SSPD'03 Conference

September 14-19 (2003), Stara Lesna, Slovakia

Solution of Ge containing zeolites by applying direct methods to powder data

by Jordi Rius

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synchrotron radiation

inorganic structures

whole profile fitting

FIPS (Estermann et al.)

refinement function

systematic overlap (Rius, Miravitlles, Gies, Amigó)

accidental overlap

Integrated intensities

Refinement of phases

Structure completion

dominant scatterer:

automated ΔF recycling

lighter ligand atoms not required

weak dominant scatterers:

fragment / atom ΔF recycling

lighter ligand atoms required

FOCUS (Grosse-Kunstleve et al.)

The true structure

$$\rho(x) \leftrightarrow \mathbf{E}_H = (E_H , \varphi_H)$$

$$\mathbf{E}_H = 1/N^{1/2} \Sigma_j \exp i2\pi H x_j$$

$$= E_H \exp i\varphi_H$$

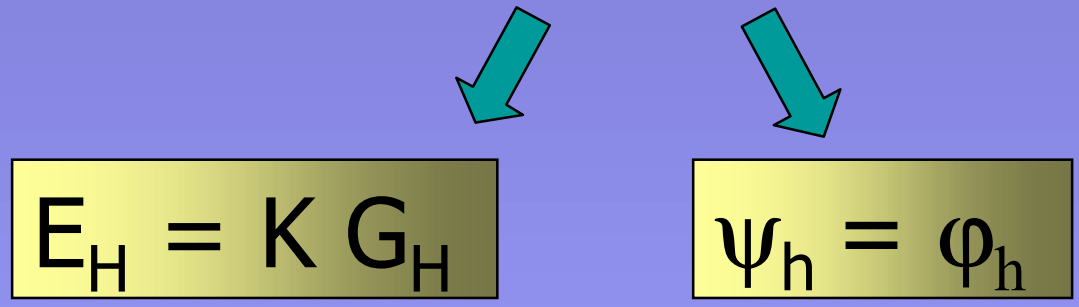
$$\Phi = \{\dots , \varphi_h, \dots\}$$

Corrections
L,P,k
f_o,B,ε_H
<E>=1

$$E_H^2 = 1 + (1/N) \Sigma_j \Sigma_k \cos 2\pi H(x_j - x_k) \quad j \neq k$$

The squared structure

$$\rho(x)^2 \leftrightarrow \mathbf{G}_H = (G_H , \psi_H)$$



$$\mathbf{G}_H(\Phi) = \Sigma_{h'} E_{h'} E_{H-h'} \exp i(\varphi_{h'} + \varphi_{H-h'})$$

E_H in terms of the interatomic vectors

$$E_H \approx 1 + K_H \Sigma_j \Sigma_k \cos 2\pi H(x_j - x_k) \qquad j \neq k$$

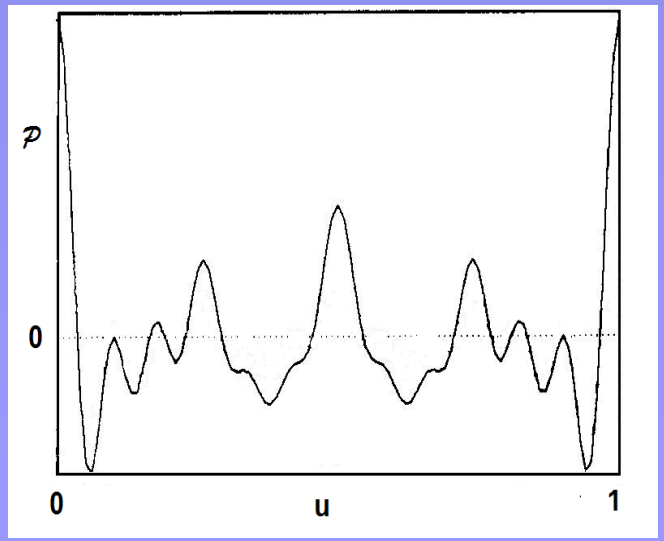
$$\uparrow$$

$$\langle E_H \rangle$$

Modulus and origin syntheses:

$$P(u) = (1/V) \Sigma_H E_H \cos 2\pi Hu$$

$$U(u) = (1/V) \Sigma_H \langle E \rangle \cos 2\pi Hu$$



E_H in terms of the phases F

$$E_H(\Phi) = K \cdot \{ \exp i\psi_{-H} \cdot \mathbf{G}_H(\Phi) \}$$

$$= K \cdot \Sigma_{h'} E_{h'} E_{H-h'} \cos(\psi_{-H}+\varphi_{h'}+\varphi_{H-h'})$$

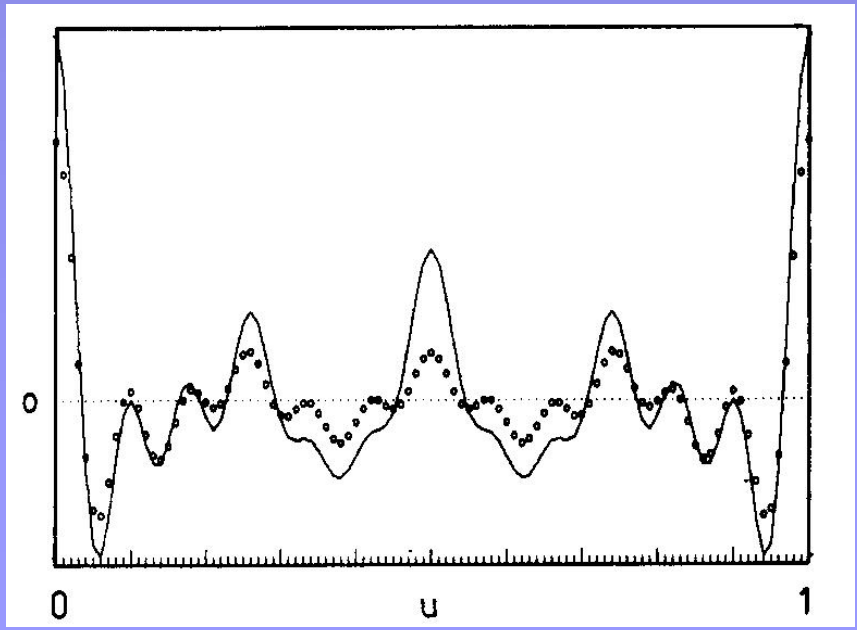
Calculated modulus synthesis:

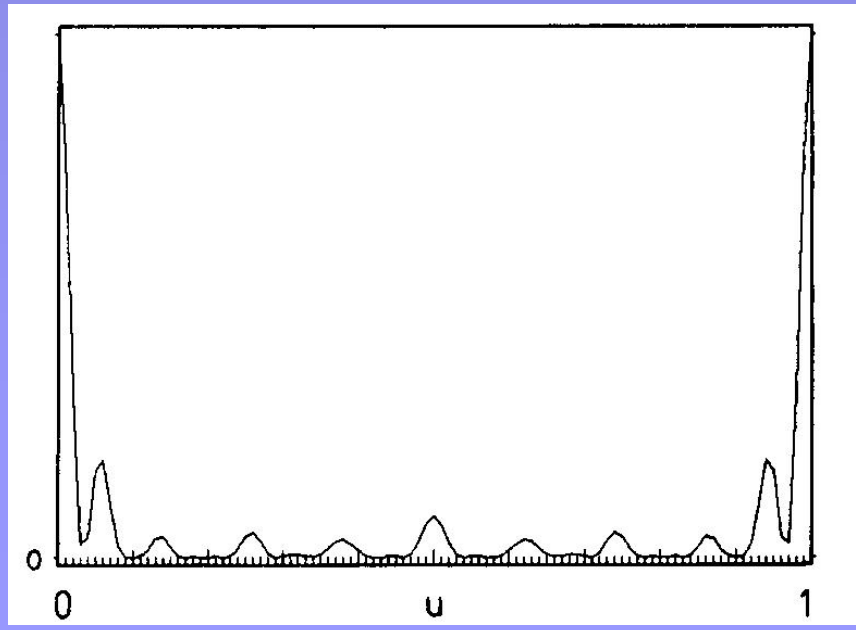
$$P(u,\Phi) = (1/V) \Sigma_H E_H(\Phi) \cos 2\pi Hu$$

The modulus sum function

$$Z(\Phi) = V^2 \int_V P(u)\, P(u,\Phi)\, du = \max!$$

$$Z(\Phi) = K \Sigma_H E_H E_H(\Phi) = \max!$$





The modulus sum function

$$Z(\Phi) = K \Sigma_H E_H \Sigma_{h'} E_{h'} E_{H-h'} \cos(\psi_{-H} + \varphi_{h'} + \varphi_{H-h'})$$

- Only the large E's are significant.

