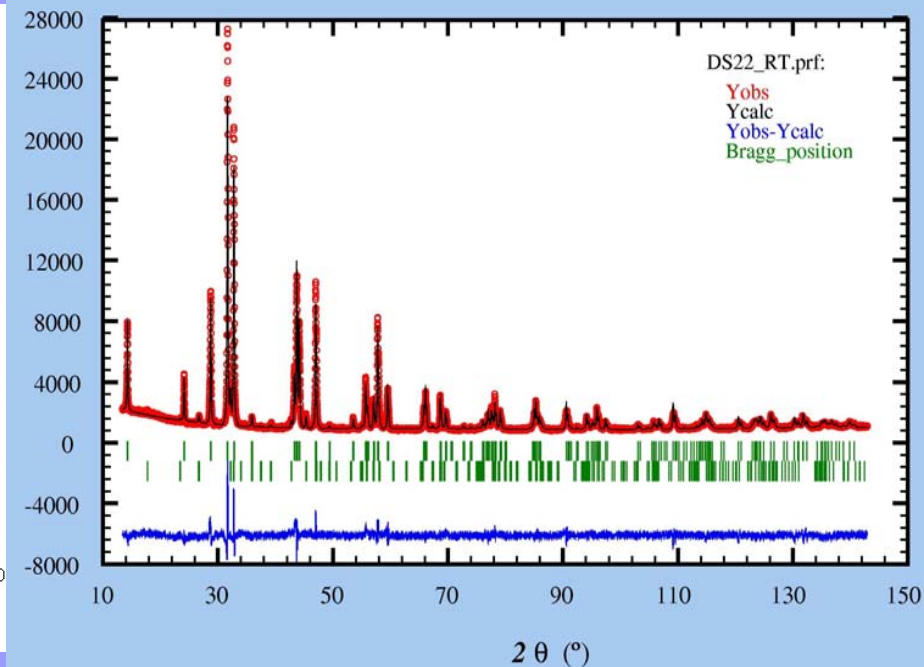
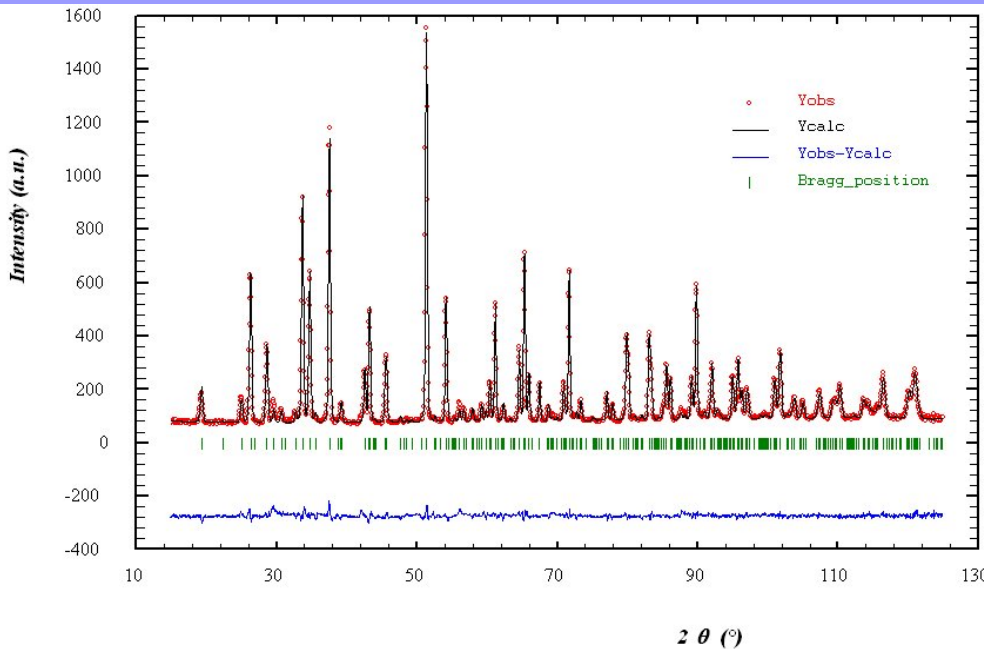
→ Beschränkung !

Kühlen und Heizen kein Problem

# Vergleich X-ray- Neutronenpulverbeugung

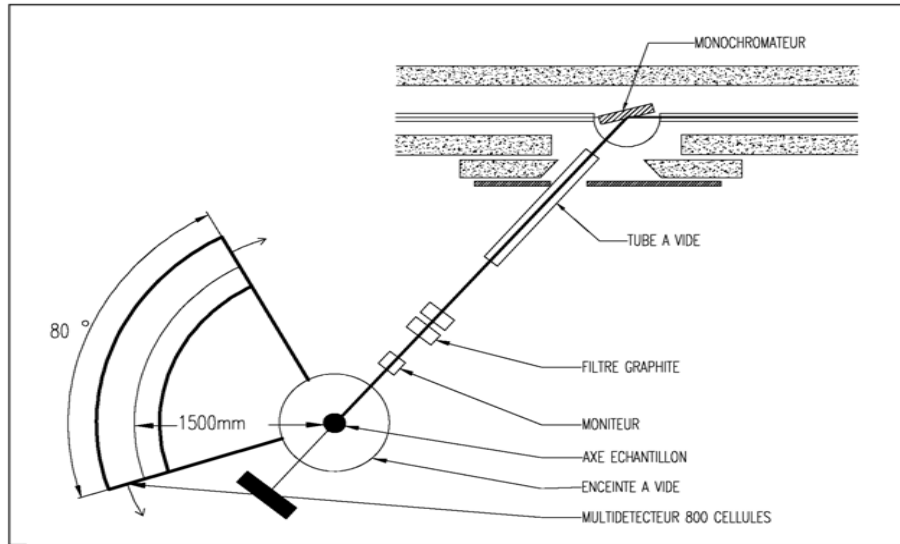
Neutronen

x-ray

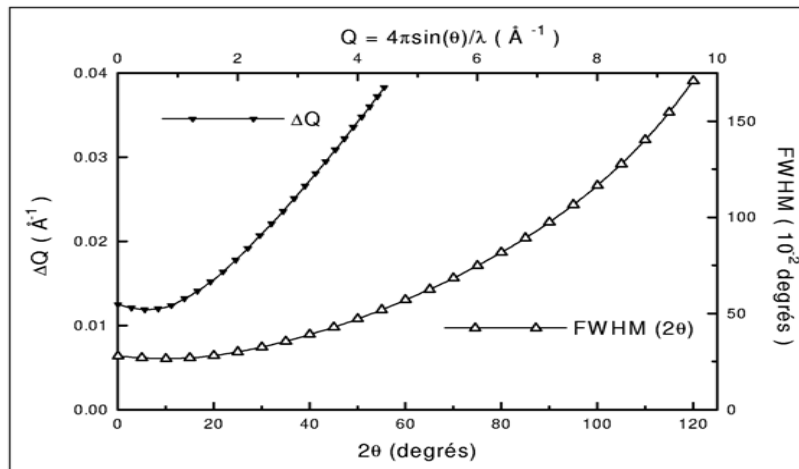


- Neutronen bieten mehr Information bei hohen Q-Werten
  - leichter beschreibbares Profil
  - bessere Wichtung der einzelnen Atome
- ➔ Bestimmung der Strukturparameter möglich

# Hochfluss G4.1 oder G6.1



*Schéma du diffractomètre G 4-1*



*Courbes de résolution : Δ largeur à mi-hauteur (FWHM) en fonction de 2θ  
▽ ΔQ en fonction de Q (λ = 2.45 Å)*

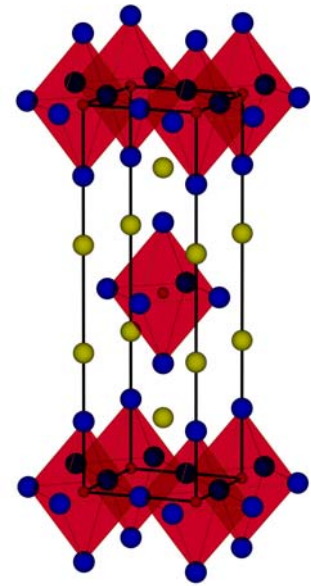
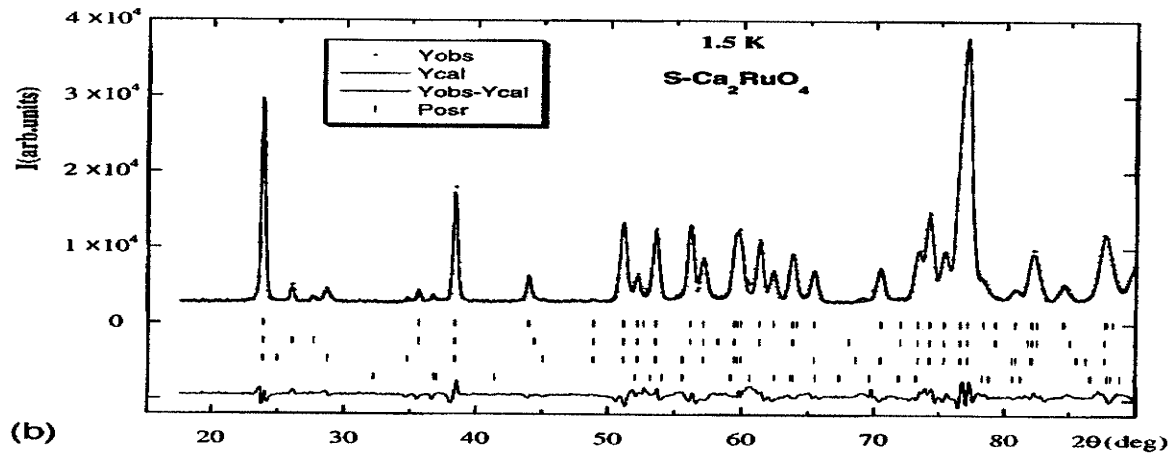
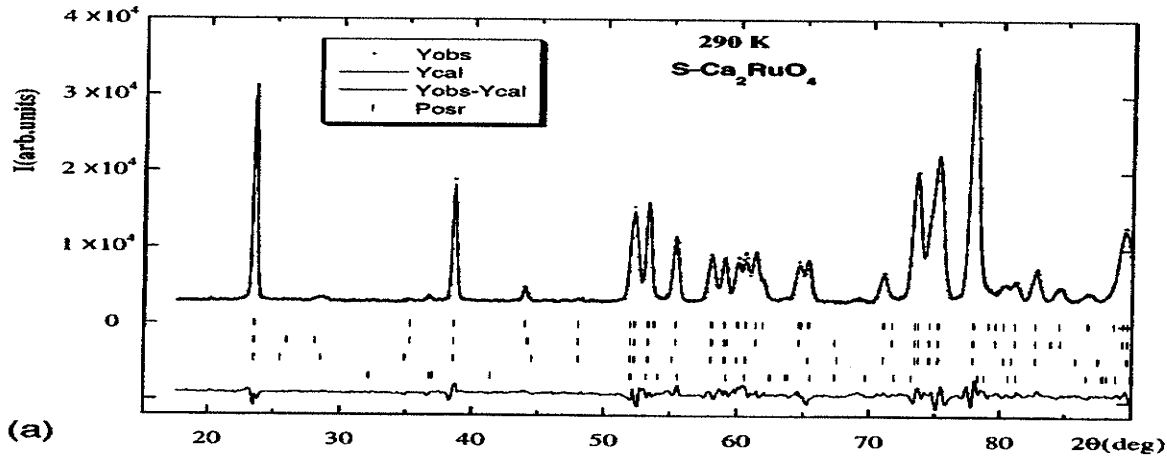
**-Wellenlänge 2.4Å  
→ hoher Fluss**

**-Detektorbank mit  
400 oder 800 Detektoren  
aber ohne Kollimation**

**- sehr schnelle Messung**



# RUTHENATE : Distorted structure Neutron diffraction with high flux

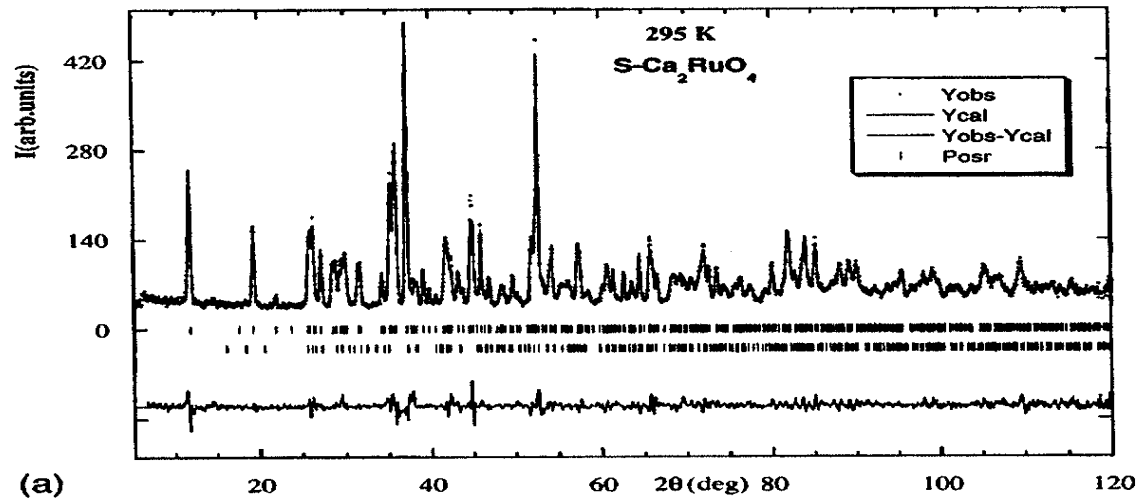


G4.1

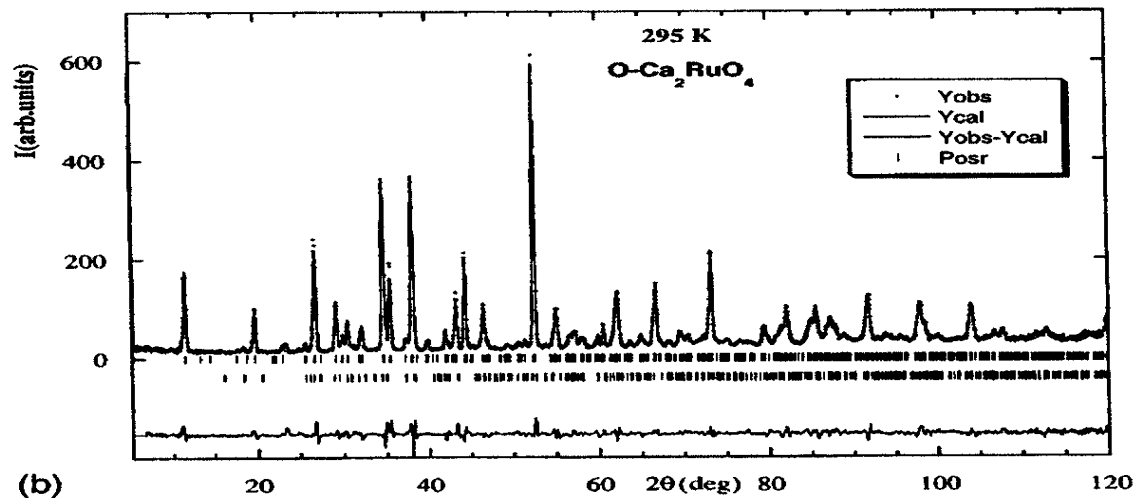
2.36 Å

800 detectors

# High resolution neutron powder diffraction



(a)



(b)

3T.2  
1.22Å  
20 detectors

# Powder diffractometers at the ILL

## PSD diffractometers

⌘ D1B

⌘ D20

⌘ High resolution 2-axis diffractometer

⌘ D1A

⌘ D2B

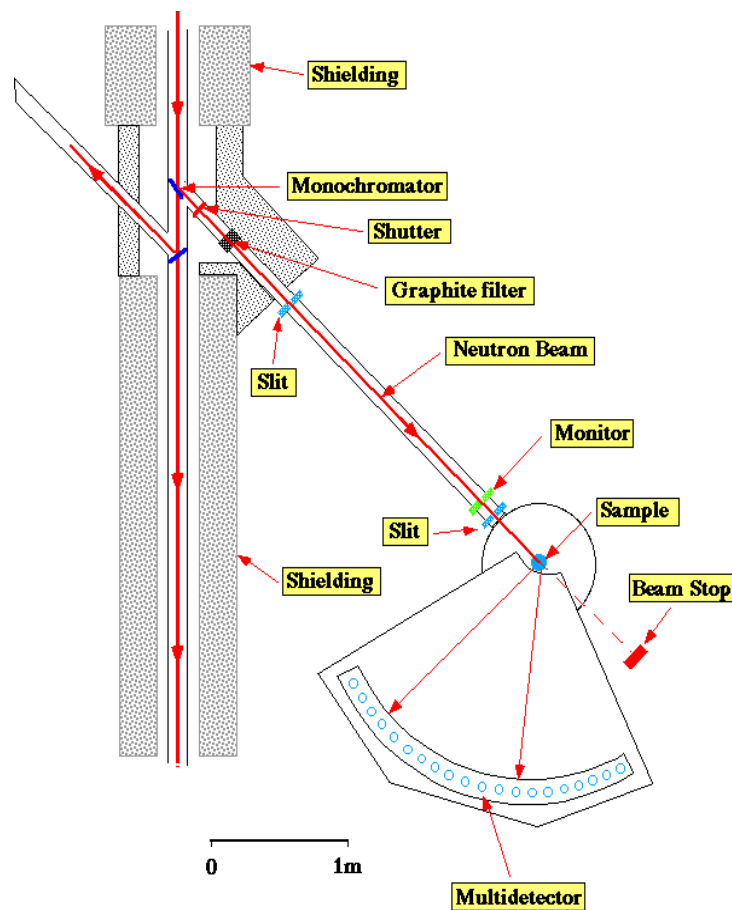
⌘ D20

⌘ Short wavelength diff. (for liquids and amorphous solids)

