

Crystal Structure Determination of Zeolite N from Synchrotron X-Ray Powder Diffraction Data

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Christensen, A. N. and Fjellvåg, H., 1997. Crystal Structure Determination of Zeolite N from Synchrotron X-Ray Powder Diffraction Data. – Acta Chem. Scand. 51: 969–973. © Acta Chemica Scandinavica 1997.

The crystal structure of zeolite N (EDI type framework) has been refined using high-resolution synchrotron powder diffraction data. The structure is pseudo-tetragonal. The orthorhombic distortion is observable as a slight line broadening, $a = 990.41(2)$, $b = 988.60(2)$, $c = 1309.00(2)$ pm, space group $I222$, No. 23, $Z = 1$, for the composition $K_{12}Al_{10}Si_{10}O_{40}Cl_2 \cdot 8H_2O$. The AlO_4 and SiO_4 tetrahedra form an ordered arrangement similar to that in edingtonite. The potassium and chlorine atoms form deformed ClK_6 octahedra positioned in the channels running along $[001]$.

During their studies of the hydrothermal chemistry of silicates and aluminosilicates Barrer *et al.*¹ and Barrer and Marcilly² found some salt-bearing aluminosilicates. The KCl- and KBr-bearing compounds were termed zeolite N and zeolite O, respectively. The present investigation concerns the crystal structure of zeolite N. Barrer and Marcilly² obtained zeolite N by treatment of the Linde sieve Na-X with KCl, and they reported the composition $K_{2.7}Al_2Si_{2.54}O_9Cl_{0.7} \cdot 0.55H_2O$. The topology of its framework structure is of the edingtonite type (EDI).^{3,4} Baerlocher and Barrer⁵ later described the structure of the closely related material Rb-D, $Rb_2Al_2Si_2O_8 \cdot 2.6H_2O$. From X-ray powder diffraction data collected on a conventional powder diffractometer using Cu $K\alpha$ radiation, they found a statistical distribution of the Al and Si in the framework. Furthermore, the determination of the water position was very incomplete. The unit cells for Rb-D and zeolite N are rather similar. The dimensions for the body-centered tetragonal cells are $a = 997.8(1)$, $c = 1321.5(2)$ pm, and $a = 983$, $c = 1310$ pm, respectively. The crystal structures appear hence to be related. Furthermore, the cation distribution may be quite different for the differently sized K and Rb atoms. Furthermore, zeolite N contains additional KCl, whereas the water content is substantially less than for Rb-D. The crystal structure problem is presently attacked by means of high-resolution, synchrotron powder diffraction data.

Experimental

The sample of zeolite N was made in a 150 ml gold-lined pressure vessel during hydrothermal synthesis. A mixture

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of 10 g zeolite 4A, $Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O$ (Fluka), 25 g KCl (Merck p.a.) and 100 ml water was kept at 300 °C for 170 h. The reaction product was washed and dried in air at room temperature. An X-ray powder pattern recorded on a Stoe-Stadi diffractometer indicated that the sample was pure zeolite N.² A thermogravimetric analysis made on a Stanton Redcroft TG-TGA simultaneous thermal analyser STA 1000/1500 using a heating rate of 10 °C min⁻¹, and a 150 ml min⁻¹ flow of Ar gas showed a weight loss of 5.2% during heating to 600 °C, which is assumed to reflect loss of water. The content of Cl⁻ was determined in a Volhard titration for a sample dissolved in nitric acid. The result was 4.0% Cl⁻. Assuming a 1:1 ratio between the Al and Si atoms, the two analyses correspond to approximately the formula $K_{2.4}Al_2Si_2O_8Cl_{0.4} \cdot H_2O$ for the synthesized zeolite N.

Synchrotron X-ray powder diffraction data of zeolite N were collected at the Swiss-Norwegian beam line, BM1, at ESRF, Grenoble, at a wavelength of 109.81(1) pm. Data were collected in Debye-Scherrer geometry over the 2θ range 6–66° with steps of $\Delta(2\theta) = 0.01^\circ$. The sample was kept in a 0.5 mm diameter silica glass capillary which was rotated at approximately 100 rpm to randomize crystallite orientation. The full pattern was recorded at 27 °C over 12 h.