- For the large reflections h it holds $\psi = \varphi$

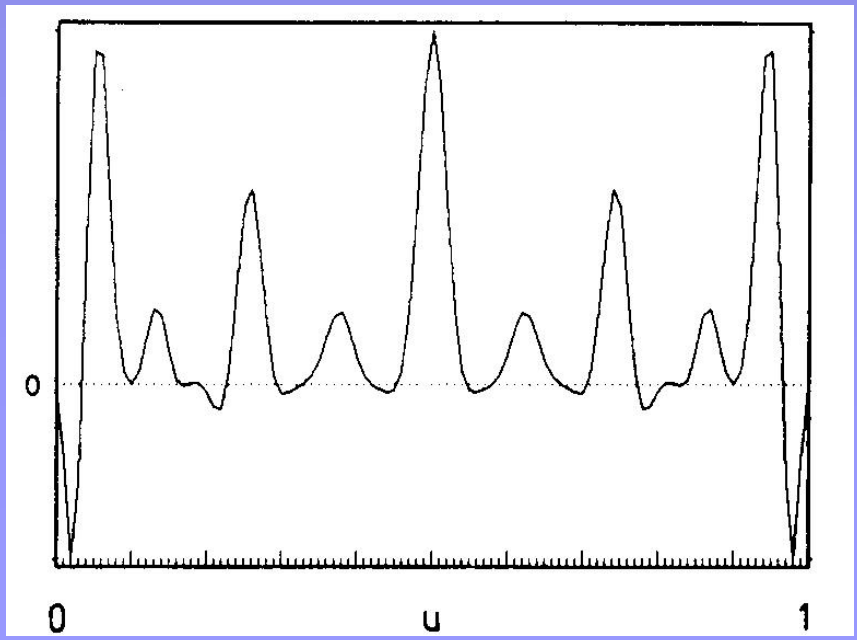
- Phase refinement with Z often leads to overconsistent triplets, i.e. for most triplets

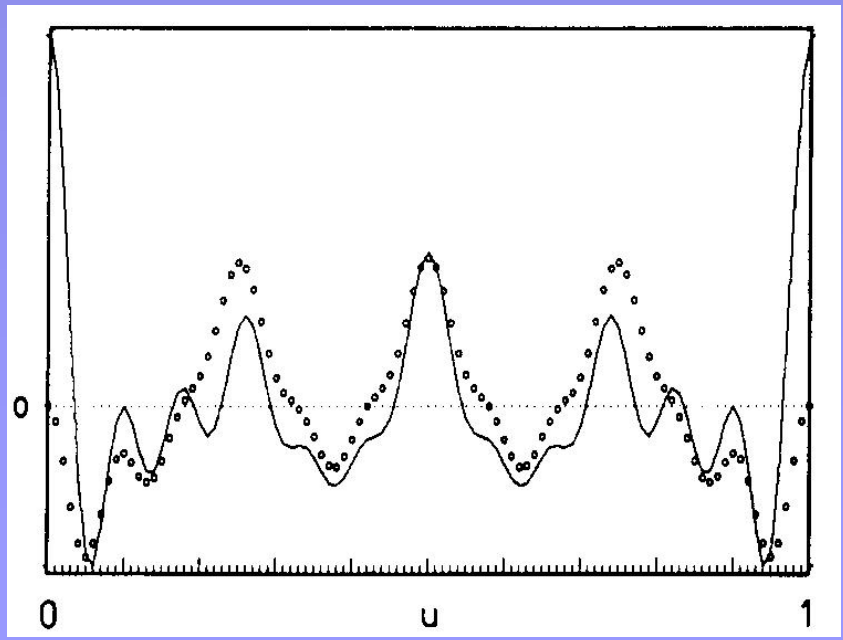
$$\varphi_{-h} + \varphi_{h'} + \varphi_{h-h'} \approx 0^o$$ (U atom solution)

The constrained modulus sum function

$$S(\Phi) = Z(\Phi) - V^2 \int_V U(u)\, U(u,\Phi)\, du = \max!$$

$$S(\Phi) = K \Sigma_H (E_H - \langle E \rangle) E_H(\Phi) = \max!$$





Computation of S(F)

$$S(\Phi) = K \Sigma_{\mathbf{h}} \Sigma_{h'} E_{-h} E_{h'} E_{h-h'}$$

$$\times [3 - \langle E \rangle (1/E_{-h} + 1/E_{h'} + 1/E_{h-h'})] /3$$

$$\times \cos(\varphi_{-h} + \varphi_{h'} + \varphi_{h-h'})$$

$$+ K \Sigma_{\mathbf{l}} \Sigma_{h} (E_{l} - \langle E \rangle) E_{-h} E_{h-l}$$

$$\times \cos(\psi_{l} + \varphi_{-h} + \varphi_{h-l}) = \max!$$

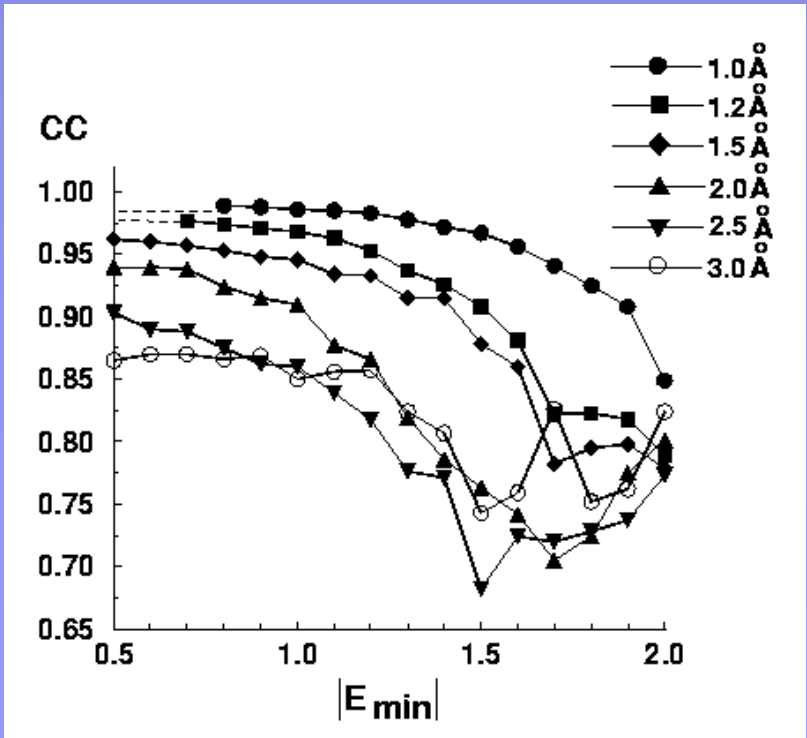
function of Φ_{old}

$E_h \leftrightarrow E_h(F) \cos(\gamma_h - j_h)$ The control parameters of S(Φ)

E_{lim} = minimum large E(h) (1.45-1.25)

d_{min} = minimum d value <=> atom types

E_{ratio} = N_l/N_h fixes the number of weak E(l)



J.Rius, X.Torrelles, C.Miravitlles, J.M.Amigó, MM.Reventós Acta Cryst. (2002) A58 21-26.

Positive triplets

$$Z(\Phi) = K \, \Sigma_H \, \Sigma_{h'} \, E_H \, E_{h'} \, E_{H-h'} \cos(\psi_{-H} + \varphi_{h'} + \varphi_{H-h'})$$

Positive and negative quartets

$$Q(\Phi) = 2/N \, \Sigma_H \, \Sigma_K \, \Sigma_L \, E_H E_K E_L E_{H-K-L}$$

$$x \, (E_{-H+K}^2 + E_{-H+L}^2 + E_{K+L}^2 - 3)$$

$$x \cos(\varphi_{-H} + \varphi_K + \varphi_L + \varphi_{H-K-L}) = \max!$$

Schenk (1974); Hauptman (1974); Giacovazzo (1976)