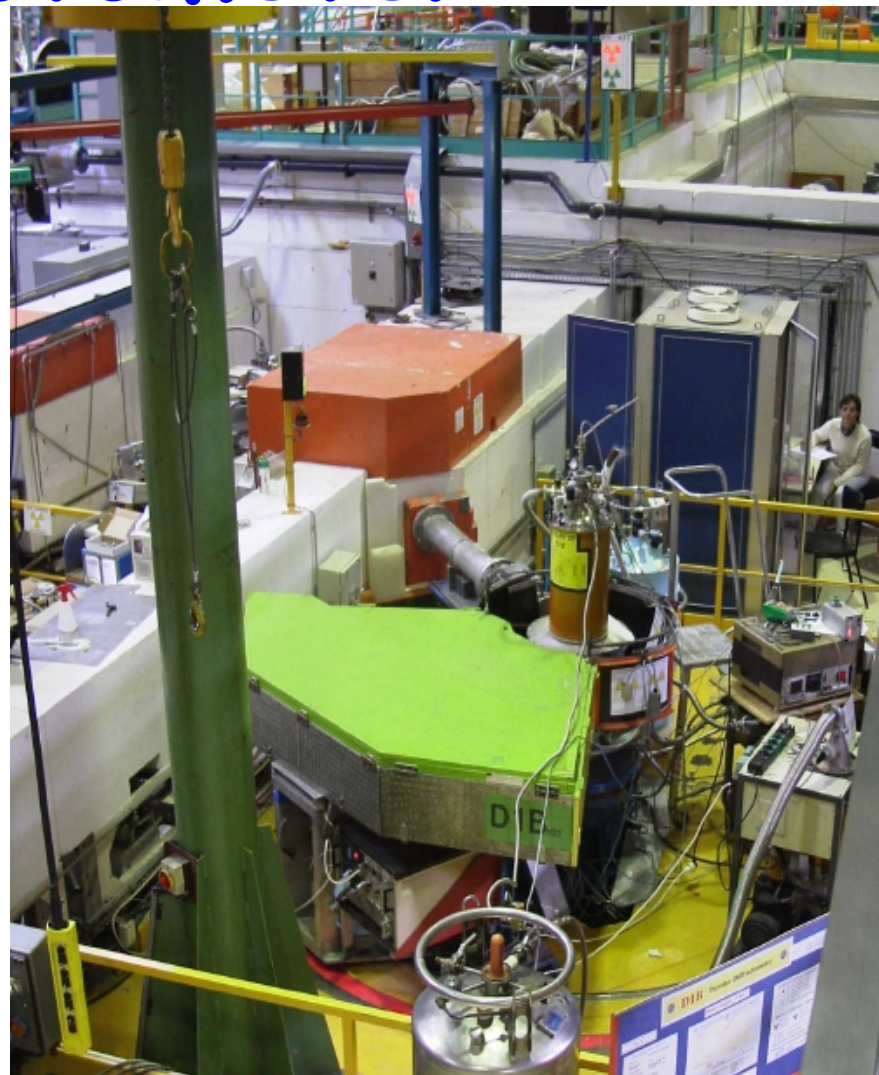
⌘ D4

# D1B high-flux diffractometer

D1B (*ILL*)



Schematic view of D1B





# D1B high-flux diffractometer

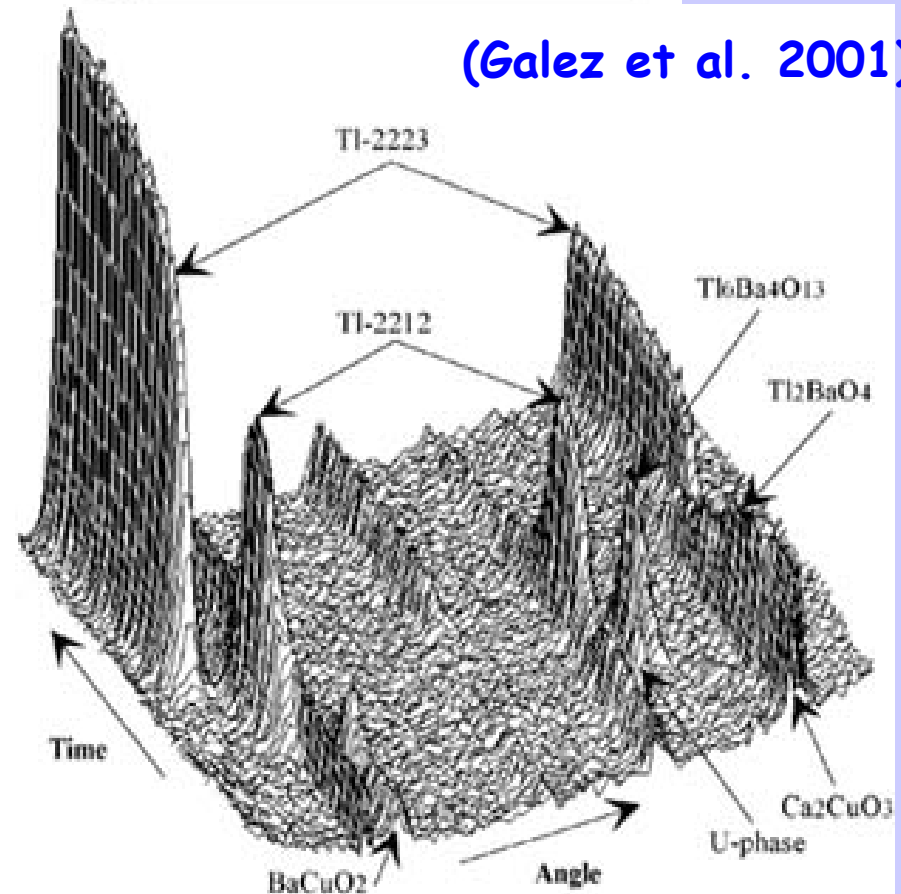
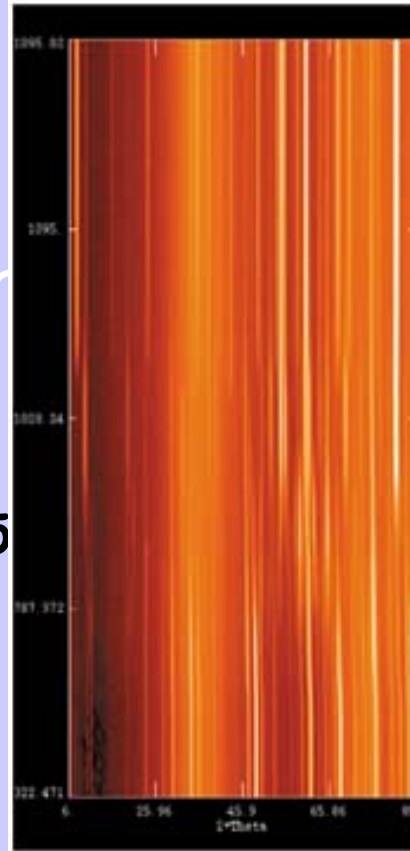
Magnetic structure  
Determination

Thermodiffractometry

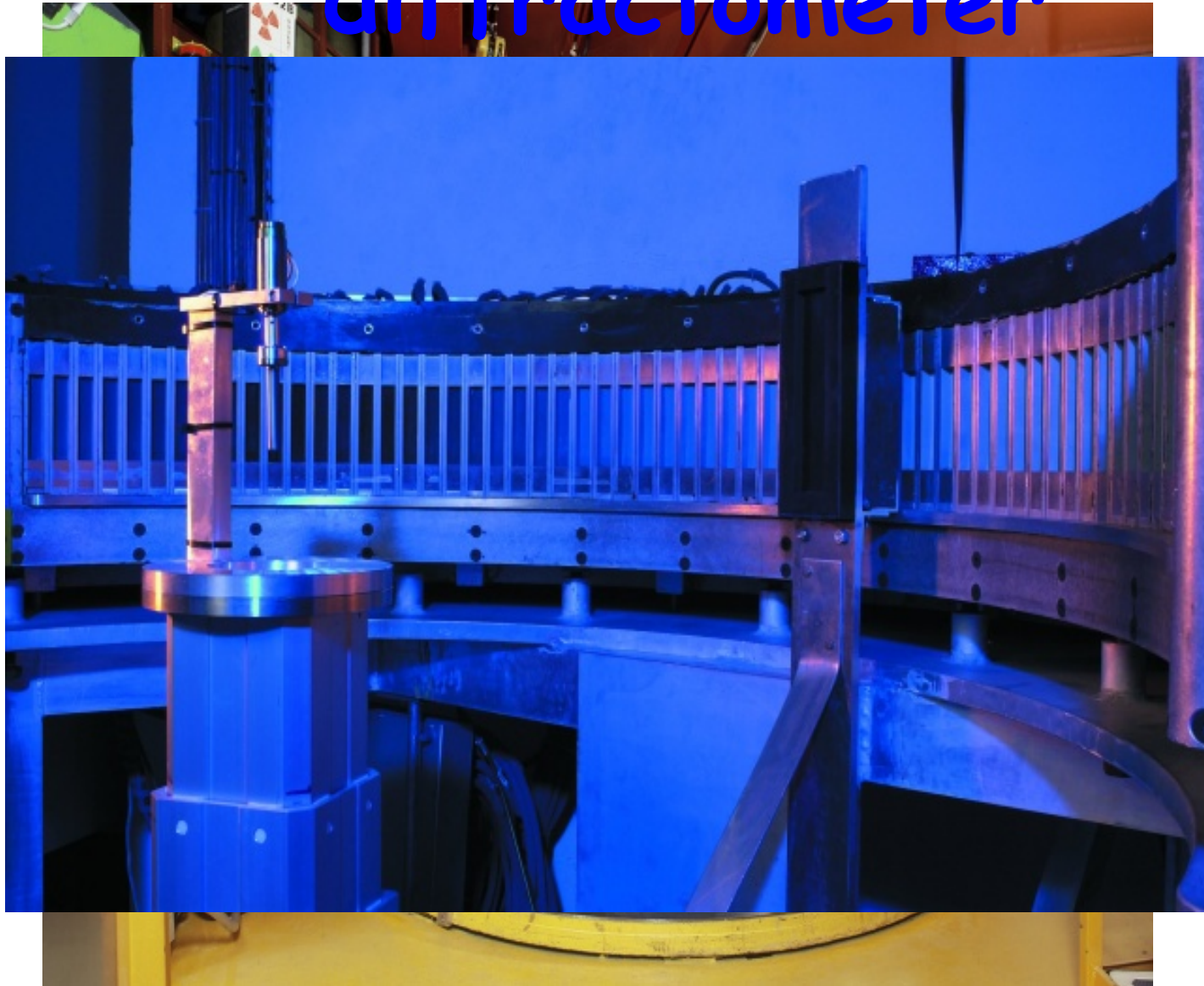
High flux

Long wavelength (2.5

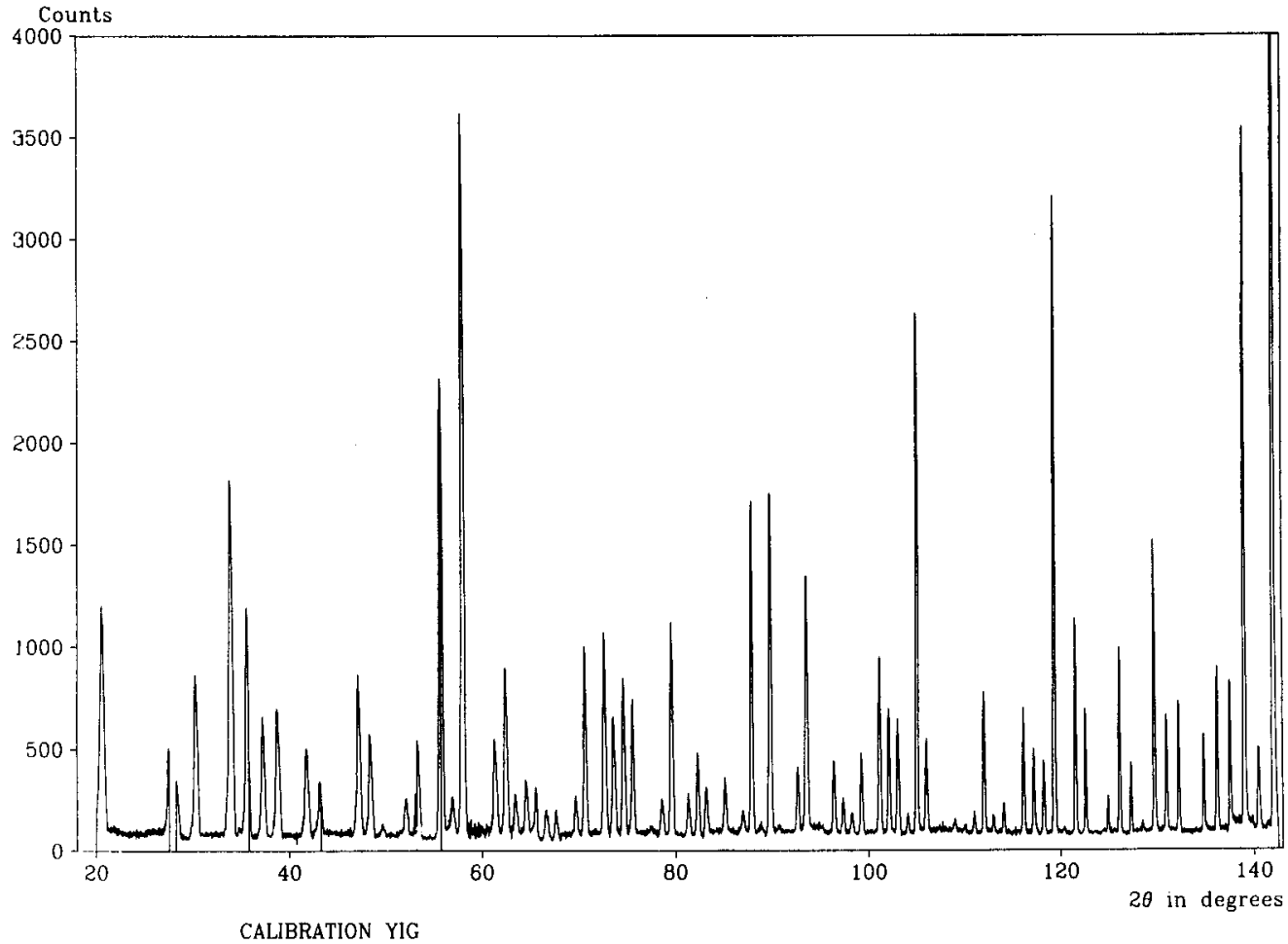
PSD



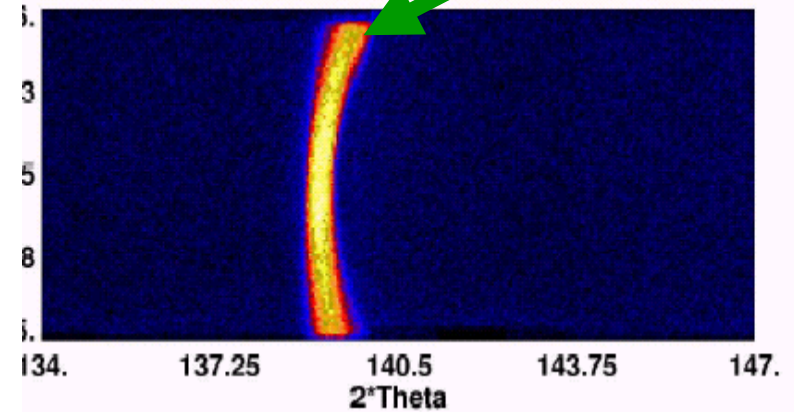
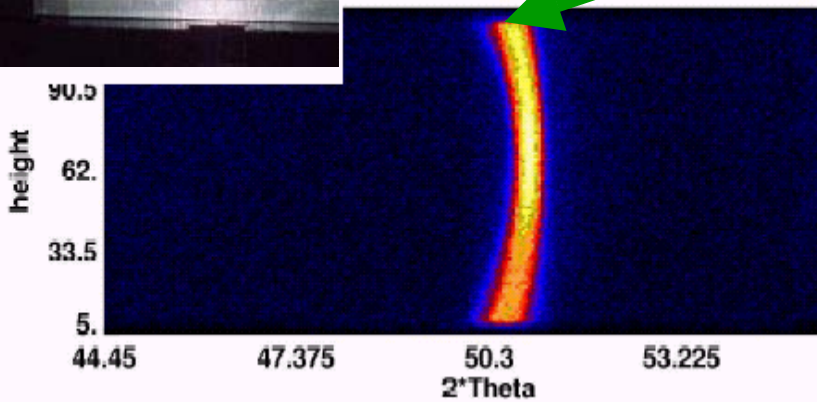
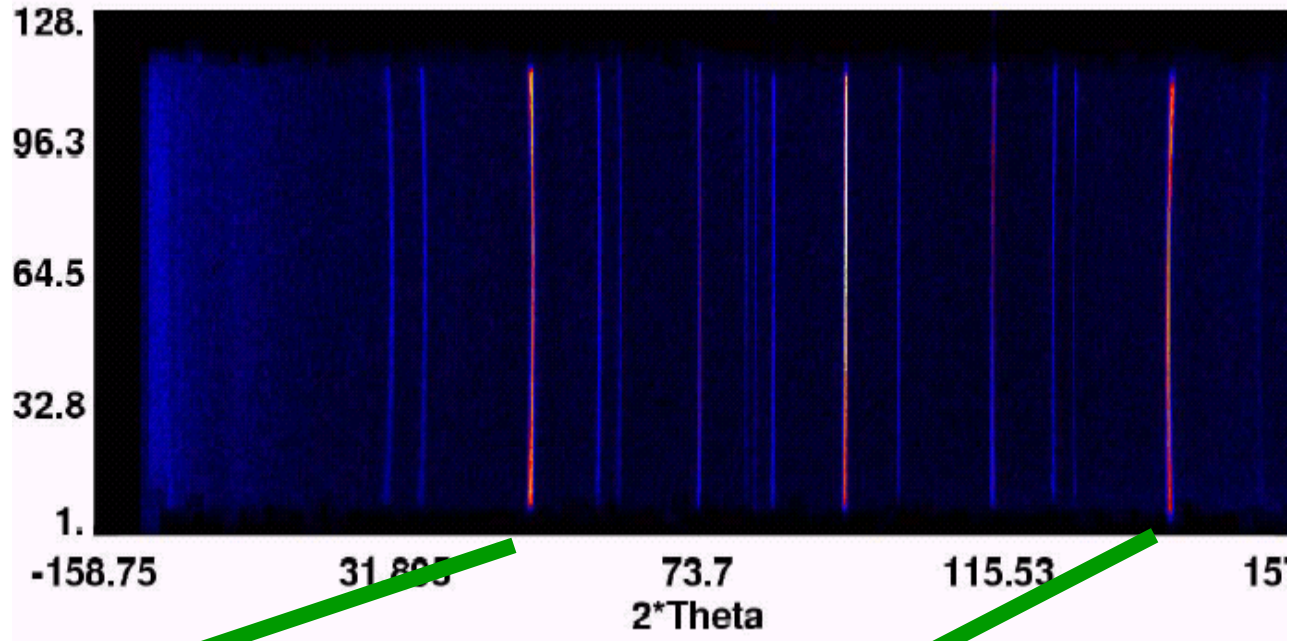
# D2B high-resolution diffractometer