Structure determination

The synchrotron X-ray powder diffraction pattern was indexed with the program DICVOL91.⁶ It suggested a tetragonal unit cell with volume 1283×10^6 pm³ and $a = 989.1(1)$, $c = 1309.4(3)$ pm. The figure of merit $M(20) = 46.8$. The observed reflections were in agreement with the extinction rules of the space group $I42m$. The

structural description in this space group imposes a statistical distribution of the Al and Si atoms over the tetrahedral framework. Baerlocher and Barrer⁵ refined the structure of zeolite Rb-D in the space group $I222$, in which it is possible to describe an ordered distribution of the Al and Si atoms. However, the quality of their data did not permit such a detailed description. Hence they describe Rb-D with a statistical Al-/Si-distribution. These zeolites with EDI topology have naturally close relationship to edingtonite, which has an ordered distribution of Al and Si atoms in the framework.⁷ Presently, both disordered and ordered models were considered.

The profile refinement followed the procedure described by Rietveld.⁸ The least-squares program FullProf⁹ was used. Starting values for the positional parameters were taken from the description of the structure of Rb-D⁵ in space group $I\bar{4}2m$. The refinements converged with the profile R -factor, $R_p=0.146$, which was far from satisfactory. Further analysis was performed with the GSAS program system.¹⁰

Careful inspection of the line profiles (Fig. 1) showed that the peak widths, FWHM, varied somewhat with hkl . Reflections with intensity contributions from hkl and khl had larger FWHM than reflections of the type hhl . This clearly indicated that the a - and b -axes are of different lengths, although their ratio is too small to provoke line splittings. The final refinements were hence performed in space group $I222$. Starting parameters were again taken from the description of Rb-D.⁵ Comparison of different models favoured the description with an ordered distribution of Al and Si atoms. 5539 data points and 399 reflections entered into the final refinements. The background, after subtraction of a broad hump caused by the capillary, was modelled in terms of a cosine Fourier series (16 terms); the line profiles were described with a pseudo-Voigt function. During the refinements the Al-O distances were restrained to 175(2) pm and the Si-O distances to 164(2) pm. The Al-O-Si angles were restrained by means of the Al-Si distances; 318(1) pm was adopted. The following parameters were entered as free variables, one scale factor, six profile parameters, one zero-point parameter, three unit-cell dimensions, 31 positional parameters, five occupation numbers for non-framework atoms, 16 background parameters, and three isotropic displacement parameters (one for the Al and Si atoms, one for the oxygen framework atoms, one for the non-framework atoms). Via repeated refinement and difference Fourier cycles, the non-framework K, Cl and O atoms were located. The final R -factors are $R_p=0.049$, $R(F_2)=0.075$. Atomic coordinates are listed in Table 1, interatomic distances in Table 2. Fig. 2 shows a stereoscopic drawing of the structure. Observed and difference between observed and calculated powder diffraction data are shown in Fig. 3.

Discussion

The results indicate an ordered arrangement of the AlO_4 and SiO_4 tetrahedra in the crystal structure. The ortho-