$$\int_V P'(u) \, P(u,\Phi) \, du$$

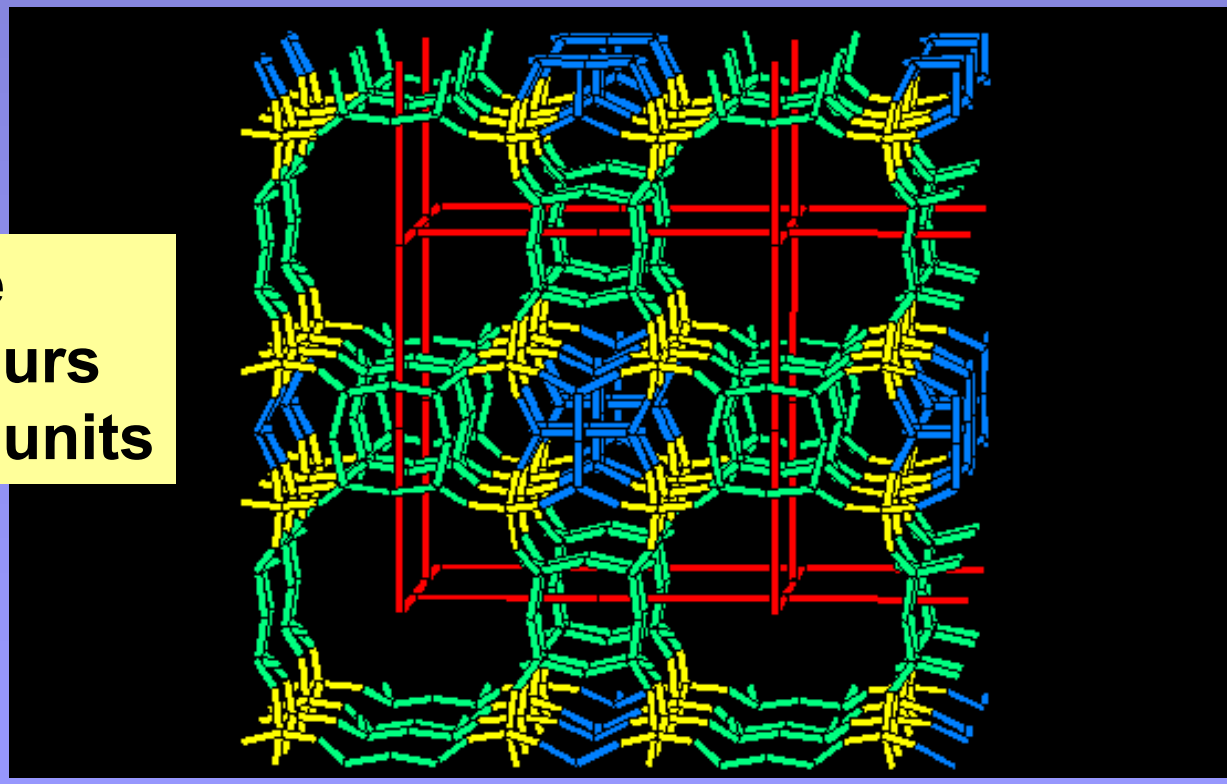
Rius et al. (1997)

$$\int_V P'(u) \, P(u,\Phi) \, du$$

Rius (1993)

Framework Isomorphous Substitution as a Structure-Directing Mechanism

F and Ge in the synthesis gel favours formation of D4MR units



Polymorph C of beta (ITQ17)