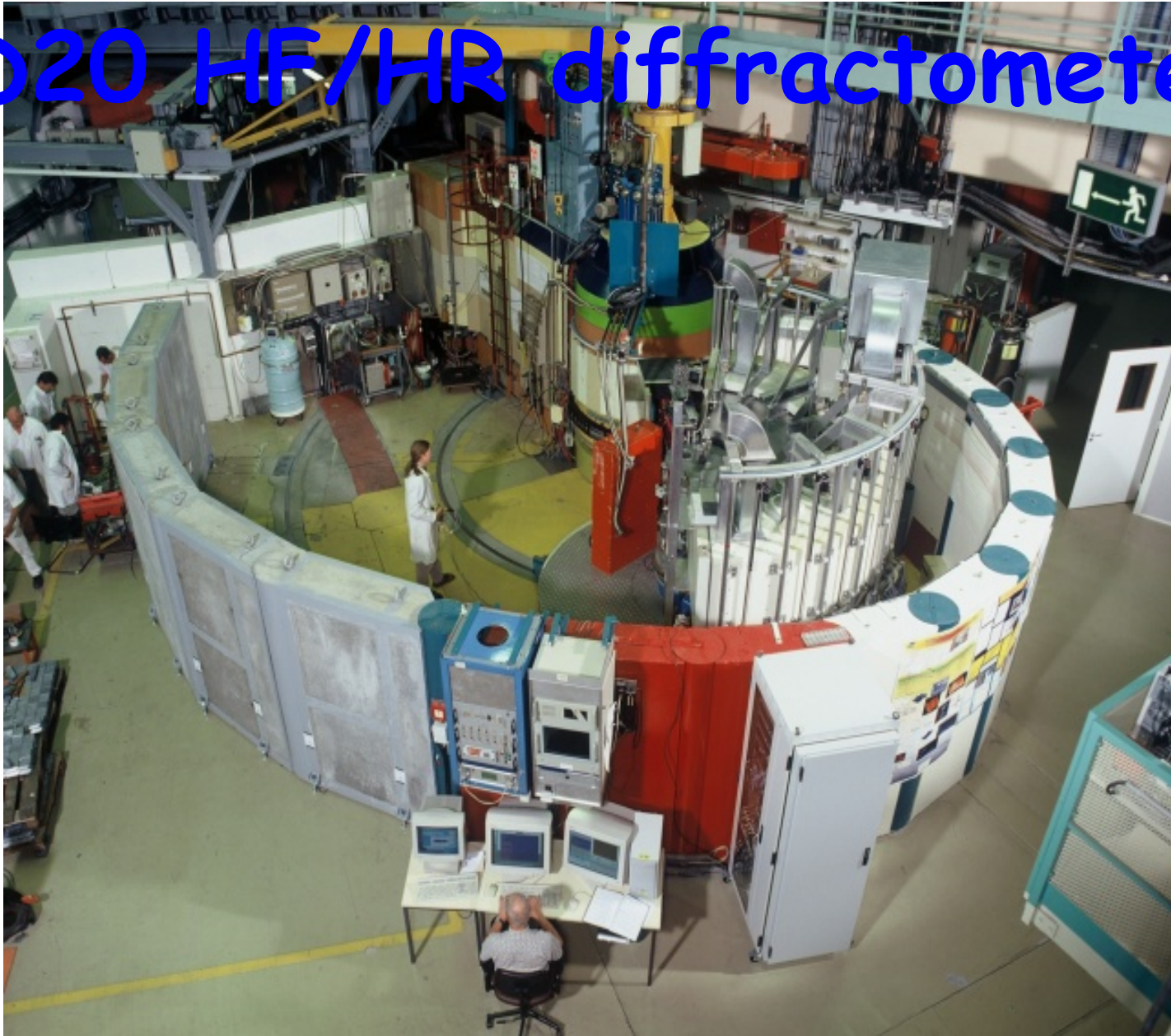
# D2B high-resolution diffractometer



# D2B high-resolution diffractometer

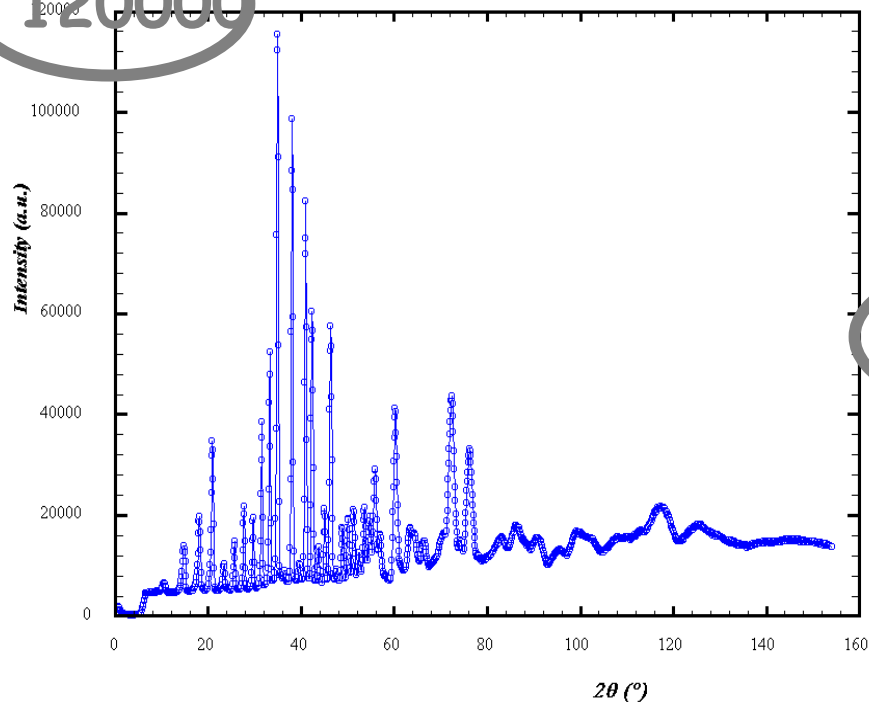


# D20 HF/HR diffractometer



# D20 HF/HR diffractometer

120000

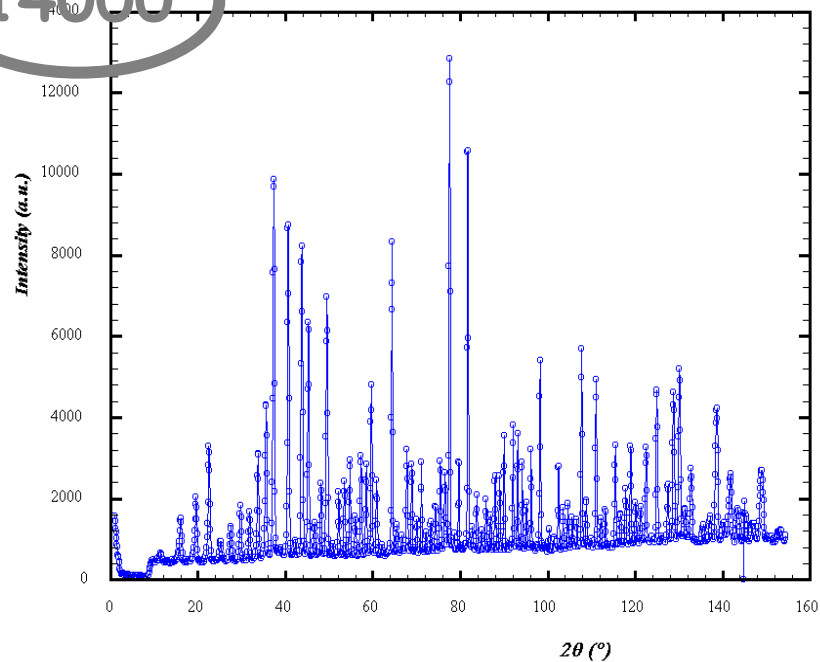


$\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$

1 cm<sup>3</sup>

2 min

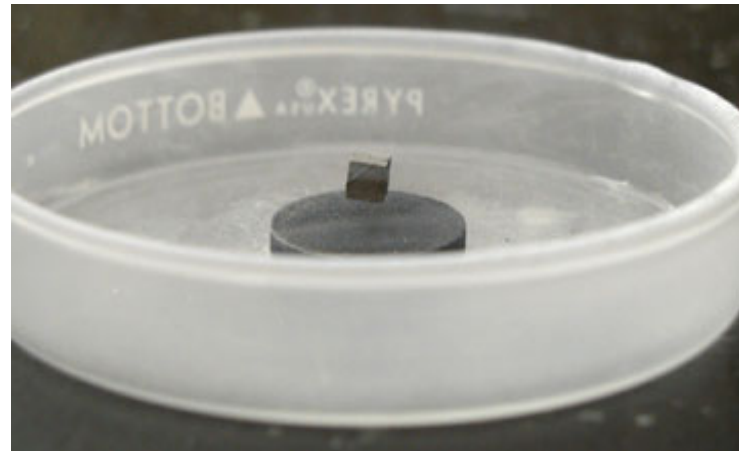
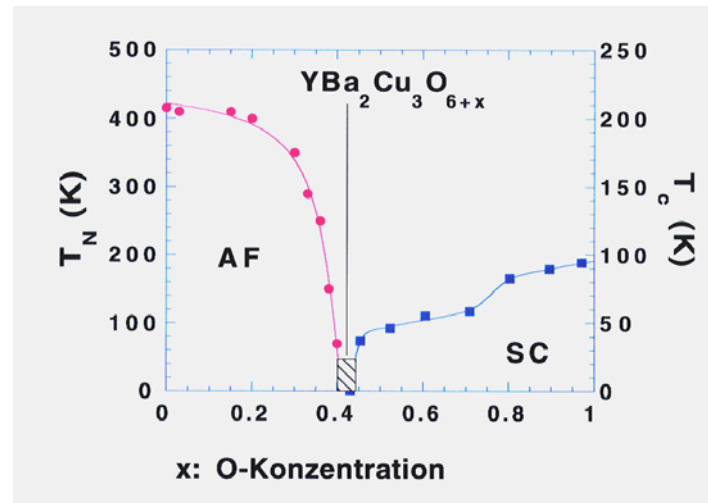
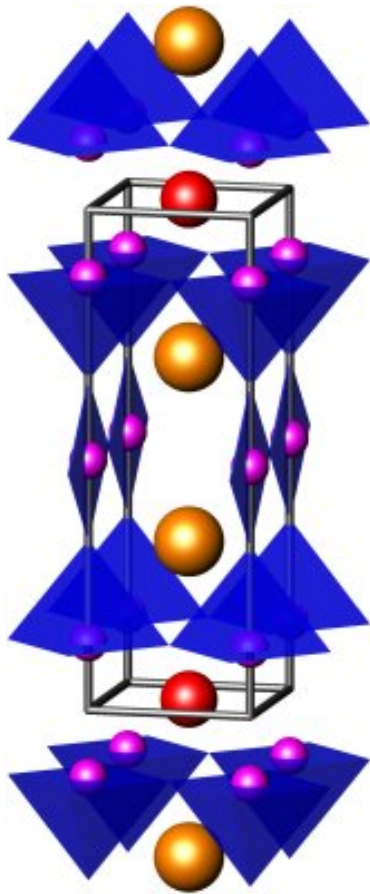
14000



# **II.IV high impact Beispiele**

- A. Struktur von  $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$**
- B. Ladungsordnungs-Phänomene**
- C. Modulierte Strukturen in Bi2212**

# 90K-Phase : $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$



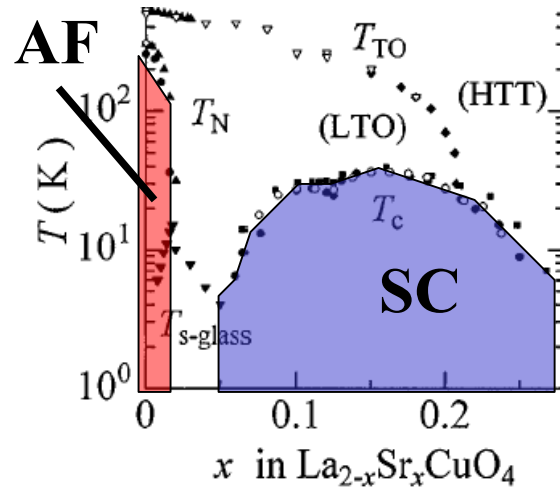
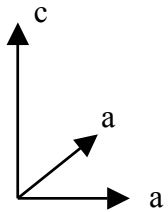
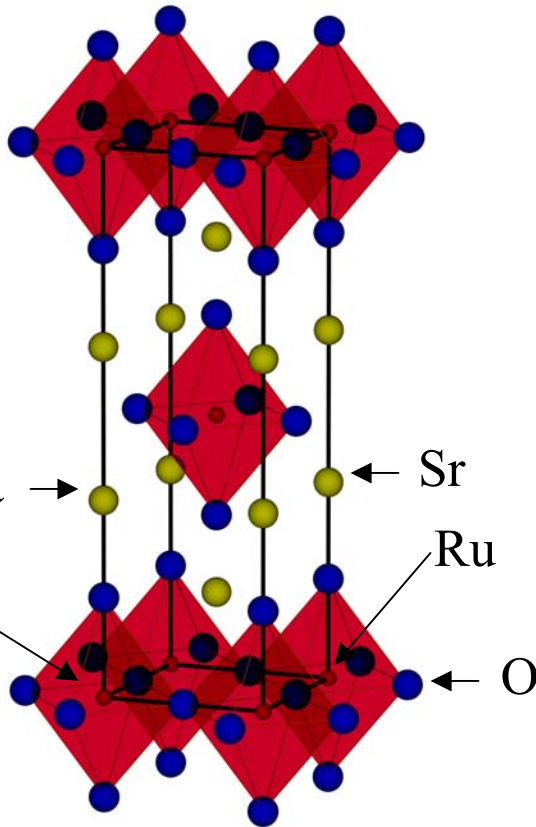
**1987 90K**  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (liquid nitrogen barrier broken) Wu et al.,  
*Physical Review Letters*. 58 (1987): 908-910.



# Supraleitung in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ und $\text{Sr}_2\text{RuO}_4$



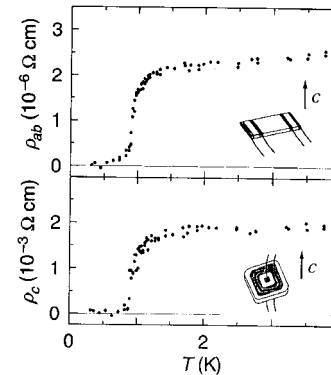
$T_c \sim 35 \text{ K}$



- Takagi *et al.* (1989a)(SQUID)
- ◆ Takagi *et al.* (1992a)(synchrotron X-ray)
- ▲ Cho *et al.* (1993)(SQUID,  $^{139}\text{La}$ -NQR)
- Nagano *et al.* (1993)(SQUID)
- ▼ Chou *et al.* (1993,1995)( $^{139}\text{La}$ -NQR)
- Radaelli *et al.* (1994) (ac-susceptibility)
- ◇ Imai *et al.* (1993)( $^{63}\text{Cu}$ -NQR)
- ▽ Keimer *et al.* (1992)(neutron)

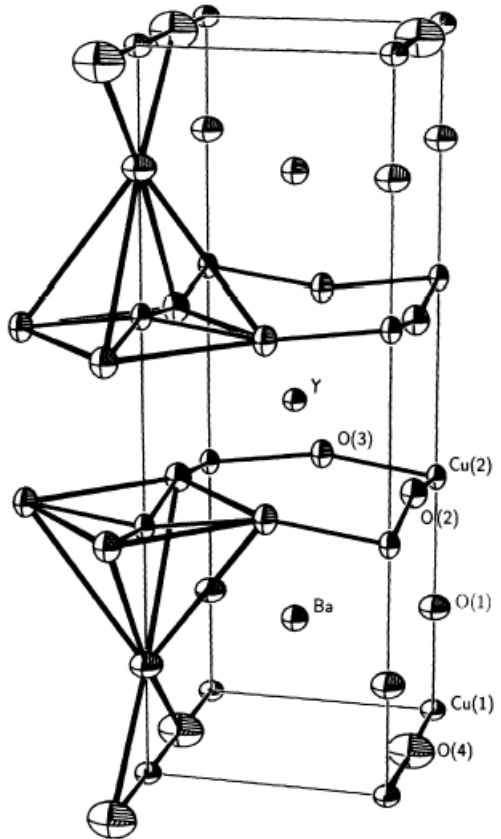


$T_c \sim 1.5 \text{ K}$



Y. Maeno *et al.*,  
Nature 1994

# Dotierung $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$



**$\text{YBa}_2\text{Cu}_3\text{O}_6$  :**

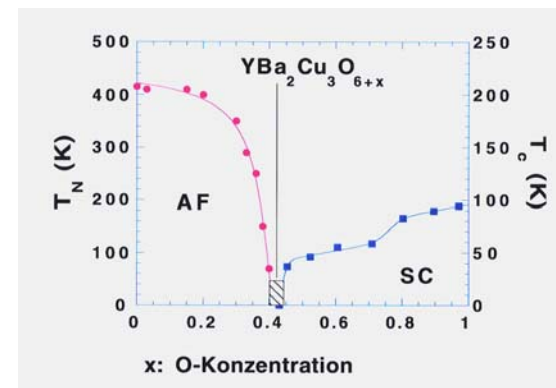
**Cu-Kette 1+**

**Cu-Ebene 2+**

**zusätzlicher Sauerstoff**

**→ Oxidation von Cu  
aber welcher ?**

**-> zunächst nur in Kette**



# STRUCTURAL ANOMALIES, OXYGEN ORDERING AND SUPERCONDUCTIVITY IN OXYGEN DEFICIENT $\text{Ba}_2\text{YCu}_3\text{O}_x$

R.J. CAVA <sup>a</sup>, A.W. HEWAT <sup>b</sup>, E.A. HEWAT <sup>c</sup>, B. BATLOGG <sup>a</sup>, M. MAREZIO <sup>d,a</sup>, K.M. RABE <sup>e</sup>, J.J. KRAJEWSKI <sup>a</sup>, W.F. PECK Jr. <sup>a</sup> and L.W. RUPP Jr. <sup>a</sup>

<sup>a</sup> AT&T Bell Laboratories, Murray Hill, New Jersey 07974, USA

<sup>b</sup> Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France

<sup>c</sup> Centre d'Etudes Nucleaires de Grenoble, 85X, 38041 Grenoble Cedex, France

<sup>d</sup> Laboratoire de Cristallographie, CNRS, 166X, 38042 Grenoble Cedex, France

<sup>e</sup> Department of Applied Physics, Yale University, New Haven, Connecticut 06520, USA

Received 21 November 1989

Revised manuscript received 15 December 1989

We report the characterization of series of oxygen deficient  $\text{Ba}_2\text{YCu}_3\text{O}_x$  samples for  $7 \geq x \geq 6$  prepared by Zr gettered annealing at 440°C. Measurements include complete crystal structure analysis at 5 K by powder neutron diffraction, electron microscopy study of the oxygen ordering, and magnetic measurements of the superconducting transitions, with particular attention to the transition widths. The results show for the first time that the 90 K and 60 K plateaus in  $T_c$  as a function of oxygen stoichiometry are associated with plateaus in the effective valence of the plane coppers. We also correlate the disappearance of superconductivity for  $x < 6.5$  with an abrupt transfer of negative charge into the  $\text{CuO}_2$  planes. We propose that different ordering schemes of oxygen have different characteristic  $T_c$ 's between 90 and 60 K.

**Physica C 165, 419-433 (1990)**

**929 ( in 2005 : 892) citations !** (Streifen haben 1420)

**dritt-häufigstes Zitat in Hoch- $T_c$  nach**

**Original-Arbeit von Bednorz und Müller ~7000 Zitate**

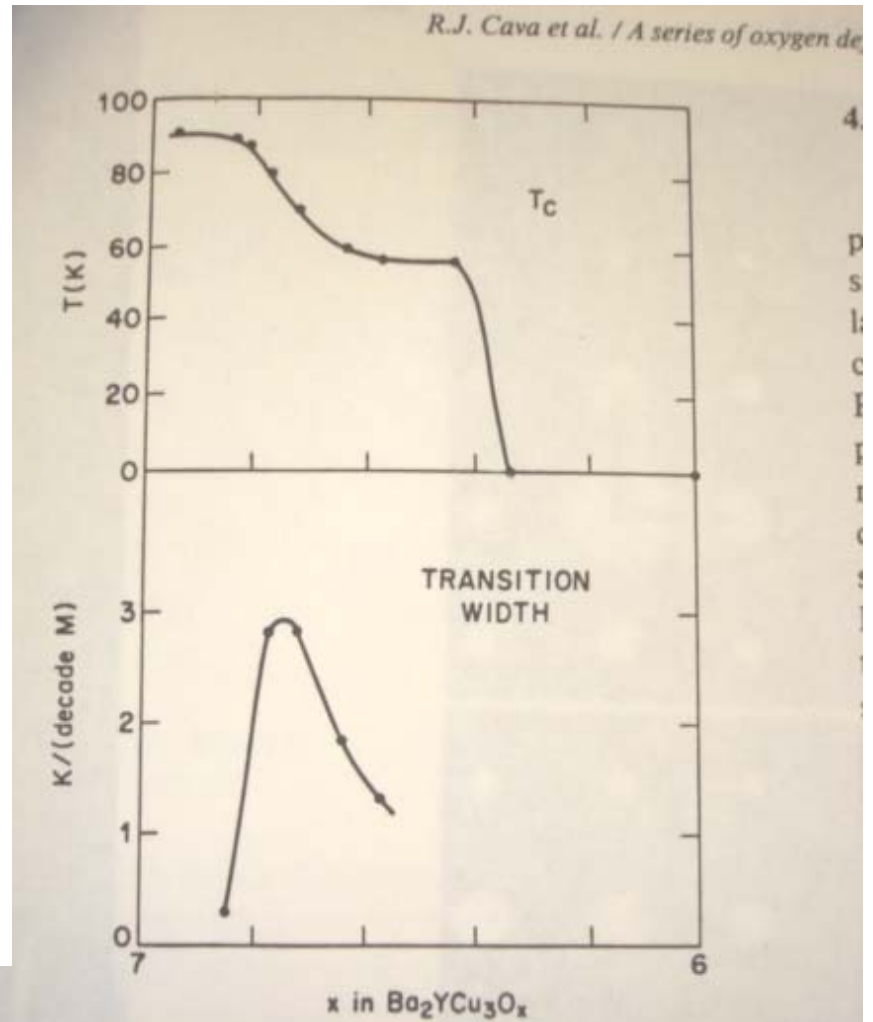
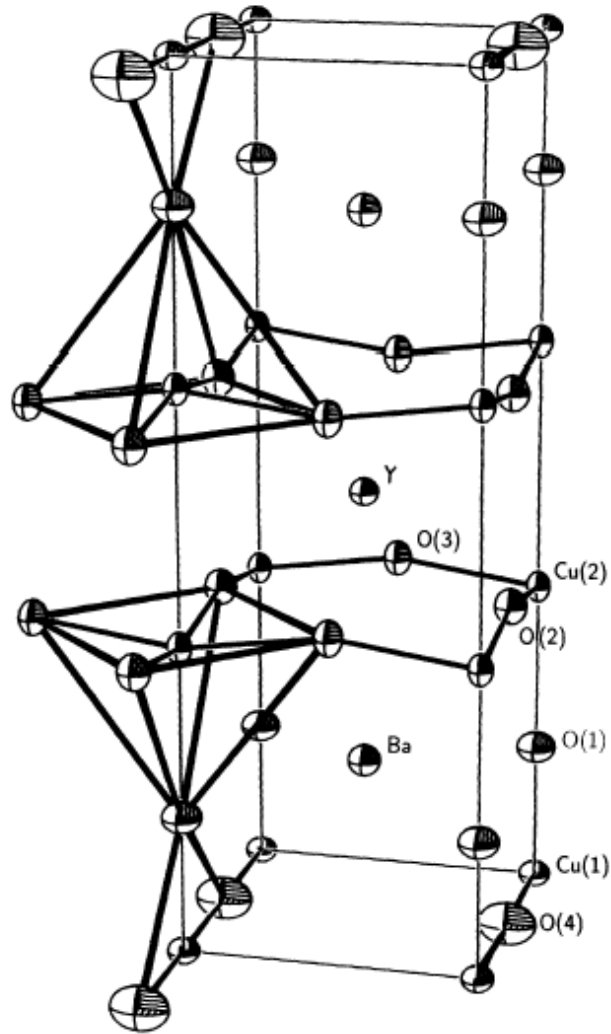


Fig. 1. Superconductive transition temperature  $T_c$  for the ten samples of  $\text{Ba}_2\text{YCu}_3\text{O}_x$  employed in this study. The width of the superconducting transitions in kelvins per decade of magnetization is also shown.

Table I

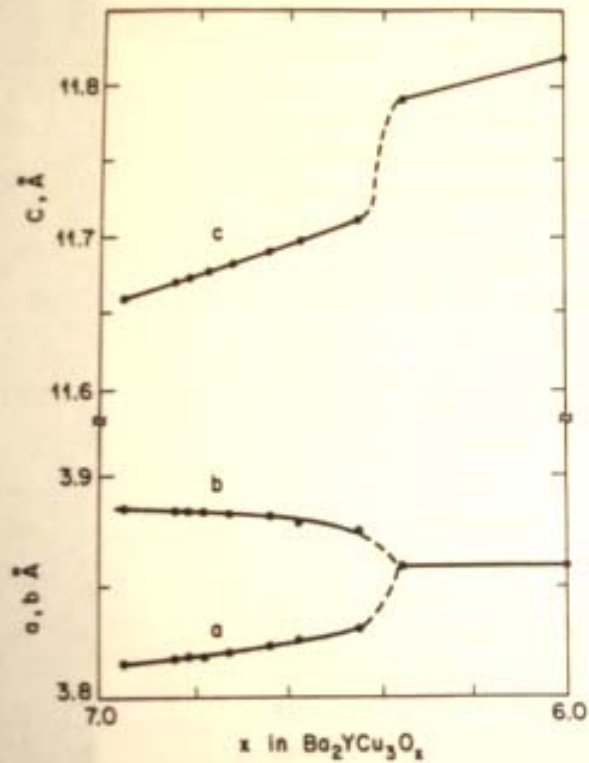
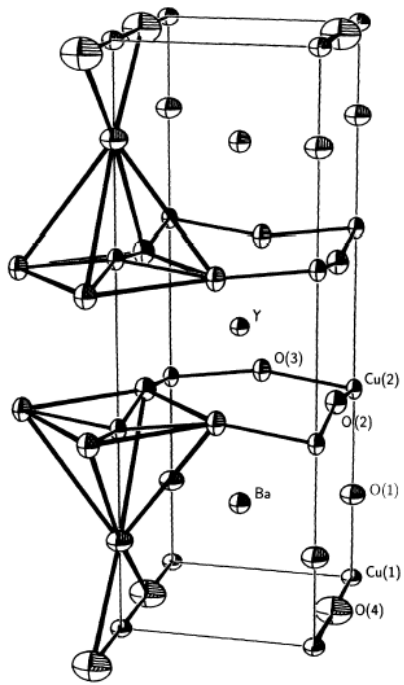


Fig. 5. Refined crystallographic cell parameters for  $\text{Ba}_2\text{YCu}_3\text{O}_x$  prepared by Zr gettering at  $440^\circ\text{C}$ .

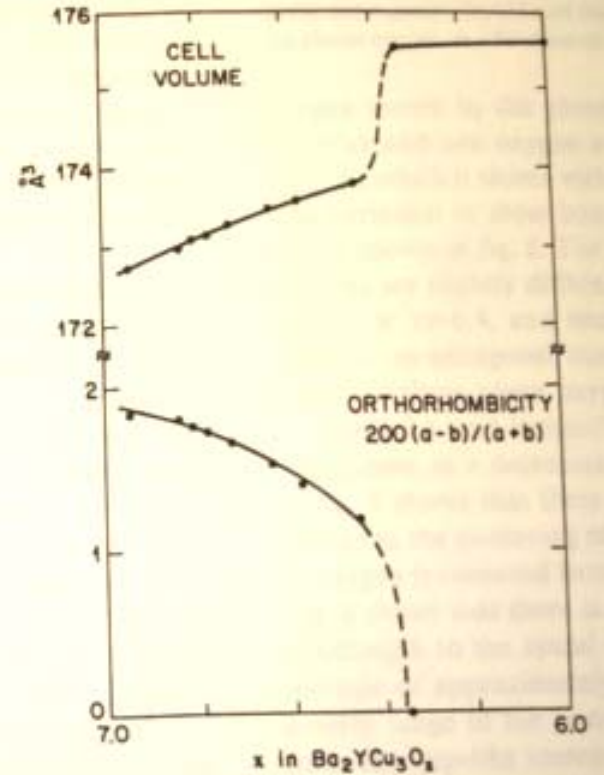


Fig. 6. Crystallographic cell volume and orthorhombicity for  $\text{Ba}_2\text{YCu}_3\text{O}_x$  prepared by Zr gettering at  $440^\circ\text{C}$ .

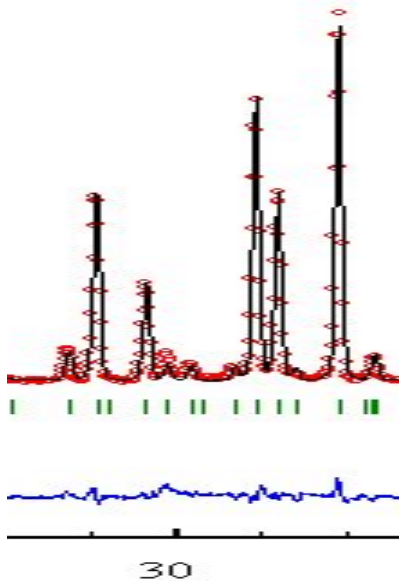
# VII. 27.11.2007

## Rietveld-Verfahren

R.A. Young: *The Rietveld Method*, Oxford University Press,  
[ISBN 0-19-855577-6](#)

Rudolf Allmann: *Röntgen-Pulver-Diffraktometrie*, Verlag Sven von Loga,  
[ISBN 3-87361-029-9](#)

C. Giacovazzo: *Fundamentals of Crystallography*, Oxford University Press,  
[ISBN 0-19-855578-4](#)



Petten, The Netherlands. (1987)

# Ketten-Cu

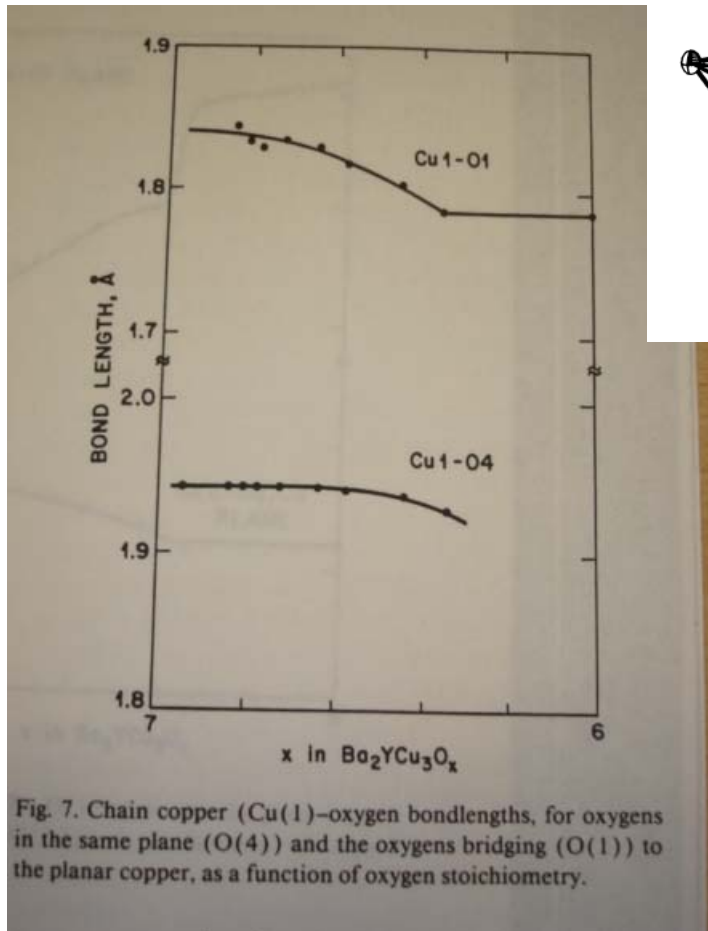
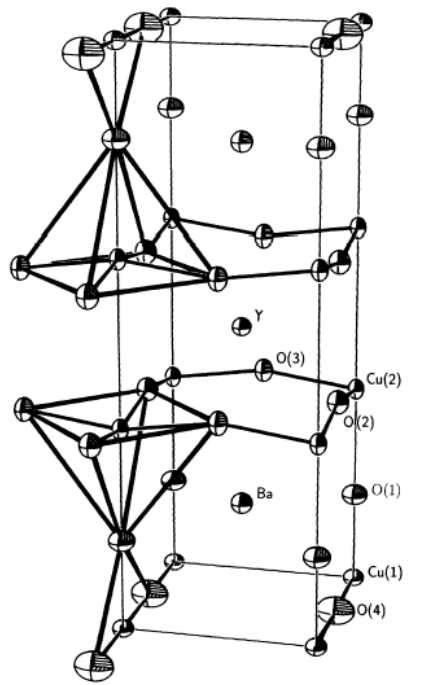


Fig. 7. Chain copper (Cu(1))–oxygen bondlengths, for oxygens in the same plane (O(4)) and the oxygens bridging (O(1)) to the planar copper, as a function of oxygen stoichiometry.



# Ebenen-Cu

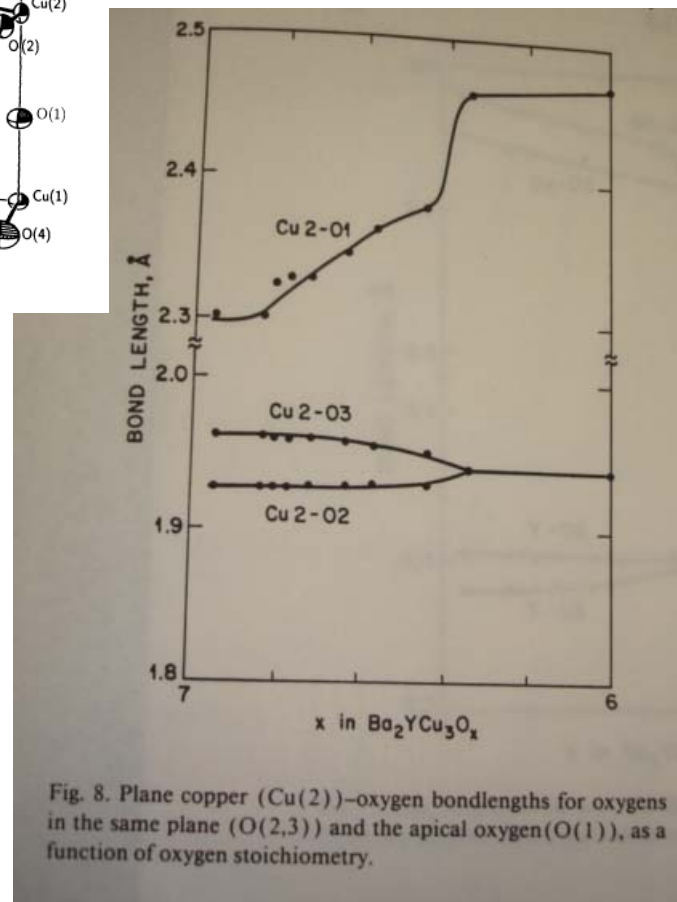


Fig. 8. Plane copper (Cu(2))–oxygen bondlengths for oxygens in the same plane (O(2,3)) and the apical oxygen (O(1)), as a function of oxygen stoichiometry.