Basic building unit of D4MR family

ITQ-17: a + a

BEC

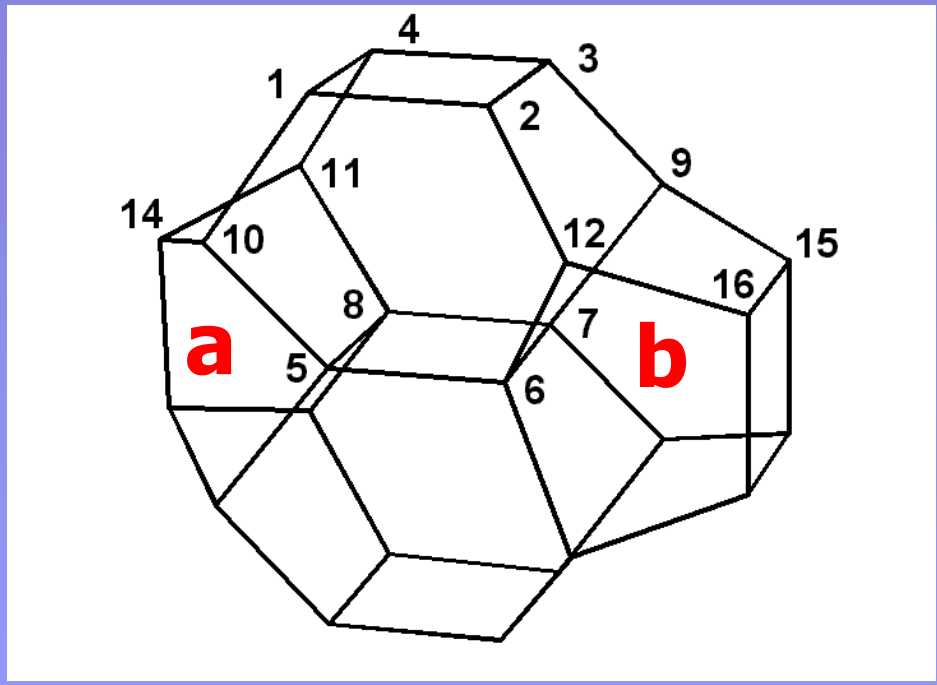
ITQ-7: a + a

ISV

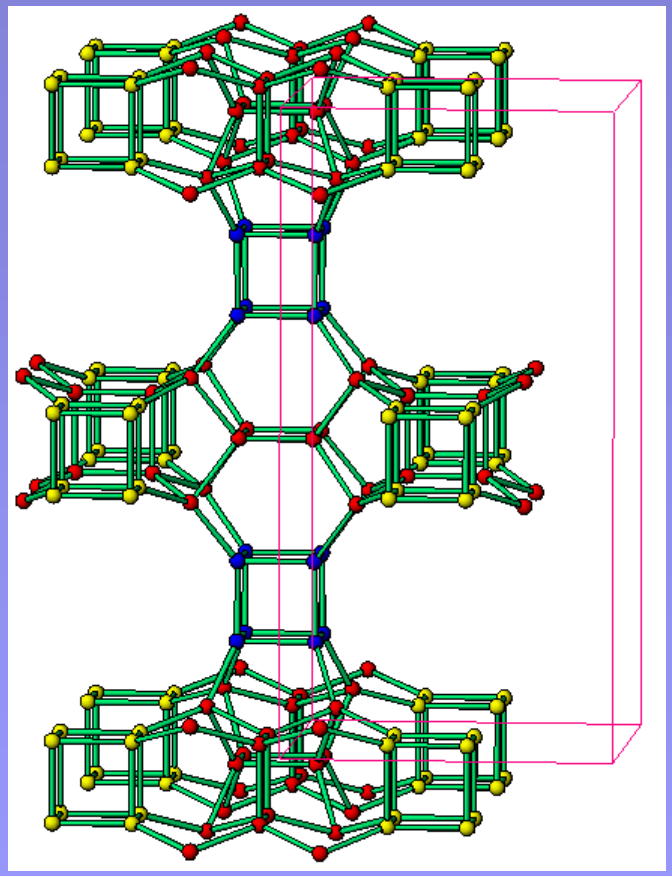
ITQ-22: a + b

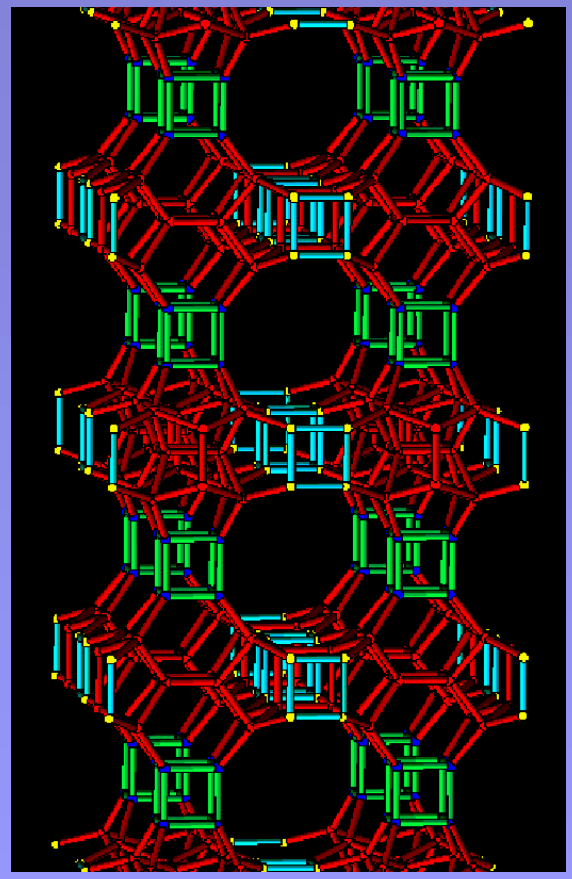
IWW

ITQ-24: b + b



Basic building unit of ITQ-7





L.Villaescusa, P.Barrett, M. Camblor

Angew. Chem. Int. Ed. 1999, 38, 1997-2000

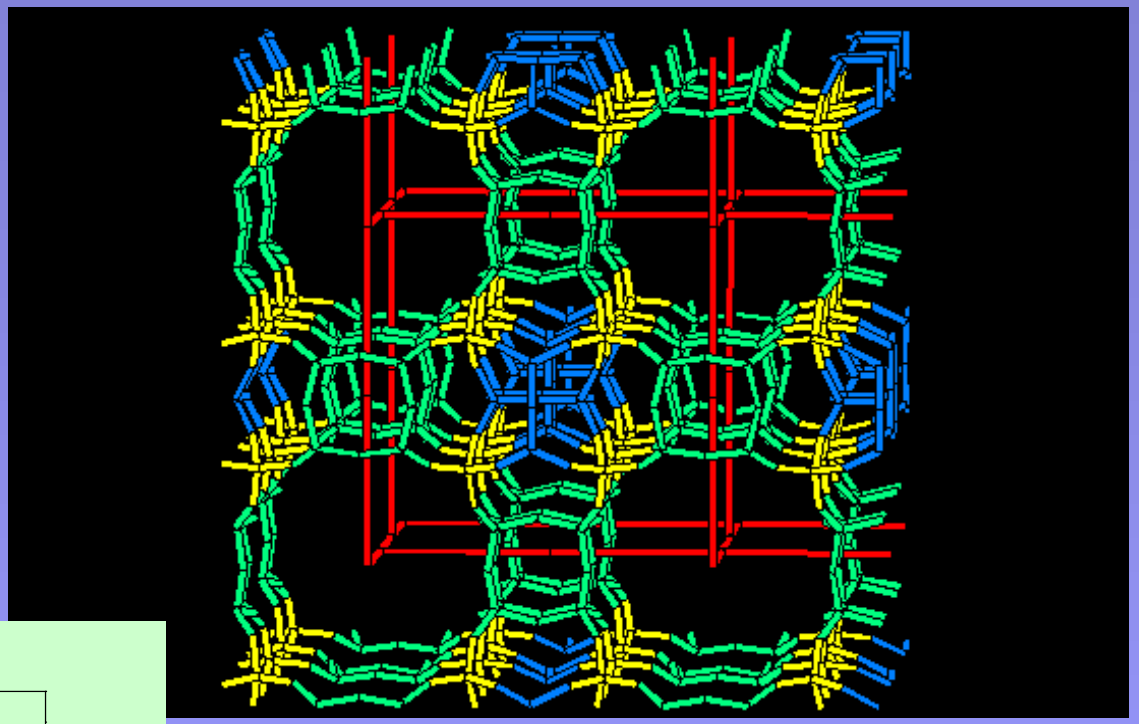
Ge distribution over the T sites in ITQ-17

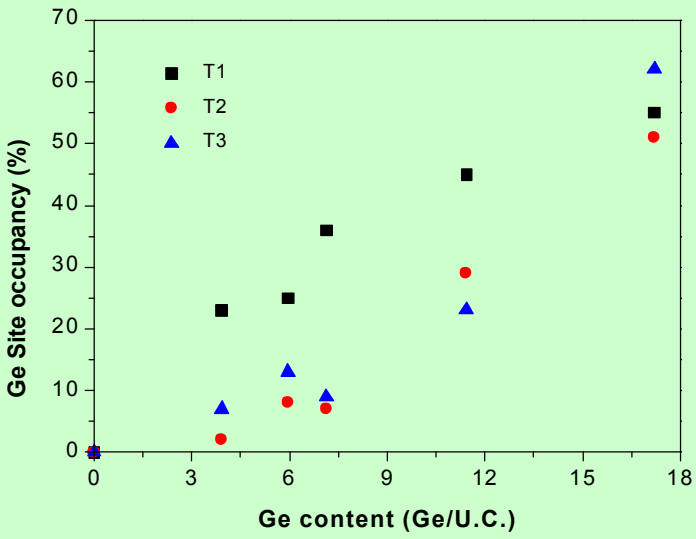
Si:Ge = 1.8

T1: 0.46 Ge

T2: 0.28 Ge

T3: 0.23 Ge





A.Corma, M.Navarro, F.Rey, J.Rius, S.Valencia *Angew. Chem. Int. Ed.* 2001, 40, 2277-2280

CSIC

ITQ22- Preliminary Data

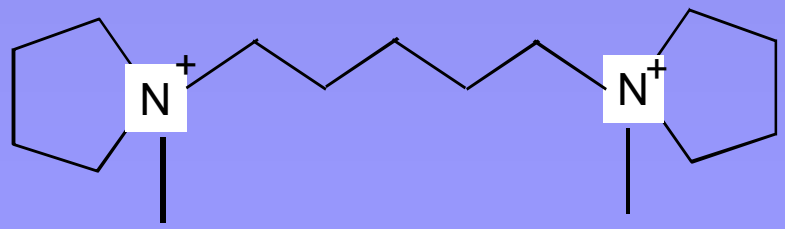
Crystal data:

a= 42.14424 Å
b= 12.99000 Å
c= 12.68428 Å
orthorhombic
V= 6944.1 Å3
Space group: Pbam (55)
r (a.s.) = 2.22 g/cm3
r (calcined) = 1.87 g/cm3

Composition:

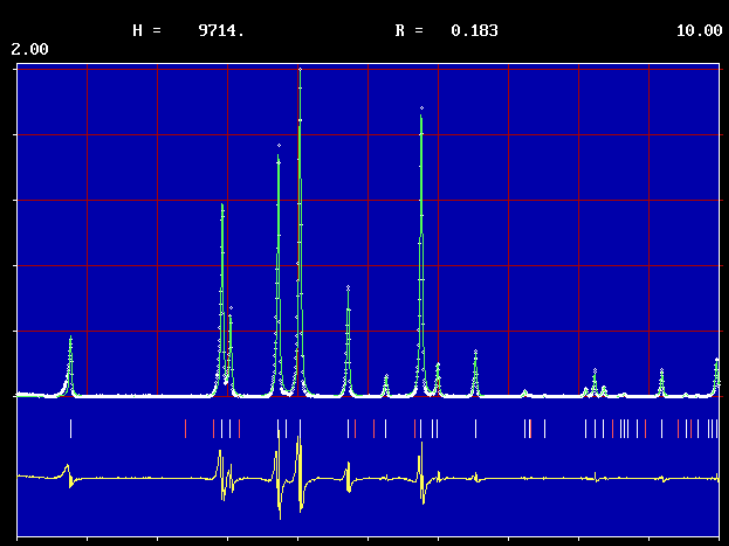
10.35359% C
1.84144% H
1.4816% N
Si/Ge=3.25
wt. loss 15.58%

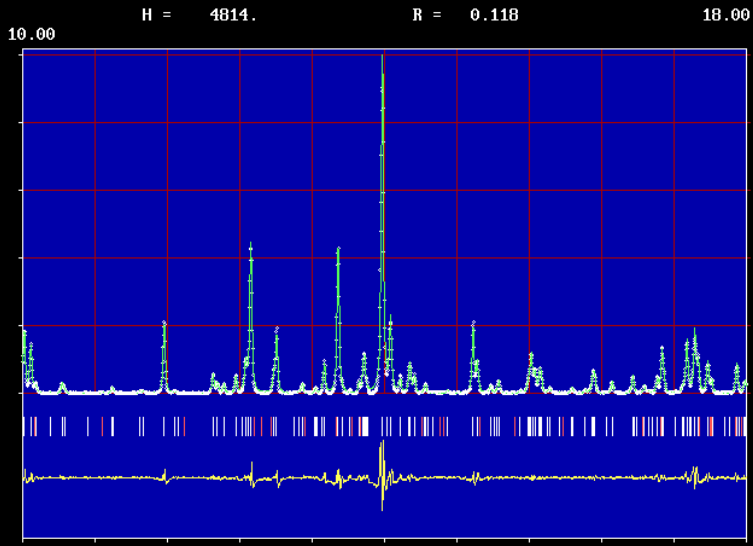
110.8 TO2/unit cell
4.9 template /unit cell

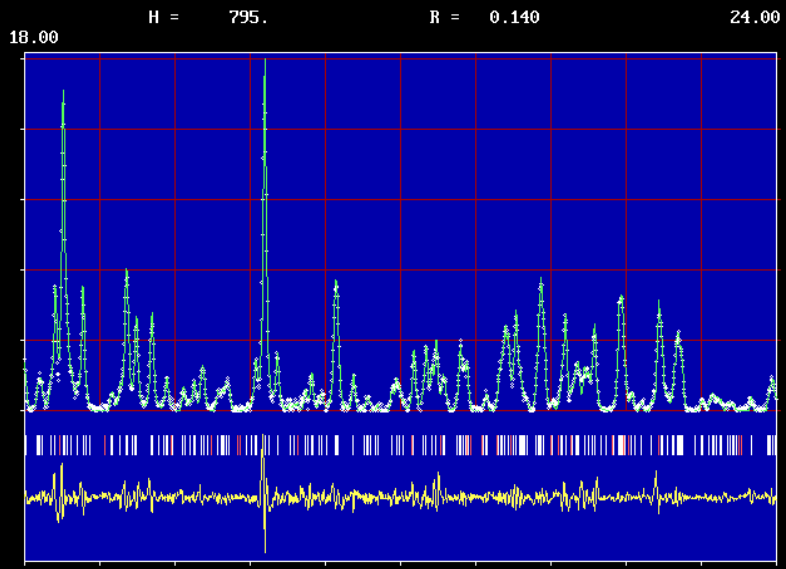


1,5-bis(metilpirrolidinium)-pentane $[C_{15}H_{32}N_2]^{2+}$

Whole-pattern fit without structure model of ITQ22







Line DW22 at LURE

l = 0.9611 Å

(Ø =1 mm)