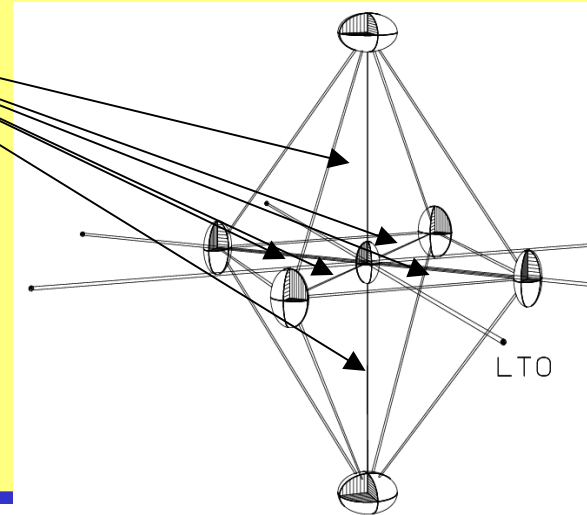
# Bindungsvalenzsummen

## Bindungslängen – Bindungsstärken – Beziehungen

$$S_i = \exp\left(\frac{R_0 - R_i}{B}\right)$$

$$Valence = \sum_i S_i$$

Zachariasen (1978);  
Brown & Altermatt (1985).  
Tabellierung von  $R_0$  und  $B$



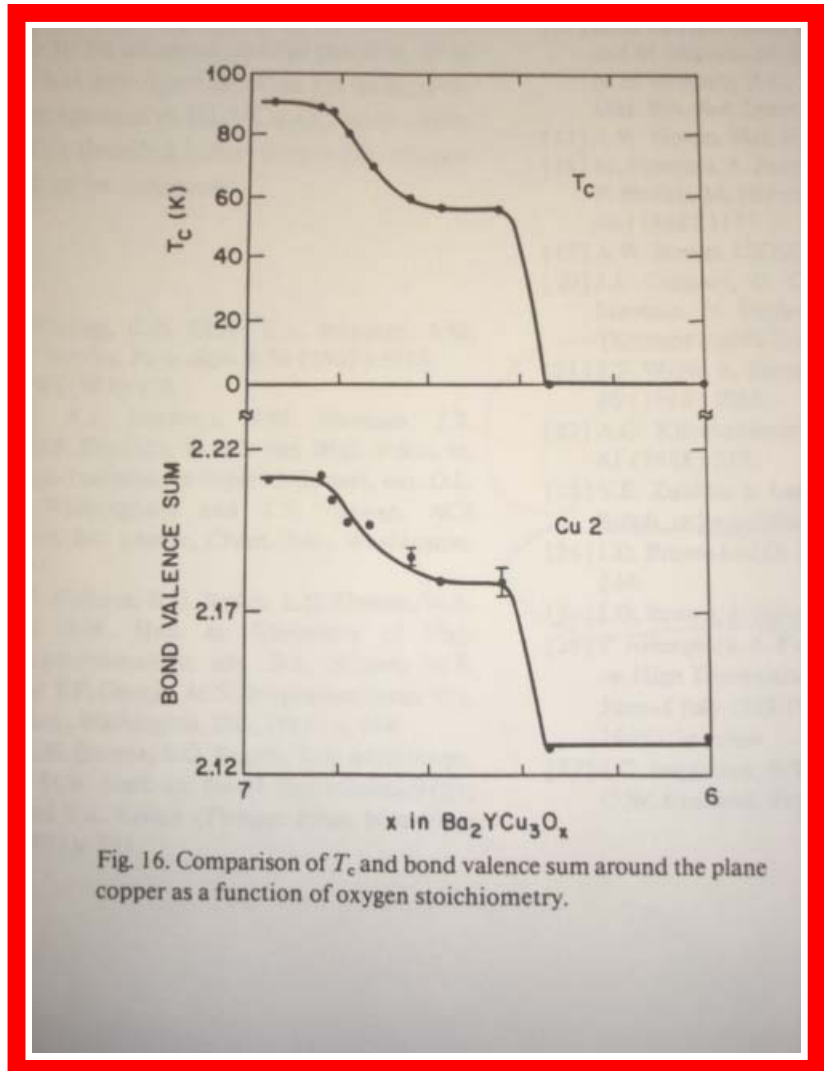
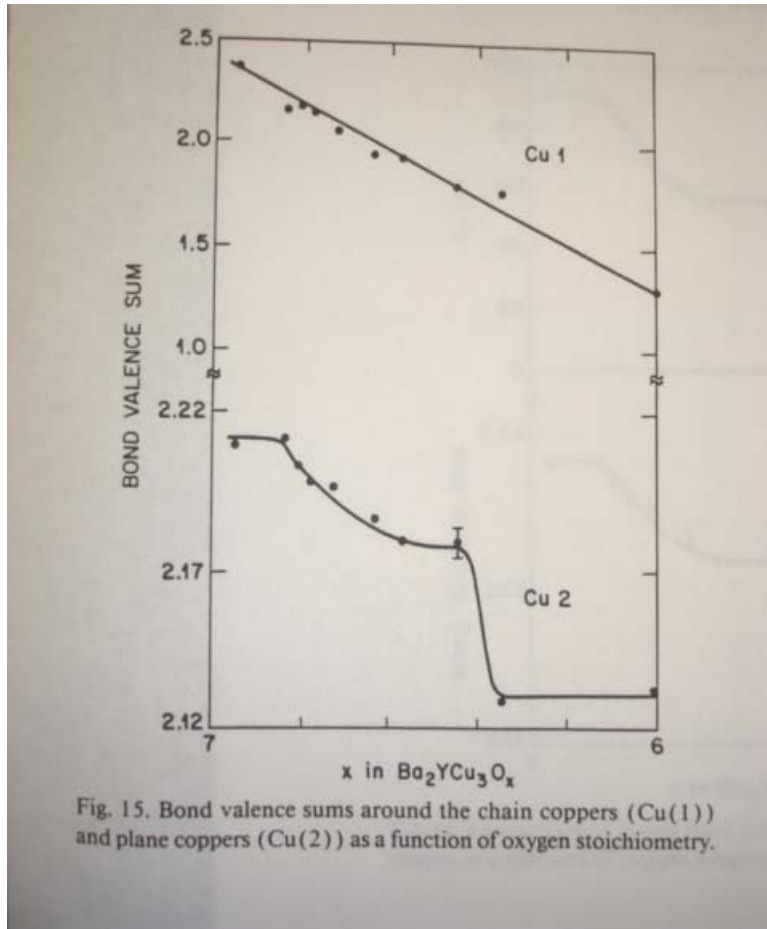
- Zuordnung : Bindung  $\rightarrow$  Bindungsvalenz

$\rightarrow$  **Bindungsvalenzsumme**

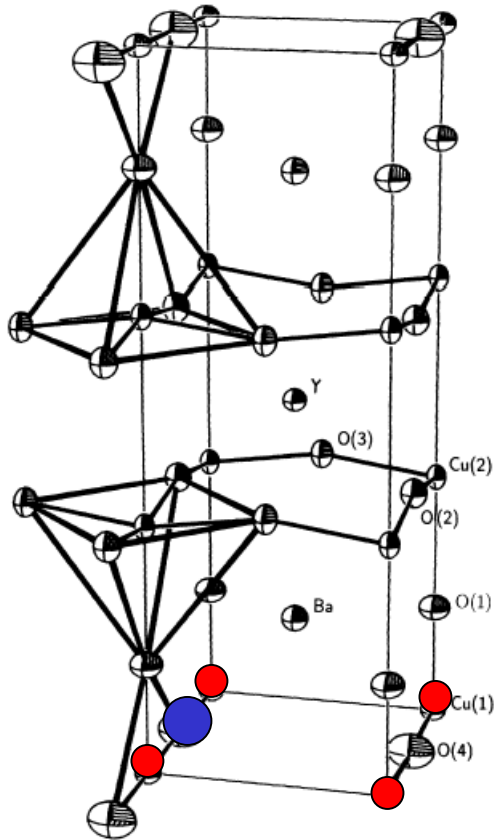
-kurze Bindungen  $\Leftrightarrow$  hohe Valenz



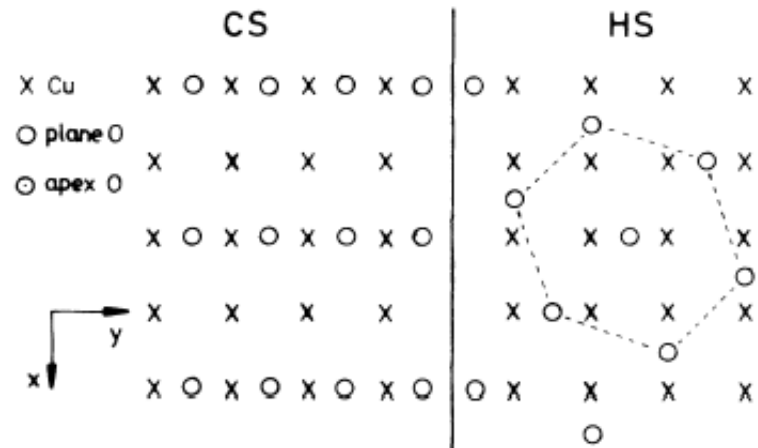
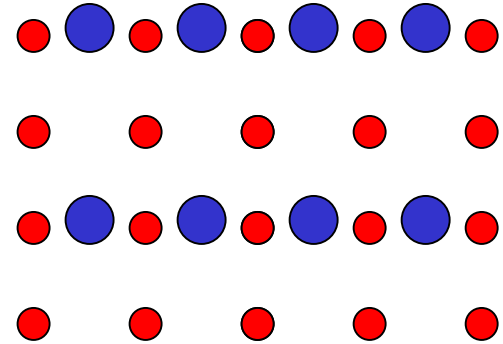
# $T_c$ skaliert mit Bindungswalenzsumme !



# Dotierung $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

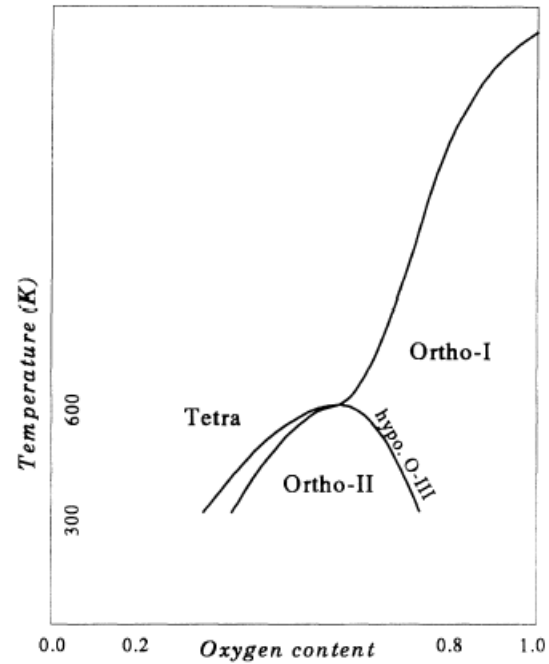
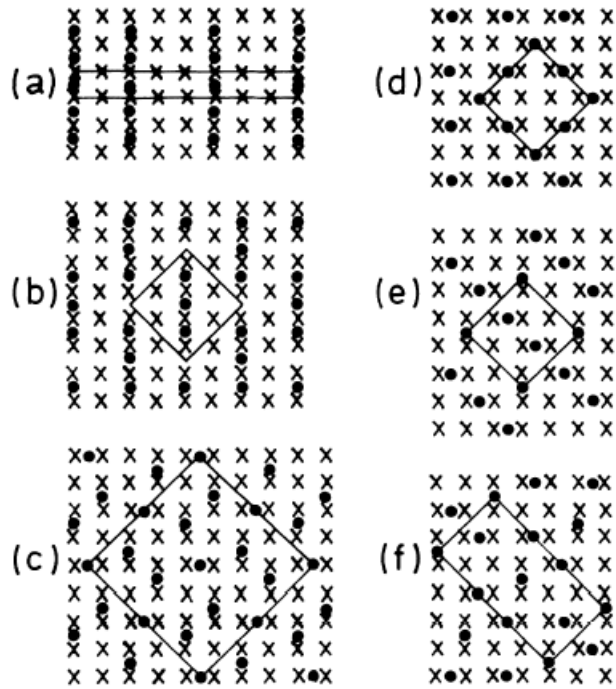


## Ketten-Cu Ebene

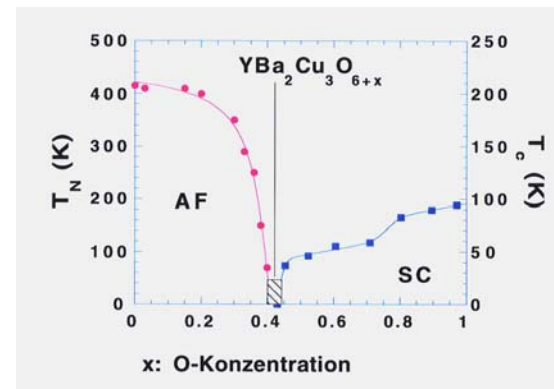


**Dotierung hängt von der Ordnung der O's ab !**

# Dotierung $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$



**Kettenformation notwendig  
Alliga, Uimin, ...**



# Hoch- $T_c$ -Kuprat-Supraleiter

- year  $T_c$  [K]
- 1986 30  $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$  J. G. Bednorz, K. A. Müller  
*Zeitschrift für Physik B*. Vol. 64: 189-193.
- 1987 90  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (liquid nitrogen barrier broken) Wu et al.,  
*Physical Review Letters*. 58 (1987): 908-910.
- 1988 115  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  H. Maeda et al  
*Jap. J. of Appl. Physics*. Vol. 27 (1988): 209.
- 1988 125  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  Z. Z. Sheng, A. M. Hermann  
*Nature*. Vol. 332 (1988): 138.
- 1993 133  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$  A. Schilling et al.  
*Nature*. Vol. 363 (1993): 56-58.
- 1995 **138**  $\text{Hg}_{0.8}\text{Tl}_{0.2}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.33}$  P. Dai et al.,  
(highest critical temperature of any material)  
*Physica C*. 243 No. 3&4 (1995): 201-206.
- 1994 164  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$  (under 30 GPa pressure) Gao et al.,  
*Physical Review B*. Vol. 50 (1994): 4260-4263.

# Hoch- $T_c$ -Kuprat-Supraleiter

$(La,M)_2CuO_4$	1986	$TlBa_2(Eu,Ce)_2Cu_2O_9$	1992
$La_2CuO_{4+x}$	1988		
$La_2CuO_4F_x$	1988	(Tl,Pb)SrCaCu variants of Tl, Ba, Ca compounds	1988
$(Nd,Sr,Ce)_2CuO_4$	1989		
$(Nd,Ce)_2CuO_4$	1989		
$Nd_2CuO_{4-x}F_x$	1989	$GaSr_2(Y,Ca)Cu_2O_7$	1991
$Sr_2CuO_{3+x}$	1993	$GaSr_2Ca_{n-1}Cu_nO_x$	1994
$Sr_2CuO_2F_{2+x}$	1994	$n = 3, 4$	
$(Ca,Na)_2CuO_2Cl_2$	1994	$AuSr_2CaCu_2O_7$	1997
$(Ca,Na)_3Cu_2O_4Cl_2$	1995	$NbSr_2(Nd,Ce)_2Cu_2O_{10}$	1992
(Sr,K) versions of previous two also are superconducting		$RuSr_2(Nd,Ce)_2Cu_2O_{10}$	1996
		and others in "1222" type with a mix of Cu and M on first Cu site (e.g., Ti, V, Cr) also known	
$(La,Sr)_2CaCu_2O_6$	1990		
$(Sr,Ca)_2(Sr,Ca)_{n-1}Cu_nO_x$	1993	$Cu(Eu,Ce)_2(Eu,Sr)_2Cu_2O_9$	1989
$(n = 2, 3, 4)$		and others in this type with a mix of Cu and M on first Cu site (e.g., Pb, Ga) also known	
$PbBaSr(Y,Ca)Cu_3O_x$	1990		
$Sr_{1-x}Nd_xCuO_2$	1991		
$YBa_2Cu_3O_7$	1987		
$YBa_2Cu_4O_8$	1988	$HgBa_2Ca_{n-1}Cu_nO_{2n+2}$	1993
$Y_2Ba_4Cu_7O_{15}$	1988	$n = 1, 2, 3, 4, 5, 6$	
$(Cu,M)Sr_2(Y,Ca)Cu_2O_7$	1988	$Hg_2Ba_2(Y,Ca)Cu_2O_8$	1994
M stabilized Sr 123		$(Hg_{0.5}Cr_{0.5})Sr_2CuO_5$	1995
M = Pb, Ga, Fe, B, $SO_4$ , $CO_3$ , Al, (Bi + Cd)		$(Hg_{0.5}Cr_{0.5})Sr_4Cu_2O_7CO_3$	1995
		$(Ba,Sr)_2Cu_{1+x}(CO_2)_{1-x}O_y$	1992
$Pb_2Sr_2(Y,Ca)Cu_3O_8$	1988	$(Cu_{1-x}(CO_2)_x)_m(Ba,Sr)_2Ca_{n-1}Cu_nO_y$	1994
$Pb_2(Sr,La)_2Cu_2O_6$	1988	$m = 1; n = 2, 3, 4, 5; x \neq 0 \text{ or } x = 0$	
		$m = 2; n = 3, 4, 5; x \neq 0$	
" $Bi_2Sr_2CuO_6$ "	1987		
$Bi_2Sr_2CaCu_2O_8$	1988	$Bi_2Sr_4Cu_2O_8CO_3$	1993
$Bi_2Sr_2Ca_2Cu_3O_{10}$	1988	$Bi_2Sr_2Cu_3O_{10}(CO_3)_2$	1994
$Bi_2Sr_2(Ln,Ce)_2Cu_2O_{10}$	1990	(Tl,Pb)Sr <sub>4</sub> Cu <sub>2</sub> O <sub>7</sub> CO <sub>3</sub>	1993
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$	1988	$Ca_{13.5}Sr_{0.5}Cu_{24}O_{41}$	1996
$n = 1, 2, 3, 4$		(60 kbar (6 MPa) applied pressure only)	
$TlBa_2Ca_{n-1}Cu_nO_{2n+3}$	1988		
$n = 1, 2, 3$			

# Einige Kristallstrukturen

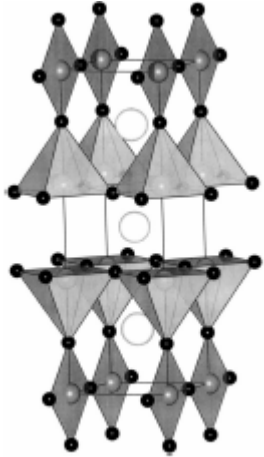


Fig. 13. Crystal structure of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (see Fig. 9 for legend).<sup>22</sup>

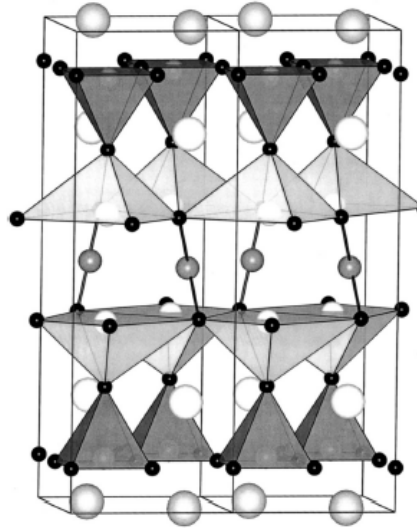


Fig. 16. Crystal structure of Pb<sub>2</sub>Sr<sub>2</sub>YCu<sub>3</sub>O<sub>8</sub> (see Fig. 9 for legend).

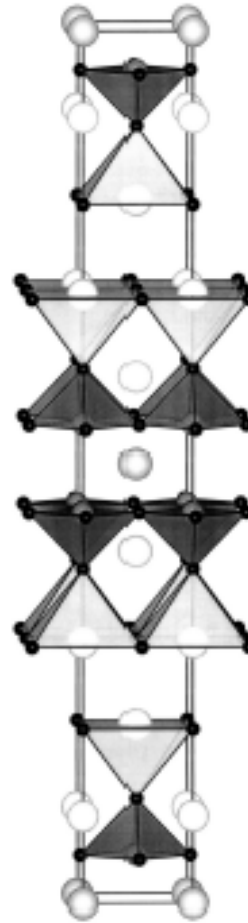


Fig. 14. Crystal structure of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> (see Fig. 9 for legend).<sup>22</sup>

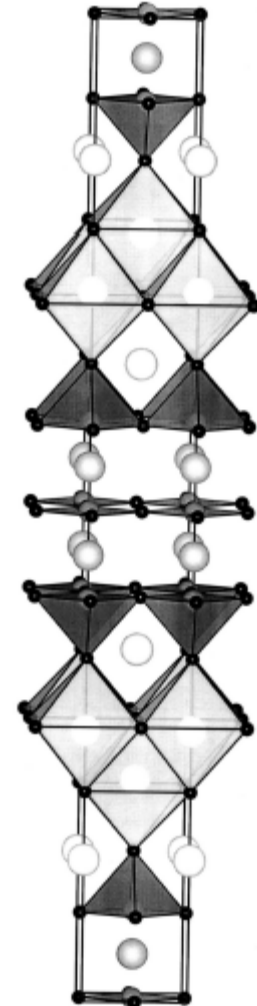
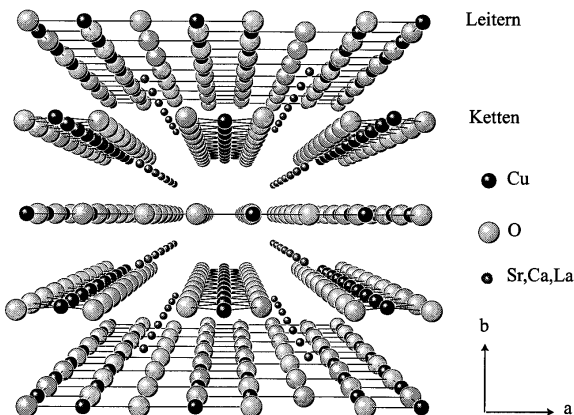
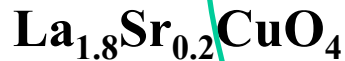


Fig. 15. Crystal structure of Tl<sub>2</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> (see Fig. 9 for legend).<sup>22</sup>



# Schema der Kristallstrukturen: ein wenig Chemie

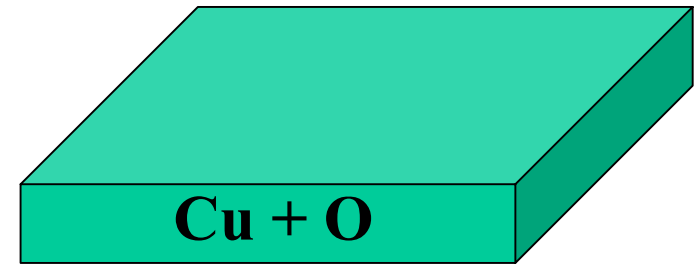
## Hoch-Temperatur-Supraleiter Formeln



**Cu = Copper**

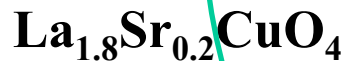
**O = Oxygen**

**CuO = CopperOxide**



# Schema der Kristallstrukturen: ein wenig Chemie

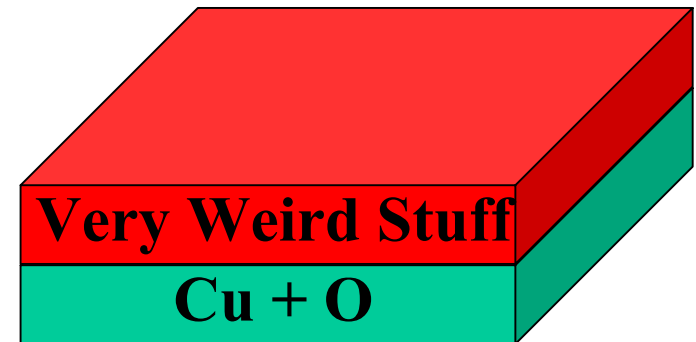
## Hoch-Temperatur-Supraleiter Formeln



**Cu = Copper**

**O = Oxygen**

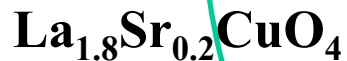
**CuO = CopperOxide**





# Schema der Kristallstrukturen: ein wenig Chemie

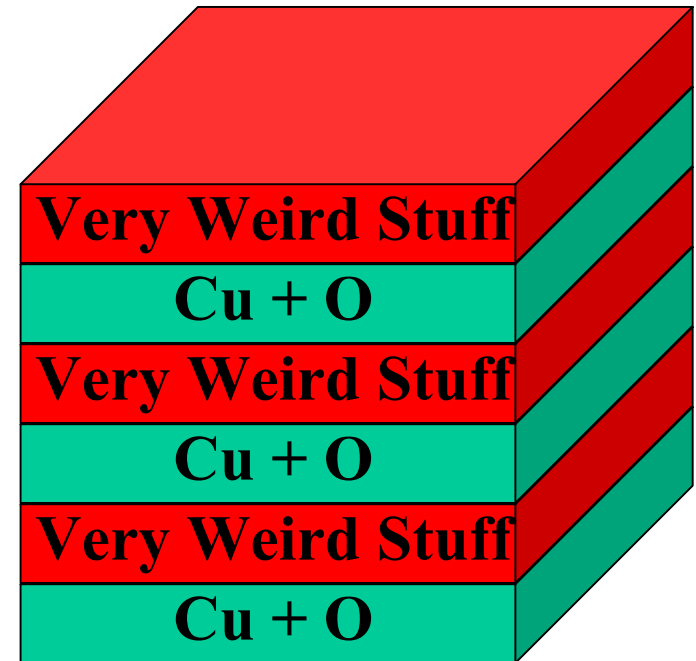
## Hoch-Temperatur-Supraleiter Formeln



**Cu = Copper**

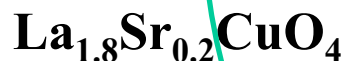
**O = Oxygen**

**CuO = CopperOxide**



# Schema der Kristallstrukturen: ein wenig Chemie

## Hoch-Temperatur-Supraleiter Formeln



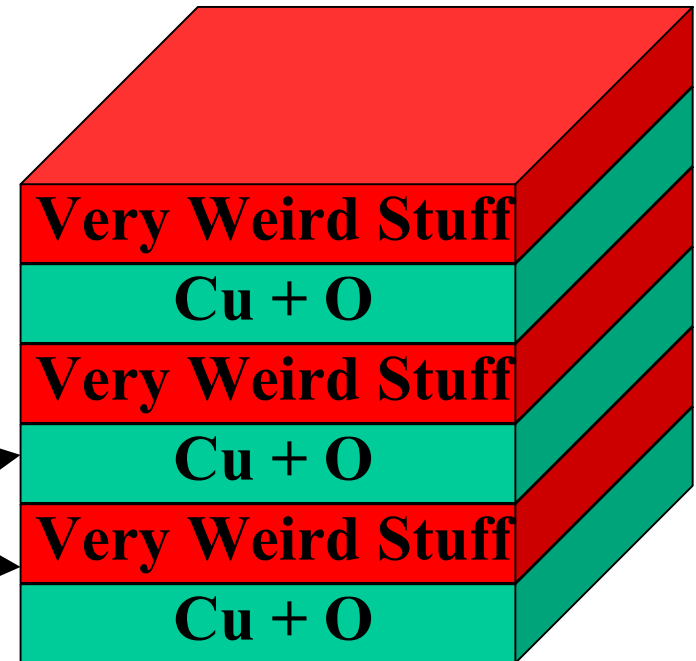
**Cu = Copper**

**O = Oxygen**

**CuO = CopperOxide**

Supraleitung ist hier !!!

auch wichtig!



# C. Modulierte Struktur von Bi2212



- Struktur ist komplizierter
  - BiO- und CuO-Ebene passen nicht zu einander
    - strukt. Verzerrung
    - hier inkommensurabel
- modulierte Strukturen

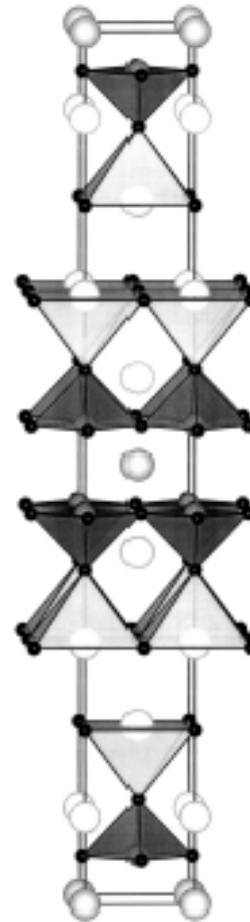


Fig. 14. Crystal structure of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> [see Fig. 9 for legend].<sup>11</sup>

## Rietveld analysis of the modulated structure in the superconducting oxide $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+x}$

Akiji Yamamoto, Mitsuko Onoda, Eiji Takayama-Muromachi, and Fujio Izumi  
*National Institute for Research in Inorganic Materials, Tsukuba 305, Japan*

Tōru Ishigaki and Hajime Asano  
*Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan*  
(Received 16 June 1989; revised manuscript received 27 December 1989)

The modulated structure of the high- $T_c$  superconductor  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+x}$  was analyzed with a newly developed Rietveld refinement program for modulated structures. The structure refinement was made by the simultaneous refinement method using x-ray and time-of-flight neutron-diffraction data. It has a one-dimensionally modulated structure with  $N$   $Bbmb/\bar{1}11$ ,  $a = 5.3957(3)$ ,  $b = 5.3971(3)$ ,  $c = 30.649(1)$  Å, and  $\mathbf{k} = 0.2118(1)\mathbf{b}^*$ . Atoms in Bi-O, Sr-O, Cu-O, and Ca layers are all greatly displaced from their average positions. In particular Bi atoms are displaced mainly along the  $b$  axis, forming Bi-condensed and Bi-dilute regions. The characteristic feature of the structure is the existence of extra oxygens, giving  $x = 1.0$ , in the Bi-dilute region of the Bi-O layer. Bi has a distorted rocksalt-type oxygen coordination with four short Bi—O bonds in the Bi-condensed region and a deformed square pyramidal coordination with five Bi—O bonds in the Bi-dilute region. The apical oxygen of a  $\text{CuO}_4$  pyramid, which joins Cu to Bi, moves along with Bi, distorting the pyramid considerably.

# Fundamental-Struktur

RIETVELD ANALYSIS OF THE MODULATED STRUCTURE IN ...

TABLE I. The structural parameters of the fundamental structure.

Atom	Wyckoff position	$x$	$y$	$z$	$p$
Bi	8l	0.25	0.5	0.0528	1.0
Sr	8l	0.25	0.0	0.1409	1.0
Ca	4e	0.25	0.0	0.25	1.0
Cu	8l	0.25	0.5	0.1963	1.0
O(1)	8g	0.0	0.25	0.1963	1.0
O(2)	8g	0.5	0.25	0.1963	1.0
O(3)	8l	0.25	0.5	0.1170	1.0
O(4)	8l	0.25	0.0	0.0528	0.5
O(5)	8g	0.5	0.25	0.0528	0.5
O(6)	8g	0.0	0.25	0.0528	0.5

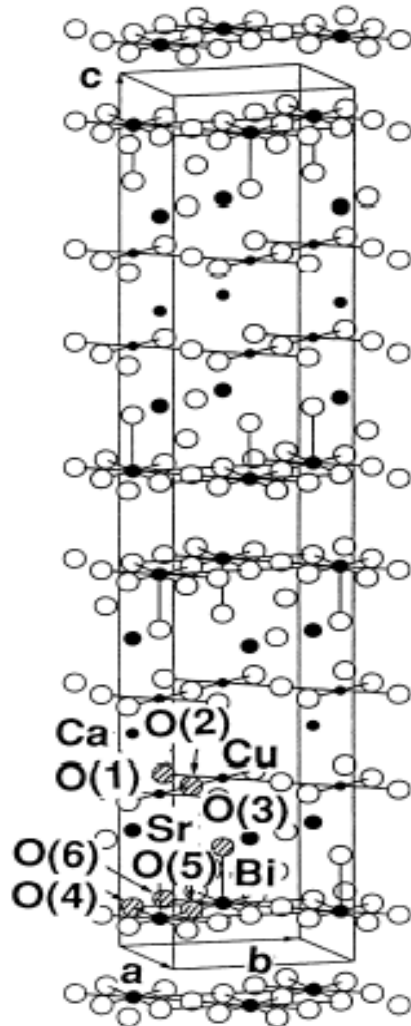


FIG. 1. The fundamental structure used in the refinement. In the Bi-O layer, the O(4)-O(6) sites are occupied with the occupation probability of  $\frac{1}{2}$ . Solid and open circles represent metal and oxygen atoms.

Modulation :

Atom bei  $\mathbf{R}=\mathbf{r}+\mathbf{T}$

Modulationsvektor  $\mathbf{k}=0.21\mathbf{b}^*$

Phase der Modulation  $t=\mathbf{R}^*\mathbf{k}$

Verschiebung :

Atom bei  $\mathbf{R}+\mathbf{u}$

mit

$$\mathbf{u}=\mathbf{u}_1\cos(2\pi t)+\mathbf{v}_1\sin(2\pi t)+\mathbf{u}_1\cos(2\pi t)+\mathbf{v}_1\sin(2\pi t)+\dots$$

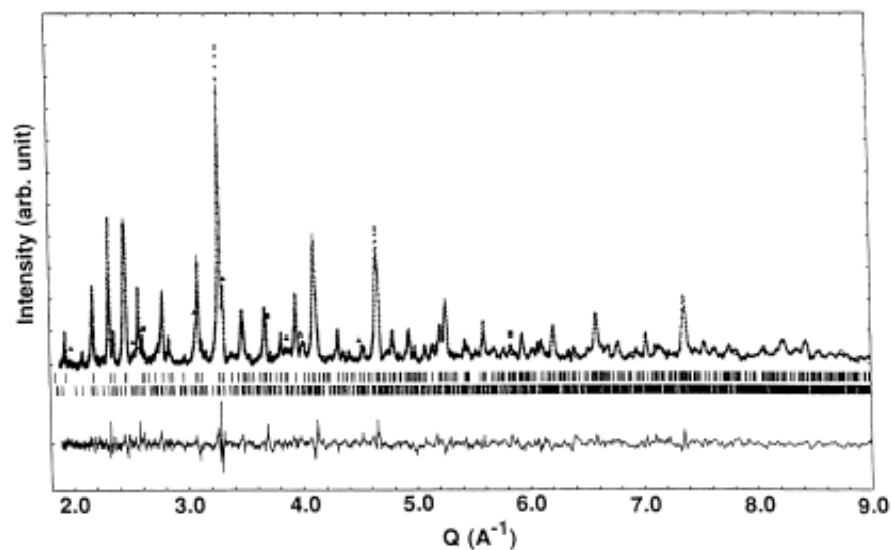


FIG. 2. Observed and calculated neutron-diffraction patterns for  $\text{Bi}_2(\text{Sr,Ca})_7\text{Cu}_2\text{O}_{8+x}$ . The background is subtracted. The lower solid line represents the difference between the observed and calculated intensities. The vertical bars below the diffraction pattern show the location of the main (upper) and satellite (lower) reflections. Small triangles and squares indicate the positions of strong reflections in  $\text{Ca}_2\text{CuO}_3$  and  $\text{CaO}$ , respectively. Peaks at corresponding positions in the difference pattern show the existence of a trace amount of such impurity phases.