Summary of intensity extraction

Method:

1. Whole pattern profile fitting by fixed point iteration → profile parameters
2. Intensity extraction by L.S. profile fitting of regions → intensities + e.s.d.'s

363 intensities for d ≥ 2.24Å

from which 49 overlapped within 2.58 - 2.24Å

ITQ22: Summary of direct methods (1)

N.shell	d_{inf}	$\Sigma F_c^2/\Sigma F^2$	N. ref	$\langle F^2 \rangle$
1	3.83	1.03	225	15285
2	3.04	1.00	217	8986
3	2.66	1.08	247	5801
4	2.41	0.72	164	6446
5	2.24	1.25	153	2829

Wilson plot

SK=0.68 B= 14 Å^2 $\langle |E^2-1| \rangle$=0.95 **(0.97)**

ITQ22: Summary of direct methods (2)

Control parameters:

Elim = 1.46

Eratio = 0.85

dmin= 2.24Å

solved in Pba2

47 large E's (3.37-1.46)

40 small E's (0.02-0.13)

$\langle E \rangle_{large+small}$ = 1.19

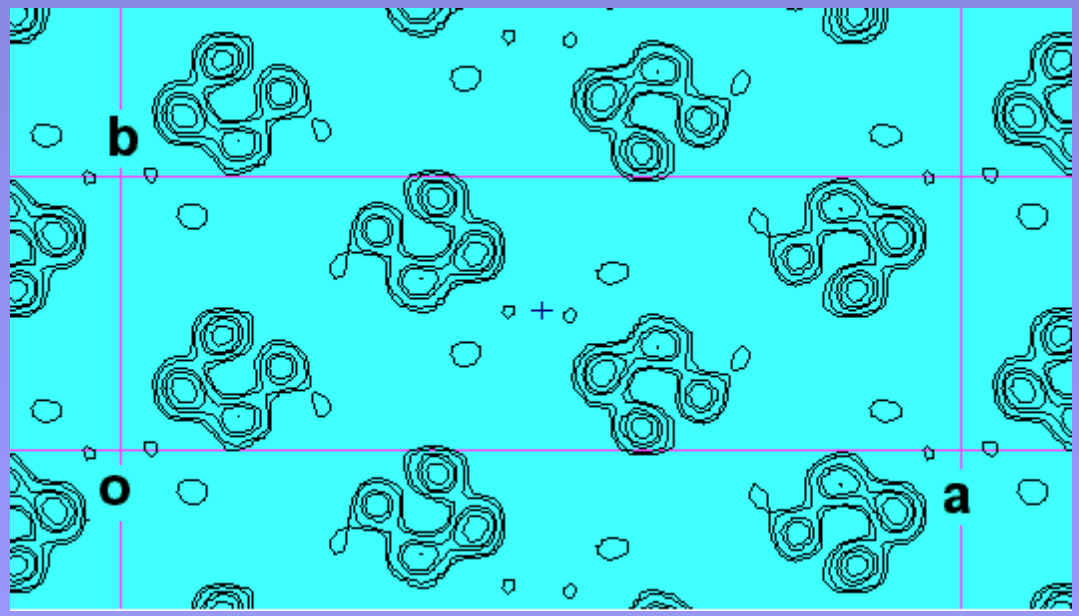
Phase refinement with S-TF **(100 sets, 20 cycles)** followed by automated ΔF recycling for each solution gives as best solution the one with the highest S / S_{exp}

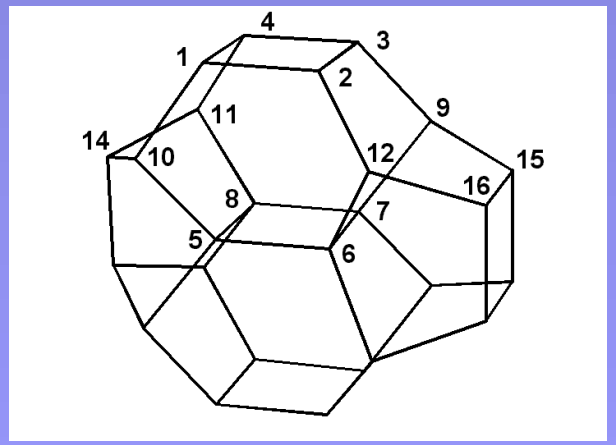
Best solution: S / S_{exp}=0.826 R_{DF}(%)=55.2*

$$R = 1000 \times \{1-[\Sigma(Fo \cdot Fc)^{1/2}]^2/(\Sigma Fo \Sigma Fc)\}$$

ITQ22: 3D-imaging at 2.24 Å resolution

S-TF + automated DF refinement → D4MR units + 7 T atoms showed up





a = 42.090 b=12.990 Å

Structure completion of ITQ-22: (1)

From the automated Forier recycling with initial phases from direct methods:

T1 to T4 + T5 to T8 + T9 to T11

From the restrained L.S. refinement with fixed occupations for T atoms and 50% Ge at T1-T4 + subsequent DF:

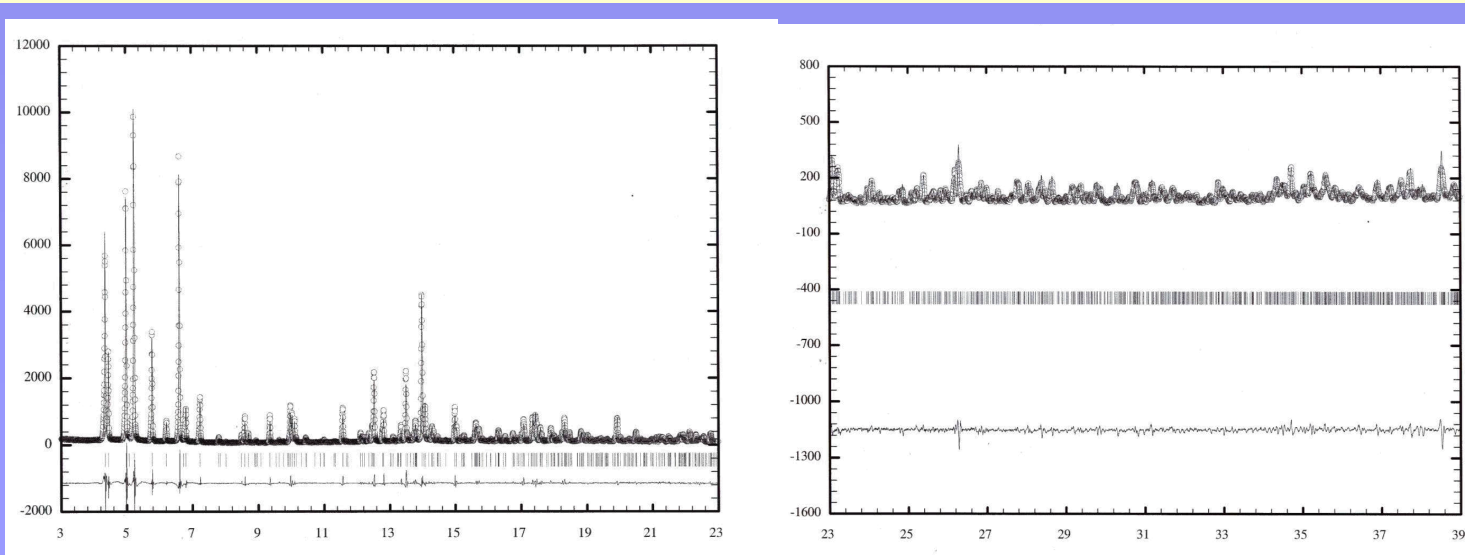
T12 **T-T= 3.15(5)Å**

Structure completion of ITQ-22: (2)

- Restrained L.S. with all T occupations fixed except for T1-T4 + ΔF => T13-T16

- L.S. with no restraints for T13-T16

d(A)	2.24	2.35	2.44	2.54	2.70	2.87	3.09	3.42	4.03	5.26	inf
Nref	40.	36.	35.	37.	34.	35.	41.	32.	36.	37.	
R1	0.582	0.532	0.399	0.402	0.332	0.342	0.256	0.261	0.175	0.148	