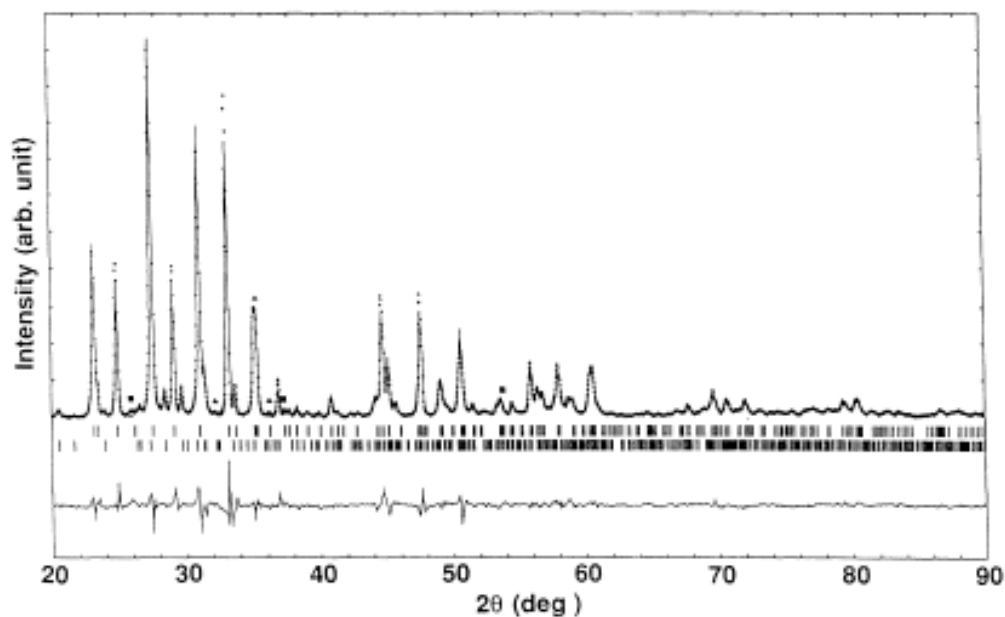


FIG. 3. Observed and calculated x-ray-diffraction patterns for  $\text{Bi}_2(\text{Sr,Ca})_7\text{Cu}_2\text{O}_{8+x}$ . The meanings of lines and symbols are the same as in Fig. 2. The contribution from  $\text{Ca}_2\text{CuO}_3$  and  $\text{CaO}$  to the intensity is also visible in the difference pattern.

TABLE IV. The structural parameters of the modulated structure. The third column (corresponding to  $l$  in the banding) represents the parameters for the average structure. The fourth and fifth columns are the amplitudes for the cosine and sine waves. The last three columns are the corresponding values by Gao *et al.* (Ref. 7). The values have been multiplied by  $10^3$  for positional parameters and  $10^4$  for thermal parameters ( $\text{\AA}^2$ ) and occupational ones. The standard deviations are in parentheses. [A common thermal parameter is assumed for O2S and O2N.]  $a$ ,  $b$ , and  $c$  occupation probabilities of Bi, Ca, and Sr. The standard deviations are estimated from the formula  $\sigma(x, y) = [A_{xy}^{-1} M_{xy}^{-1} N_{xy} - P_{xy}]^{1/2}$ , which the meaning of symbols are the same as that in Ref. 25.

Atom		Present work		Gao <i>et al.</i>		
		$l$	cos(2 $\pi x$ )	sin(2 $\pi x$ )	$l$	cos(2 $\pi x$ )
Bi	$x$	2173(14)	-180(15)	2333	-74	
	$y$	5000		5000		731
	$z$	500(1)	-32(2)	512	-61	
	$B$	152(17)				
	$P$	100	0	100		
Sr	$x$	2500(30)	1610(3)	2537	137	
	$y$	0		0		444
	$z$	140(2)	-91(2)	1408	-65	
	$B$	156(23)				
	$P$	10(18)	-49(21)	100		
a	$P$	15(18)	9(12)			
	$P$	15(18)	36(12)			
Ca	$x$	2500	142(97)	2500	0	
	$y$	0		0		
	$z$	2500	-99(3)	2500	0	
	$B$	16(81)				
	$P$	60(4)				
c	$P$	40(4)				
	$P$	40(4)				
O2	$x$	2477(29)	142(38)	2498	0	
	$y$	5000		5000		74
	$z$	1993(5)	-102(4)	1967	-91	
	$B$	42(21)				
	$P$	100		100		
O11	$x$	0		48(68)	0	
	$y$	2500		-200(77)	2500	
	$z$	1964(9)	-74(13)	1935		
	$B$	51(61)				
	$P$	100		100		
O21	$x$	5000		216(61)	5000	
	$y$	2500		173(69)	2500	
	$z$	1979(9)	-97(15)	2028		
	$B$	-20(54)				
	$P$	100		100		
O23	$x$	2121(60)	-545(92)	2000		
	$y$	5000		5000		
	$z$	1146(6)	-98(11)	1220		
	$B$	173(24)				
	$P$	100		100		
O44	$x$	1612(140)	156(197)	1500		
	$y$	0		0		
	$z$	917(39)	-103(45)	930		
	$B$	-119(72)				
	$P$	48(2)	-51(3)	100		
O45	$x$	5000		-1620(181)		
	$y$	2500		-512(164)		
	$z$	600(60)	-31(18)			
	$B$	670(169)				
	$P$	52(3)	52(3)	0		
O60	$x$	0		-1730(181)		
	$y$	2500		2107(210)		
	$z$	462(62)	261(92)			
	$B$	670(169)				
	$P$	52(3)	52(3)	0		

auch hier Symmetrie !

Super-space group

→ welche Koeffizienten  
können existieren

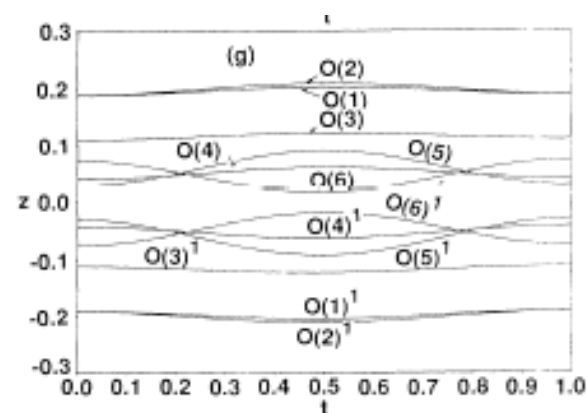
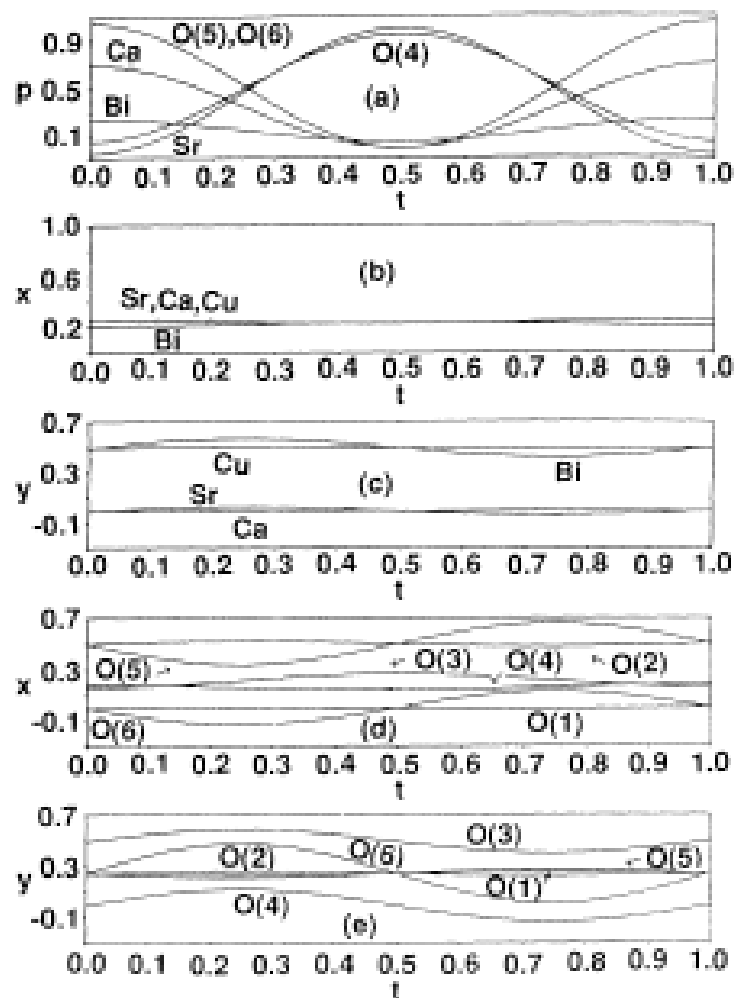


FIG. 4. Modulation waves of the occupational and displacive modulations. (a) The occupation probabilities of the metal atoms at the Sr site and of the O(4), O(5), and O(6) sites. (b) and (c) the  $x$  and  $y$  coordinates of metal atoms. (d) and (e)  $x$  and  $y$  coordinates of oxygen atoms. (f) and (g) the  $z$  coordinates of metal and oxygen atoms.  $M^1$  or  $O(i)^1$  means the atom obtained from metal  $M$  or oxygen  $O(i)$  by the symmetry operation  $-x, y, -z$ .



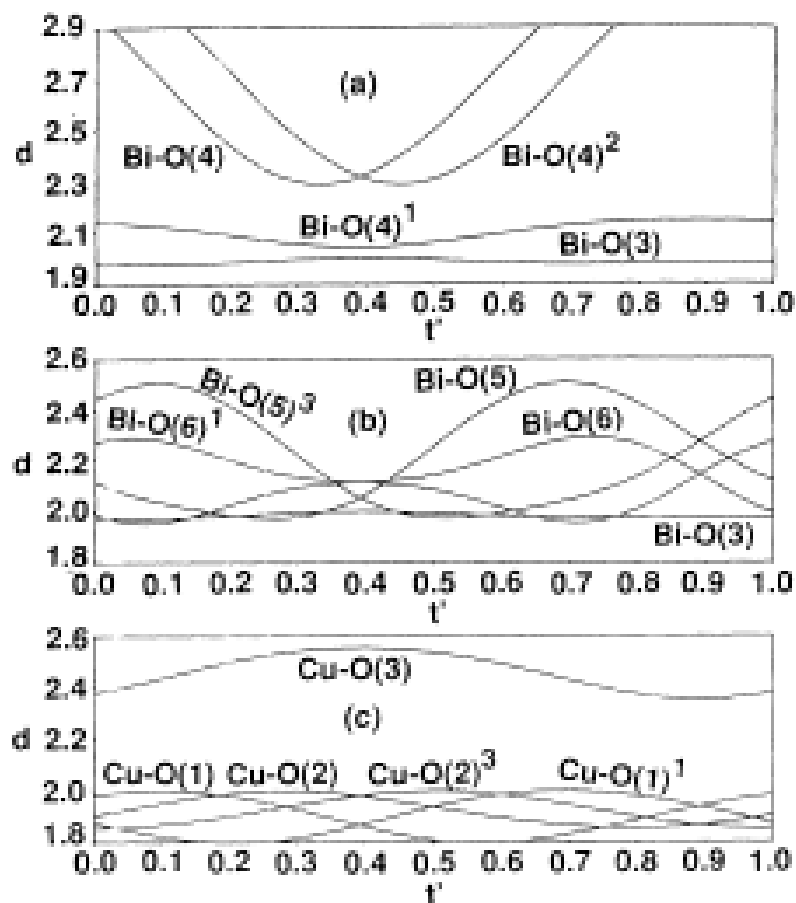


FIG. 5. Metal—oxygen distances (in Å) as a function of  $t' = t - \mathbf{k} \cdot \mathbf{X}$ . (a) Bi—O(3,4); (b) Bi—O(3,5,6); (c) Cu—O; (d) Sr—O to the oxygens in the Bi—O layer; (e) Sr—O to the oxygens in the Sr—O and Cu—O layers; (f) Ca—O.  $O(i)'$  means the atom obtained from  $O(i)$  by the  $j$ th symmetry operation shown below.

1:	$-x, y + \frac{1}{2}, z;$	2:	$x, y + 1, z;$	3:	$-x + 1, y + \frac{1}{2}, z;$
4:	$-x + 1, y - \frac{1}{2}, z;$	5:	$-x, y - \frac{1}{2}, z;$	6:	$x, y - 1, z;$
7:	$-x + \frac{1}{2}, y, -z + \frac{1}{2};$	8:	$x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2};$		
9:	$x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2};$				

# REMOS & PREMOS

<sup>15</sup>A. Yamamoto, A. Computer Program for the Refinement of Modulated Structures REMOS 82.0, National Institute for Research in Inorganic Materials (1982) (unpublished); A. Yamamoto, *Acta Crystallogr. Sec. A* **38**, 87 (1982).

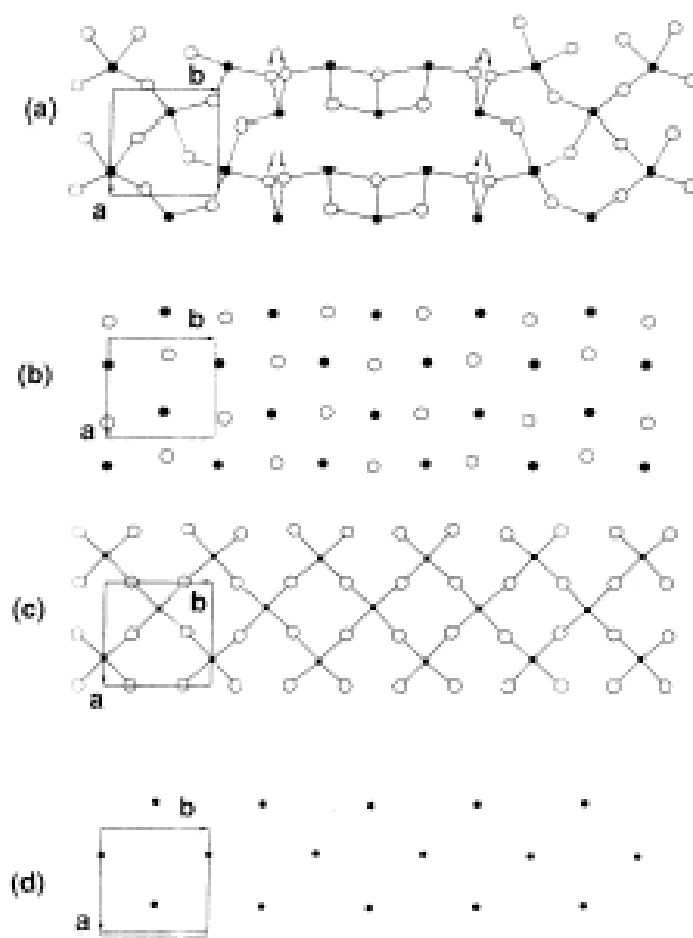


FIG. 7. The projection of metal and metal-oxygen layers normal to the  $c$  axis. (a) The Bi-O layer at  $z \approx 0.06$ ; (b) the Sr-O layer at  $z \approx 0.14$ ; (c) the Cu-O layer at  $z \approx 0.2$ ; (d) the Ca layer at  $z \approx \frac{1}{4}$ . Solid and open circles represent metal and oxygen atoms. The Cu-O bonds shorter than  $2.5 \text{ \AA}$  and the Bi-O bonds shorter than  $2.7 \text{ \AA}$  are plotted. The oxygen atoms in the Bi-O layer have the occupational modulation, so that the oxygens with the occupation probability greater than 0.4 are drawn. The arrows show that the statistically occupied two positions with the occupation probability near  $\frac{1}{2}$ . The figure shows that there are four Bi-O bonds for each Bi within the plane of the Bi-dilute region while three bonds exist in the Bi-condensed region.

auch JANA

## B. Ladungsordnungsphänomene

**Wie beobachtet man Ladungsordnung?**

**Neutronen :  $\text{Cu}^{2+}$  und  $\text{Cu}^{3+}$  haben gleiche Streulänge**



**- Röntgen : unterschiedliche Ladung variiert Wechselwirkung  
aber Effekt zu schwach und Ladung nicht so lokal !!!**



**- Elektronen : analog**



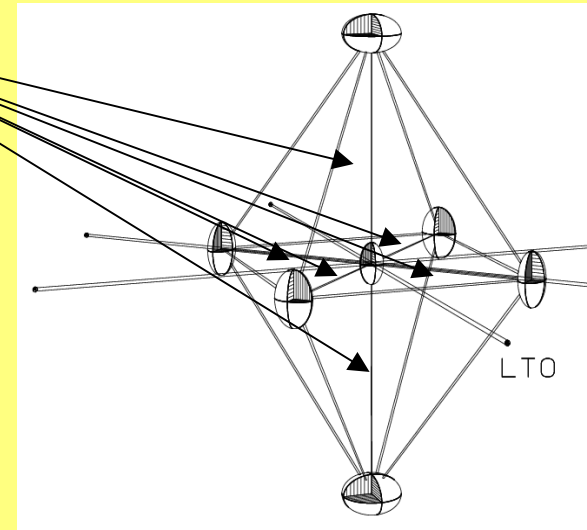
# Wie beobachtet man trotzdem Ladungsordnung?