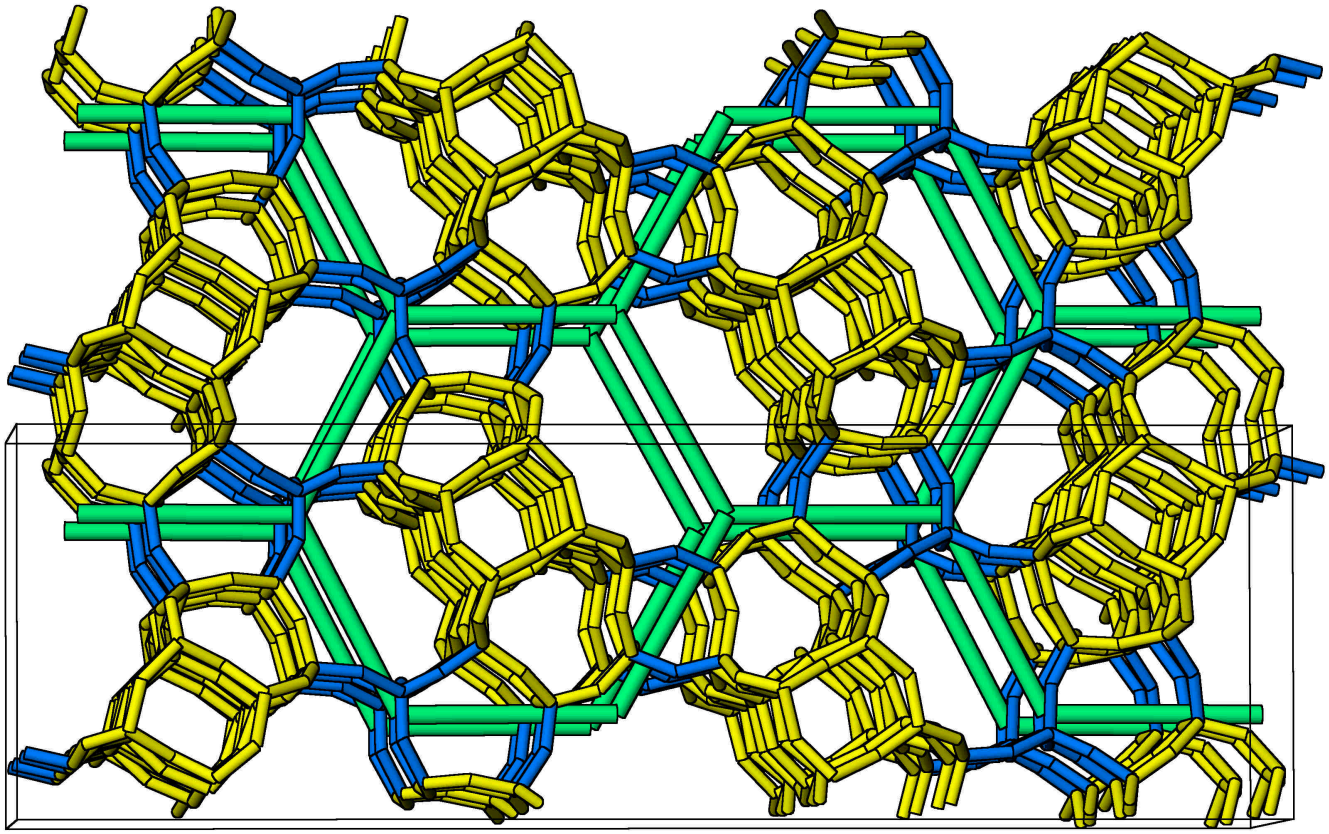
Fractional atomic coordinates of ITQ-22 (Si:Ge = 4:1)

Atom/ site	*x*	*y*	*z*	site multiplicity	%Ge[d]
T1	0.38500	0.9154	0.1275	1	62(3)
T2	0.42261	0.6981	0.1277	1	58(3)
T3	0.35640	0.5802	0.1250	1	48(3)
T4	0.31888	0.7891	0.1225	1	58(3)
T5	0.38387	0.8951	1/2	1/2	0
T6	0.41980	0.6952	1/2	1/2	0
T7	0.35708	0.5625	1/2	1/2	0
T8	0.31899	0.7708	1/2	1/2	0
T9	0.35057	0.4197	0.2980	1	0
T10	0.37882	1.0563	0.3157	1	9(2)
T11	0.27961	0.8590	0.3139	1	9(2)
T12	0.46315	0.6216	0.3125	1	10(2)
T13	0.28922	0.3018	0.3767	1	0
T14	0.30739	1.0734	0.3764	1	11(2)
T15	0.40442	0.2755	0.3769	1	8(2)
T16	0.46674	0.3964	0.3765	1	5(1)

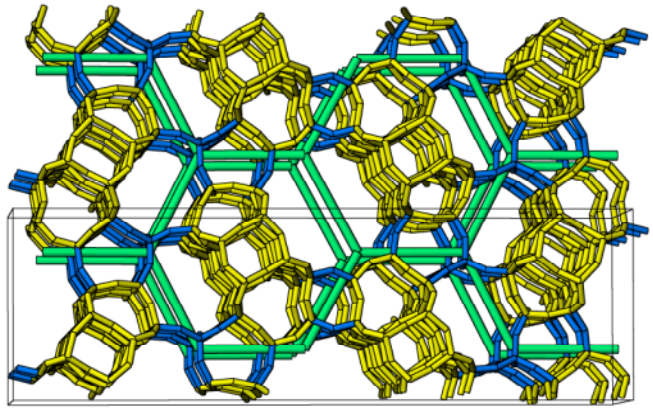
A.Corma, F.Rey, S.Valencia, JL. Jordá, J.Rius