## Bindungslängen – Bindungsstärken – Beziehungen

$$s_i = \exp\left(\frac{R_0 - R_i}{B}\right)$$

$$\text{Valence} = \sum_i s_i$$

Zachariasen (1978);  
Brown & Altermatt (1985).  
Tabellierung von  $R_0$  und  $B$



Neutronen : sehen den Sauerstoff am besten



# historisches Beispiel Magnetit $\text{Fe}_3\text{O}_4$

-Spinel  $\text{Fe}_3\text{O}_4$  sollte man auffassen  $\text{Fe}^{3+}[\text{Fe}^{2.5}]_2\text{O}_4$

A-Plätze tetrahedrisch

B-Plätze oktahedrisch

Verwey : bei 122K Ordnung auf dem B-Platz

Spinel : kubisch  $\sim 8\text{\AA}$   $\rightarrow$  monoklin

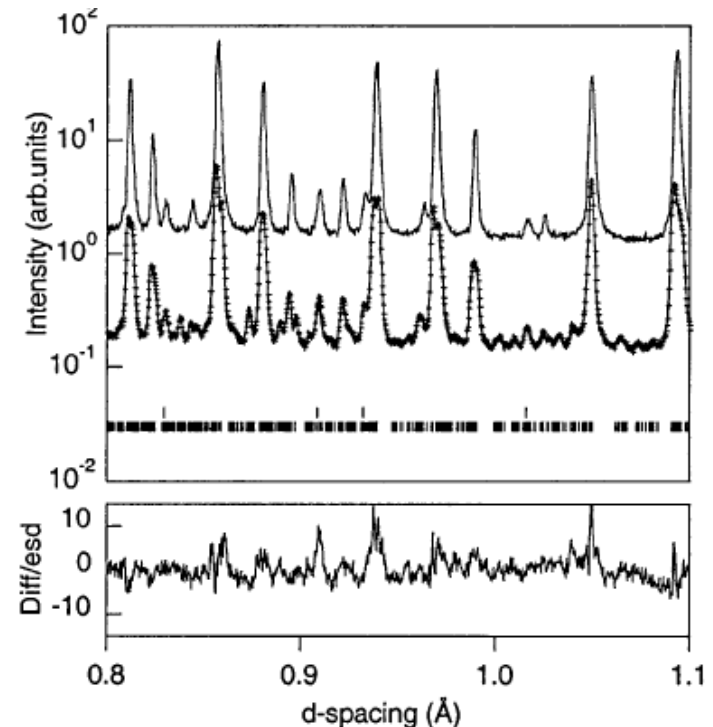
versch. Untersuchungen :

Überstrukturen

$$a_m = -(a_c + b_c),$$

$$b_m = (a_c - b_c),$$

$$c_m = 2c_c.$$



## Long Range Charge Ordering in Magnetite Below the Verwey Transition

J.P. Wright,<sup>1,\*</sup> J.P. Attfield,<sup>1,†</sup> and P.G. Radaelli<sup>2</sup>

TABLE I. Results for the distinct tetrahedral ( $A1, A2$ ) and octahedral ( $B1-B4$ ) Fe sites in the refined structure of  $\text{Fe}_3\text{O}_4$  at 90 K; individual and mean distances to the coordinating oxygens (O1–O6), bond valence sums (BVS), and the renormalized valences  $V$ .

Fe site	–O bonds	$d(\text{Fe-O})/\text{\AA}$	$\langle d(\text{Fe-O}) \rangle/\text{\AA}$	BVS	$V$
A1	–O1	1.898(4)	1.886(3)	2.80	3.00
	–O5	1.882(2)			
	–O5	1.875(2)			
	–O2	1.890(4)			
A2	–O4	1.913(5)	1.890(4)	2.77	3.00
	–O6	1.877(2)			
	–O6	1.870(2)			
	–O3	1.899(5)			
B1	–O1 ( $\times 2$ )	2.042(3)	2.072(3)	2.50	2.39
	–O2 ( $\times 2$ )	2.082(3)			
	–O6 ( $\times 2$ )	2.091(3)			
B2	–O3 ( $\times 2$ )	2.038(4)	2.043(3)	2.73	2.61
	–O4 ( $\times 2$ )	2.040(3)			
	–O5 ( $\times 2$ )	2.052(3)			
B3	–O2	1.964(5)	2.050(4)	2.71	2.59
	–O3	2.116(5)			
	–O5	2.092(3)			
	–O5	2.091(3)			
	–O6	2.019(3)			
	–O6	2.018(3)			
B4	–O1	2.033(5)	2.069(4)	2.52	2.41
	–O4	2.086(5)			
	–O5	2.094(3)			
	–O5	2.093(3)			
	–O6	2.054(3)			
	–O6	2.053(3)			

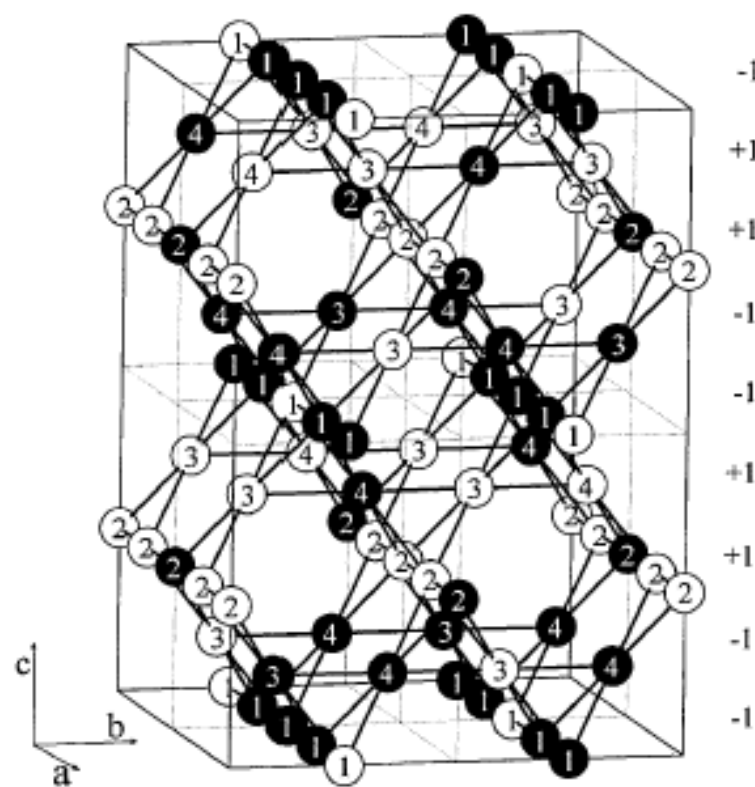


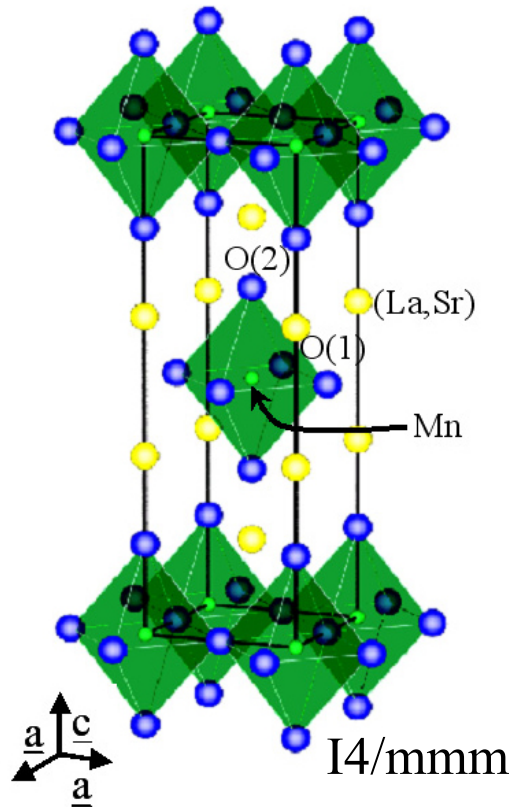
FIG. 2. A model for charge ordering on the  $B$  sites in the  $\sqrt{2}a \times \sqrt{2}a \times 2a$   $Cc$  supercell of magnetite that is consistent with the class II solutions from our refinement. The  $B$  sites are numbered as in Table I. Dark/light circles correspond to  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . The charge per four  $B$  sites relative to the average value of +10 is shown for each layer; these define a [001] charge density wave.

# Magnetit $\text{Fe}_3\text{O}_4$

- Warum nur so wenig Modulation der Ladungen?
- Ist Symmetrie überhaupt richtig?  
Verfeinerung wurde nicht in monokliner Raumgruppe durchgeführt und ein Teil der Überstrukturen kann nicht beschrieben werden!!!

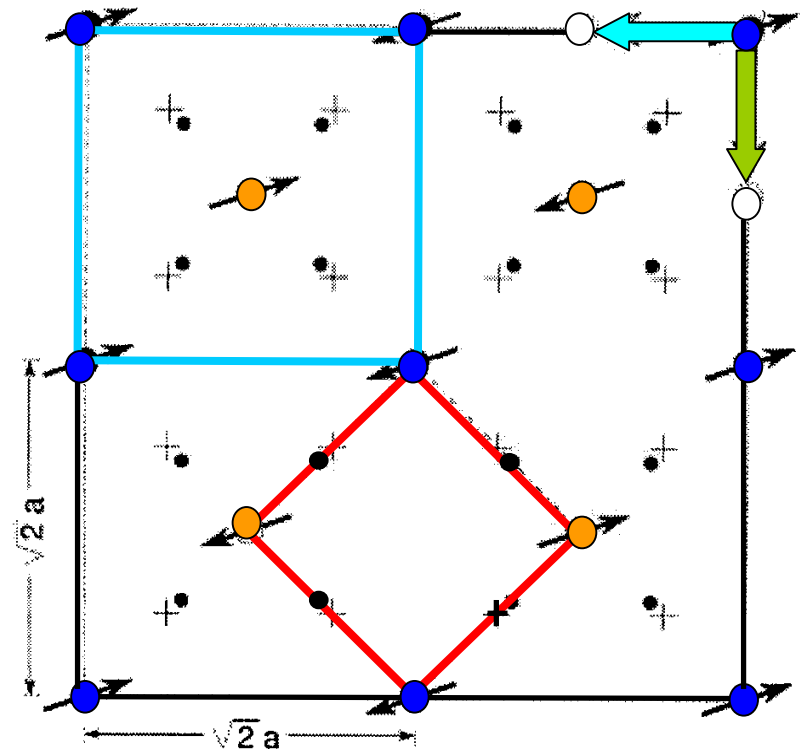
**Pulverdiffraktion sicher nicht ausreichend ! ! !**

# Schicht-Manganate ( $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ )

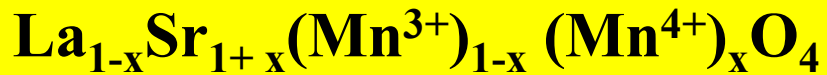


B.J. Sternlieb *et al.* PRL76(1996)2169

- $\text{Mn}^{+4}$
- $\text{Mn}^{+3}$
- c.o. oxygen position
- + I4/mmm oxygen position
- majority c/2 stacking vector
- minority c/2 stacking vector
- I4/mmm cell
- c.o. cell
- magnetic cell



**Valenz der Mangan-Ionen:**

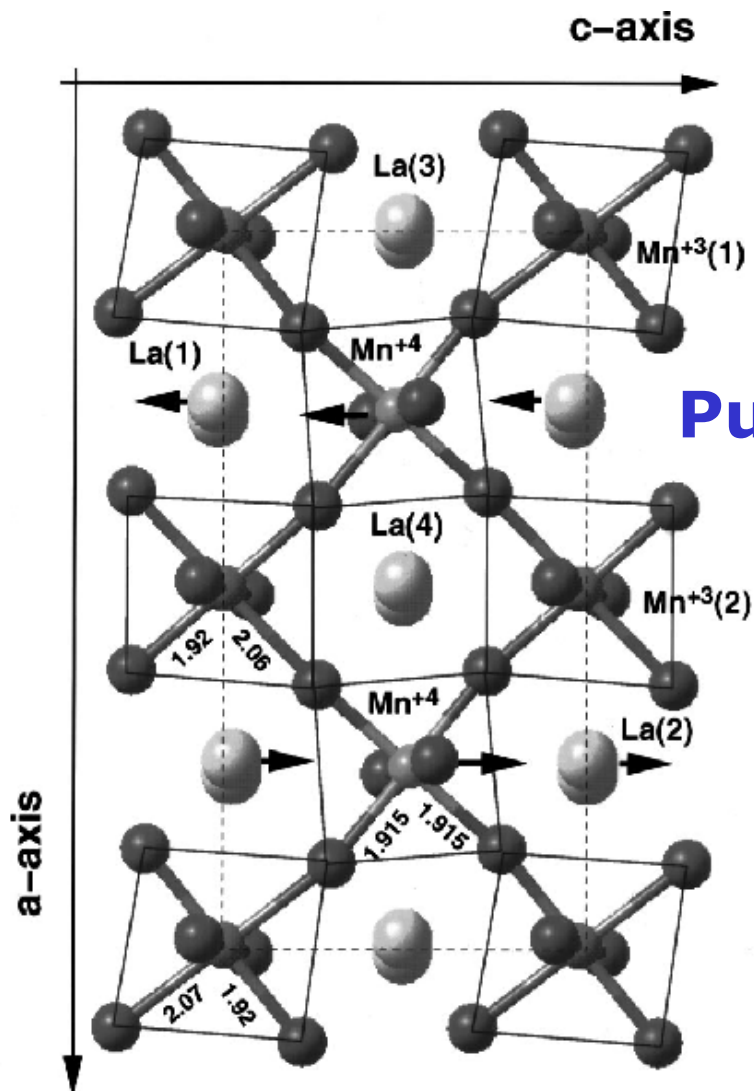


↪ Einführung von Löchern

↪  $x=0.5 \rightarrow 1:1$ -Mischung



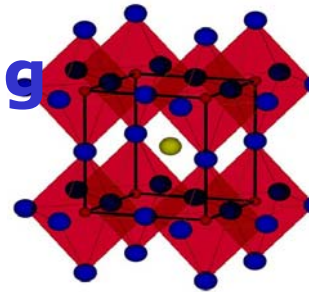
# Kubische Manganate ( $\text{SE}_{1-x}\text{EA}_x\text{MnO}_3$ )



$\text{LaMnO}_3$  nur  $\text{Mn}^{3+}$   
 Ersetzen :  $\text{La}^{3+}$  durch  $\text{Ca}^{2+}$  : Löcher  
 $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  :  
 $\text{Mn}^{3.5+} \rightarrow \text{Mn}^{3+}$  und  $\text{Mn}^{4+}$

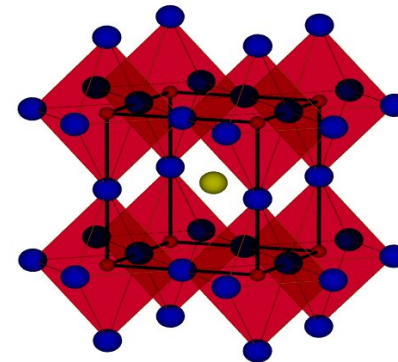
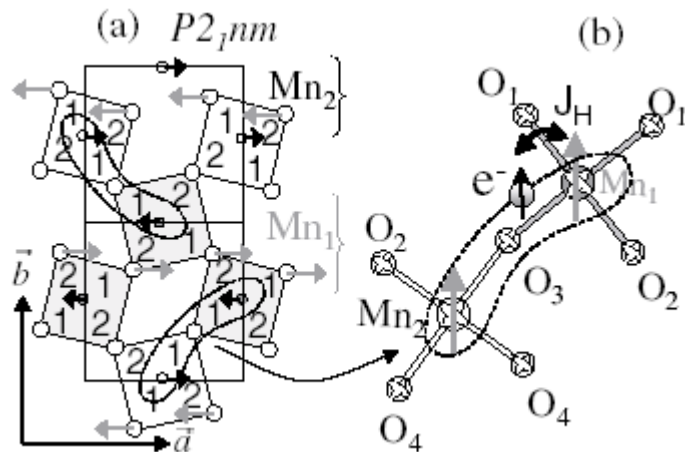
## Pulverneutronenbeugung

P. Radaelli *et al.*, PRB55(1997)3015



-Verdopplung der Pbnm-Zelle  
 monoklin  $\text{P}112_1/\text{m}$   
 -Bond-Valence-Sum-Analyse  
 $\rightarrow$  wenig Unterschied  
 (man erwartet 0.1 Å  
 Aufspaltung im MnO-Abstand)

# Kubisches Manganat ( $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ )



## Einkristallneutronenbeugung

Daoud-Aladine *et al.*, PRL89(2002)97205

TABLE I. Octahedral distortions in  $\text{Pr}_{0.60}\text{Ca}_{0.40}\text{MnO}_3$ .  $\Delta = \frac{1}{6} \sum_{i=1}^6 \left| \frac{d_{\text{MnO}_i} - \langle d_{\text{MnO}} \rangle}{\langle d_{\text{MnO}} \rangle} \right|^2$  measure the octahedral distortion. The bond valence sums (BVS), uses the  $\text{Mn}^{3+} d_0$  parameter for all sites (see Ref. [16] for definitions).

$T = 280 \text{ K}$	$T = 195 \text{ K}$	$T = 195 \text{ K}$
Mn site	Mn <sub>1</sub> site	Mn <sub>2</sub> site
Mn-O <sub>ap</sub> : 1.953(1)(×2)	Mn <sub>1</sub> -O <sub>1</sub> ' : 1.951(3)	Mn <sub>2</sub> -O <sub>3</sub> ' : 1.957(3)
Mn-O <sub>eq</sub> : 1.967(2)(×2)	Mn <sub>1</sub> -O <sub>2</sub> ' : 1.942(3)	Mn <sub>2</sub> -O <sub>4</sub> ' : 1.940(3)
Mn-O <sub>eq</sub> : 1.953(1)(×2)	Mn <sub>1</sub> -O <sub>1</sub> : 1.879(2)	Mn <sub>2</sub> -O <sub>4</sub> : 1.899(2)
	Mn <sub>1</sub> -O <sub>1</sub> : 2.053(2)	Mn <sub>2</sub> -O <sub>4</sub> : 2.028(2)
	Mn <sub>1</sub> -O <sub>3</sub> : 1.980(2)	Mn <sub>2</sub> -O <sub>3</sub> : 2.011(2)
	Mn <sub>1</sub> -O <sub>2</sub>	Mn <sub>2</sub> -O <sub>2</sub> : 1.899(2)
$d_{\text{Mn-O}} = 1.957(1) \text{ \AA}$	$d_{\text{Mn-O}} = 1.960(1) \text{ \AA}$	$d_{\text{Mn-O}} = 1.955(1) \text{ \AA}$
BVS = 3.52	BVS = 3.53(1)	BVS = 3.50(1)
$\Delta(\times 10^{-4}) = 0.12$	$\Delta(\times 10^{-4}) = 0.99$	$\Delta(\times 10^{-4}) = 0.506$

- Raumgruppe war falsch
- **P11m oder P2<sub>1</sub>nm**
- Bond-Valence-Sum :
- fast kein Unterschied