***Nature Materials* 2003, 2, 493-497**

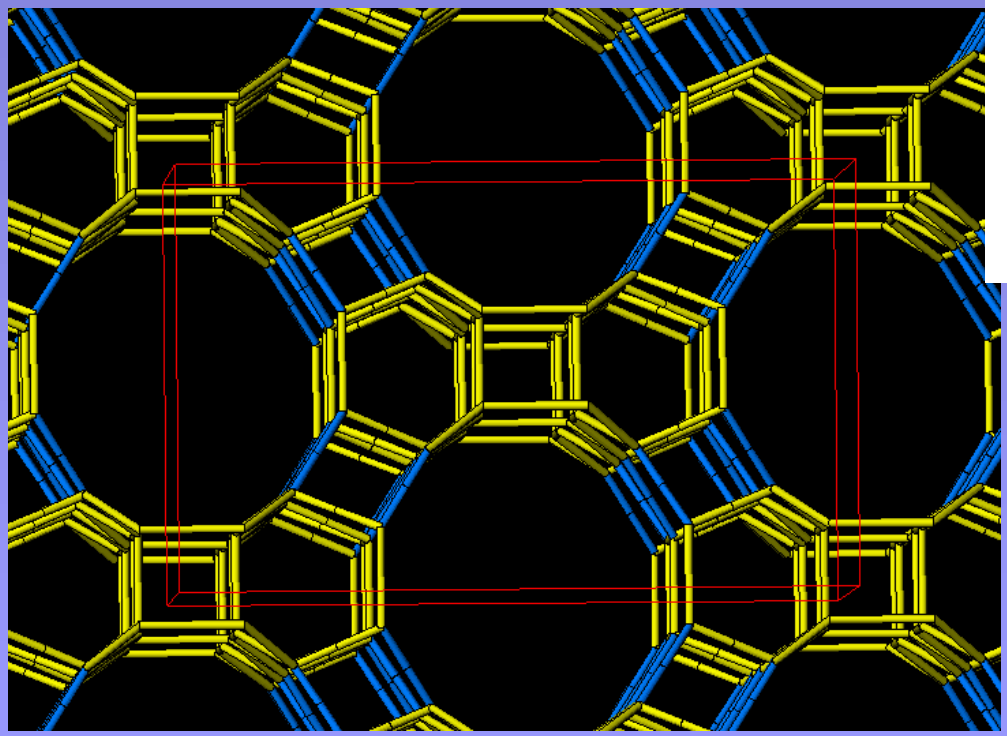
Upper view of ITQ-22



ITQ-22



Upper view of ITQ-24



R.Castañeda, A.Corma, V.Fornés, F.Rey & J.Rius **JACS (2003)**

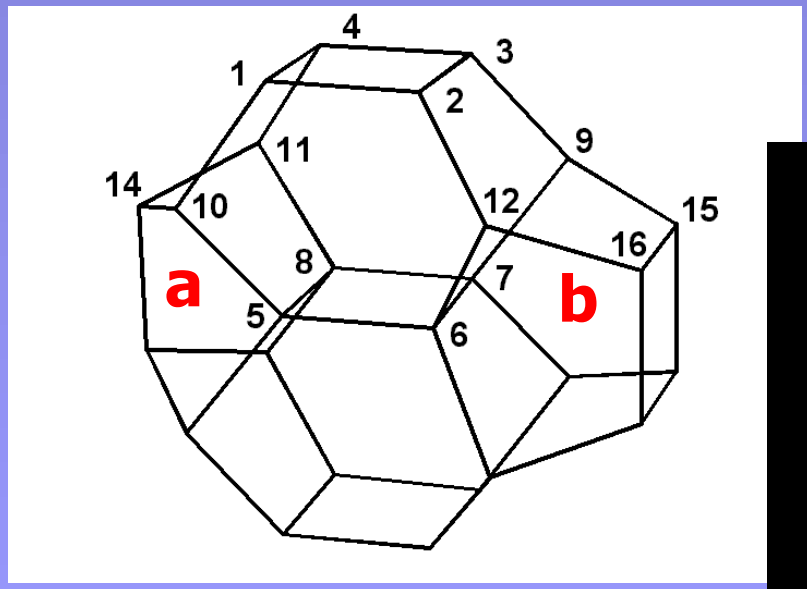
BASIC BUILDING UNITS OF D4MR FAMILY

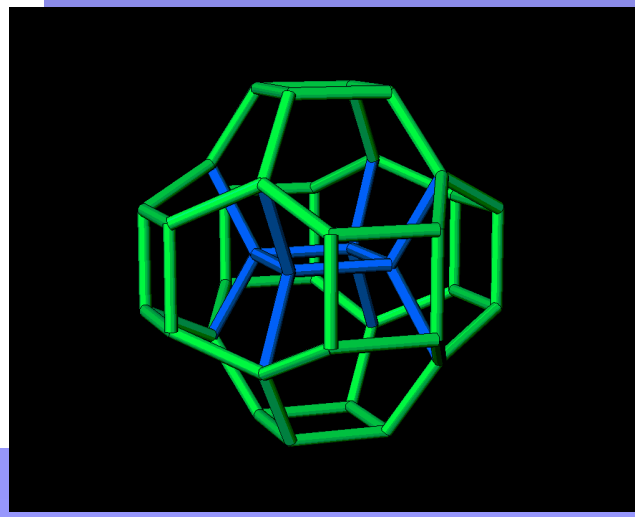
ITQ-17, ITQ-7

a + a

ITQ-22

a + b



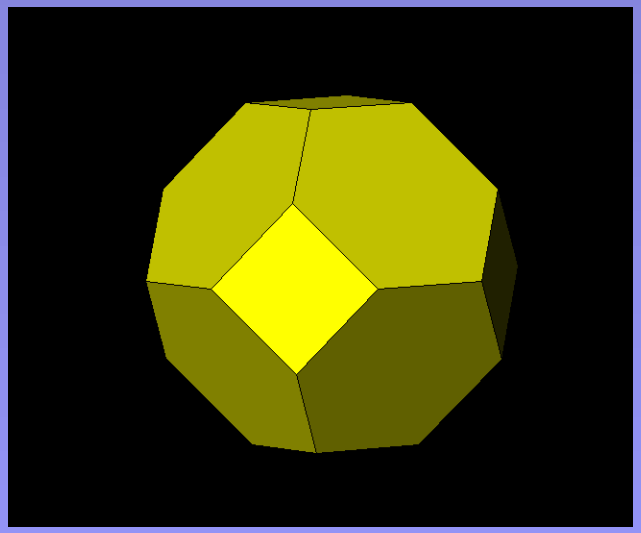


ITQ-24

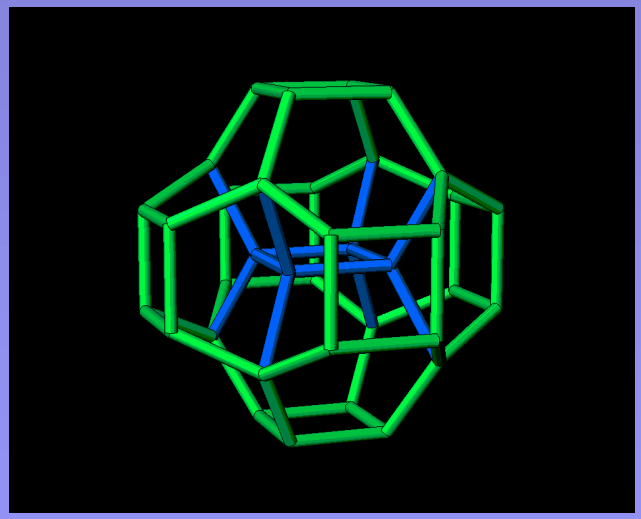
b + b

ITQ-21 4b

The building units



sodalite



ITQ-21

Basic features of some cubic zeolites

Zeolite	N. of T atoms	Window size	N. of windows	Cavity size
Sodalite	4	2.6	6	~ 9.0
Zeolite A	8	4.1	6	11.4
Faujasite	12	7.4	4	11.8

Synthesis of ITQ-21

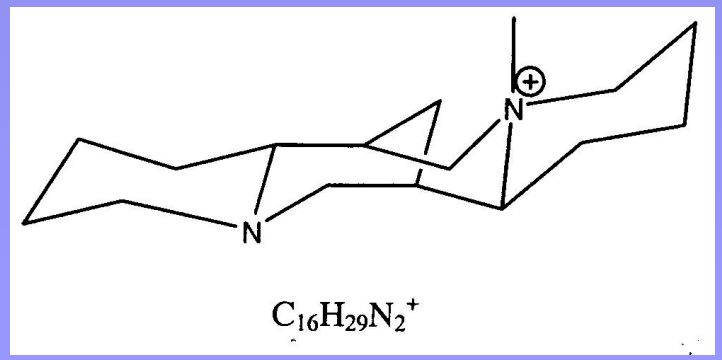
Under hydrothermal conditions at 175ºC for 3 days from gels of compositions:

$$xGeO_2 : (1-x)SiO_2 : yAl_2O_3 : 0.50MSPTOH : 0.50HF : wH_2O$$

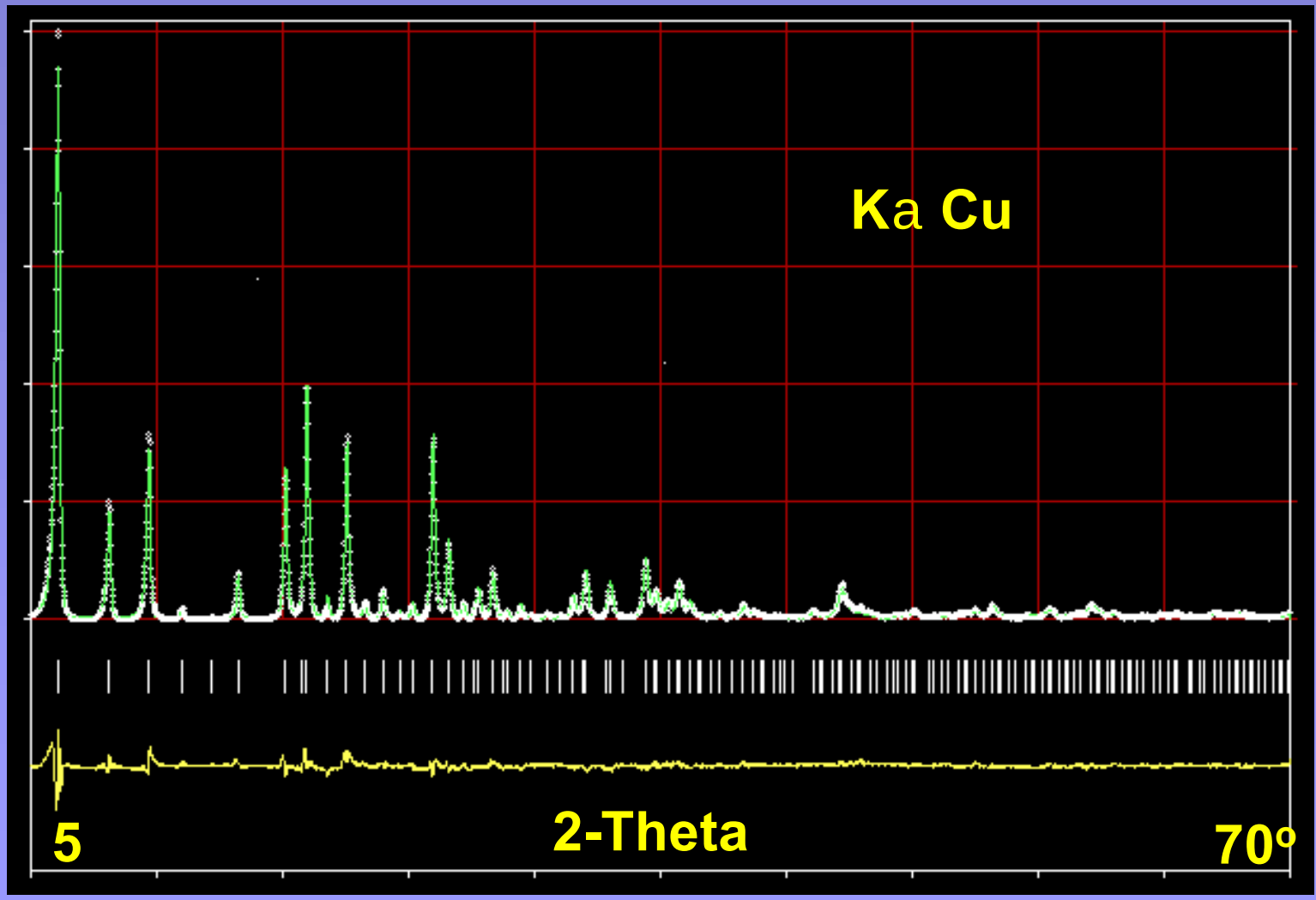
x =0.33 y =0.00 w=20

(x =0.09 y =0.02 w= 3)

MSPTOH: N-methyl-sparteinium hydroxide

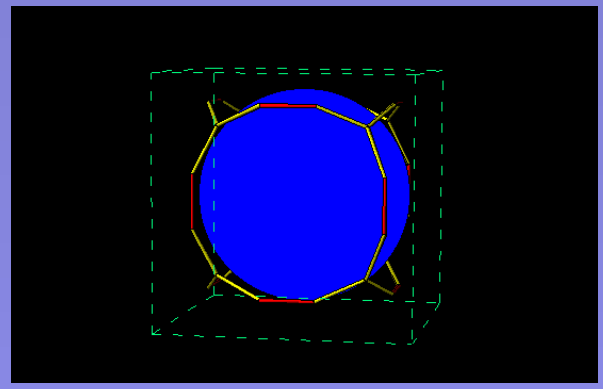


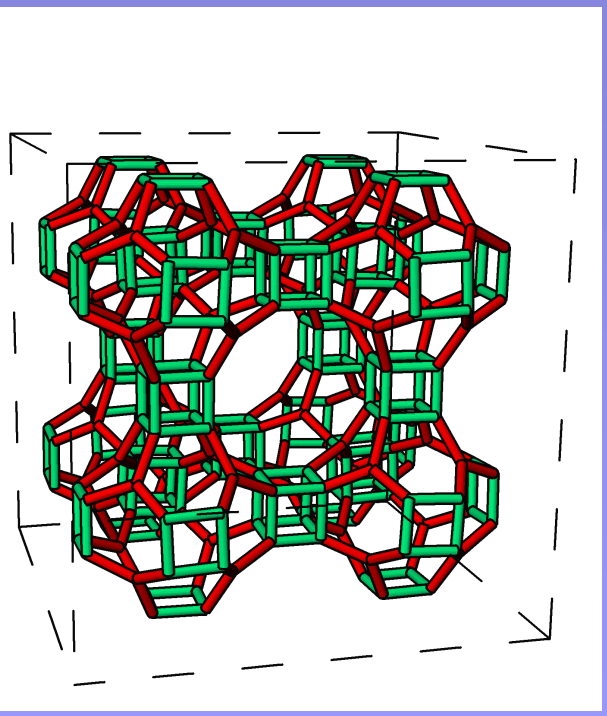
X-ray powder diffraction pattern of ITQ-21



Zeolite ITQ21

(as synthesised)





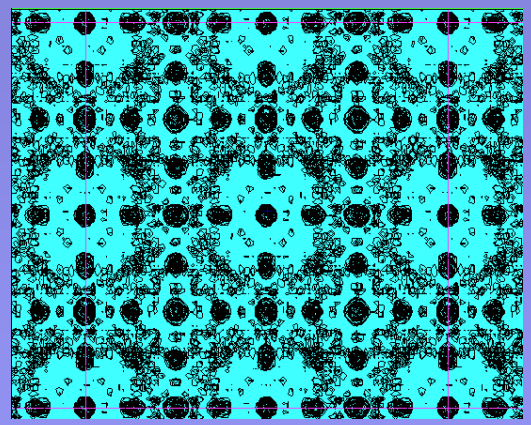
a = 27.70 Å

Fm-3c

A. Corma ... & J. Rius *Nature* (2002) 418, 514-517

3D - imaging of ITQ-21 from moderate resolution X-ray data

78 intensities



Input data at 1.5 - 1.3Å

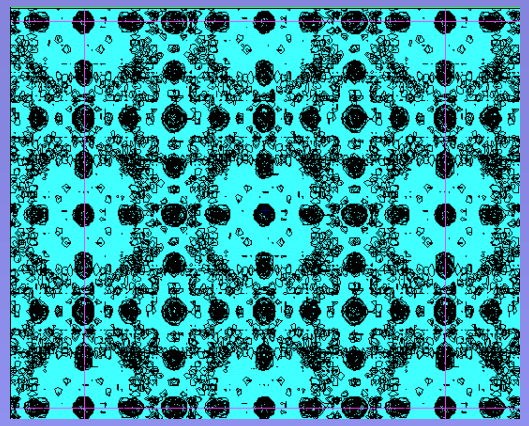
XLENS

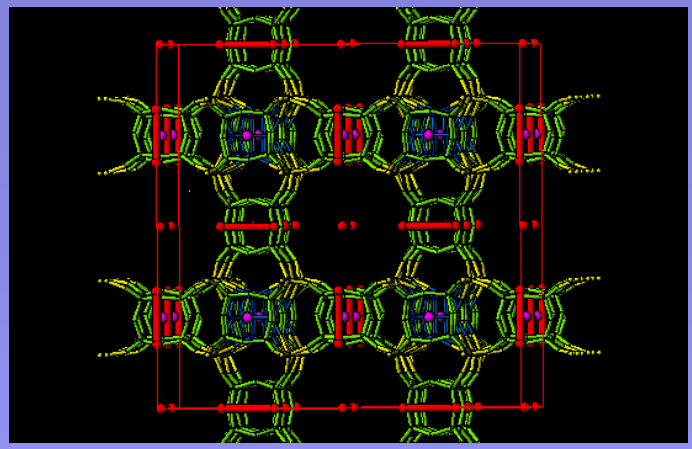
focusing by forcing the atomicity

3D - image

Rius,J. (1993) Acta Cryst. A49, 406-409

Interpretation of the XRD image



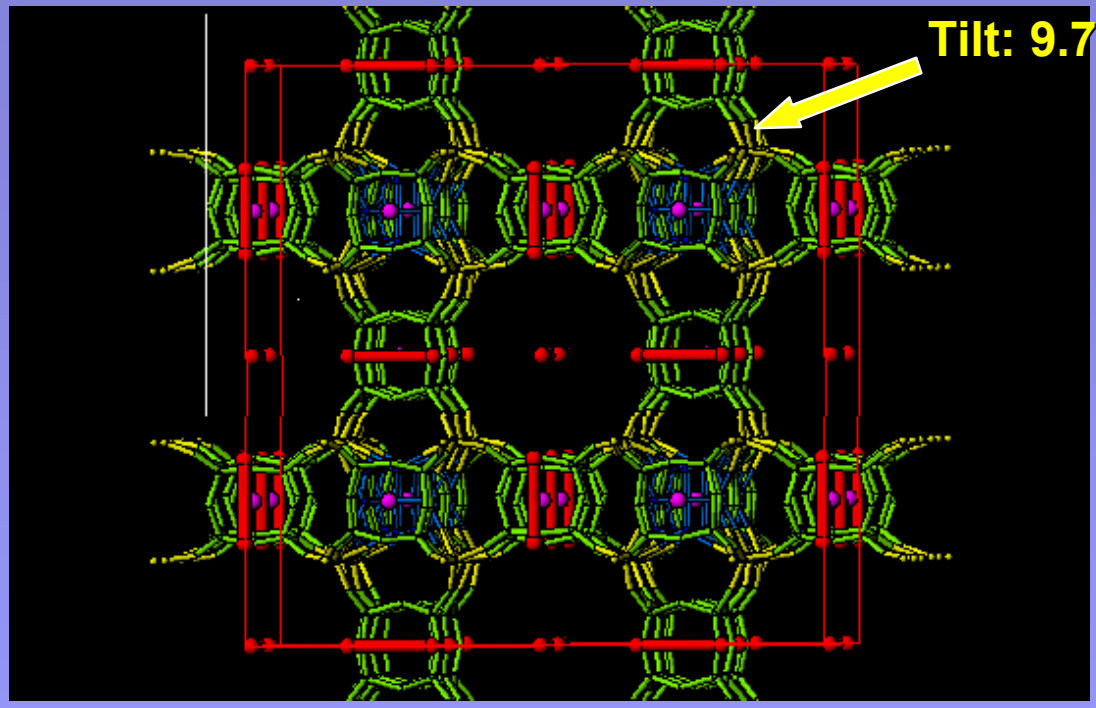


at 1.5 Å

at atomic resolution

- What are the black peaks ?
- Why is the structure F*m-3c* ?

Why is the structure face-centered ?



Averaged structure: h=2n, k=2n, l=2n (strong)

Superstructure: Rest of reflections (weak)

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