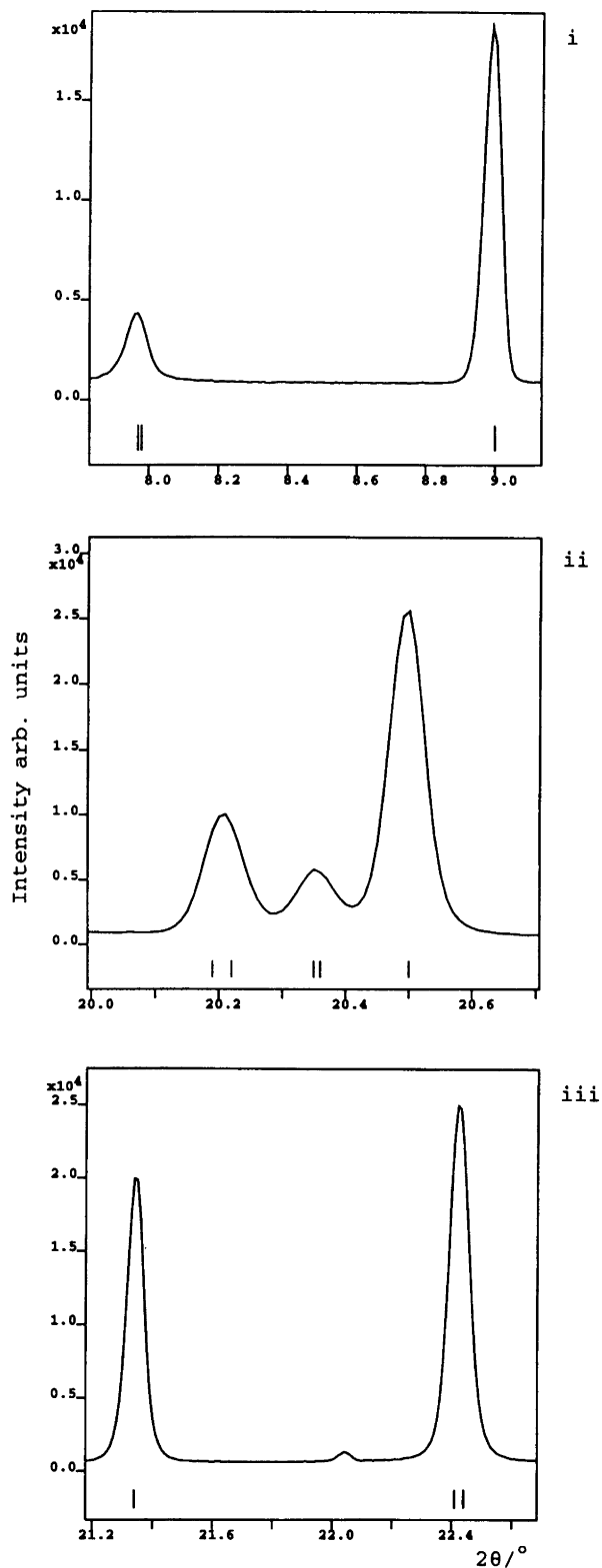


Fig. 1. Sections of the observed powder pattern in the 2θ ranges (i) 7.8–9.1, (ii) 20.0–20.7 and (iii) 21.2–22.7°. The ticks mark the positions of the reflections. FWHM values calculated from the profile fit are listed in brackets. (i) 101 + 011 [0.065°], 110 [0.063°]; (ii) 310 + 130 [0.080°], 213 + 123 [0.075°], 222 [0.071°]; (iii) 114 [0.072°], 312 + 132 [0.082°].

Table 1. Refined positional and displacement parameters for the structure of zeolite N.^a

Atom	Site	Occupancy factor ^b	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B/Å</i> ²
Al1	2 <i>b</i>	1.0	1/2	0	0	1.30(6)
Si1	2 <i>d</i>	1.0	0	1/2	0	1.30(6)
Al2	8 <i>k</i>	1.0	0.3430(4)	-0.1151(4)	0.3089(3)	1.30(6)
Si2	8 <i>k</i>	1.0	0.3862(4)	0.1584(4)	0.1920(3)	1.30(6)
O1	8 <i>k</i>	1.0	0.3967(8)	0.0996(8)	0.0753(6)	1.44(8)
O2	8 <i>k</i>	1.0	0.4001(8)	0.9003(7)	0.4353(6)	1.44(8)
O3	8 <i>k</i>	1.0	0.3106(9)	0.0446(7)	0.2569(8)	1.44(8)
O4	8 <i>k</i>	1.0	0.5406(8)	0.1911(9)	0.2291(7)	1.44(8)
O5	8 <i>k</i>	1.0	0.3044(7)	0.2960(7)	0.1894(4)	1.44(8)
K1	4 <i>i</i>	0.970(5)	0	0	0.2499(3)	3.30(8)
K2	8 <i>k</i>	0.970(4)	0.2115(4)	0.2121(4)	0.4363(2)	3.30(8)
OW1	8 <i>k</i>	0.5 ^c	0.424(2)	0.346(2)	0.425(1)	3.30(8)
OW2	8 <i>k</i>	0.5 ^c	0.361(1)	0.476(2)	0.441(1)	3.30(8)
Cl	2 <i>c</i>	0.914(6)	0	0	1/2	3.30(8)

^aSpace group *I*222. *a*=990.41(2), *b*=988.60(2), *c*=1309.00(2) pm. Calculated standard deviations are in parentheses.

^bCalculated composition from the structure determinations: K_{11.6}Al₁₀Si₁₀O₄₀Cl_{1.83}·8H₂O. ^cFixed, see text.

Table 2. Interatomic distances (in pm) for the structure of zeolite N.

Al(1)–O(1)	172.8(5) (× 4)	Al(2)–O(2)	175.5(7)
		Al(2)–O(3)	175.0(7)
		Al(2)–O(4)	172.7(7)
		Al(2)–O(5)	170.4(8)
Si(1)–O(2)	163.3(5) (× 4)	Si(2)–O(1)	163.8(6)
		Si(2)–O(4)	163.7(8)
		Si(2)–O(3)	159.6(7)
		Si(2)–O(5)	158.4(8)
K(1)–O(3)	310.9(9) (× 2)	K(2)–O(1)	281.5(10)
K(1)–O(4)	309.2(9) (× 2)	K(2)–O(2)	274.8(10)
K(1)–O(5)	290.7(6) (× 2)	K(2)–O(3)	303.5(11)
K(1)–OW(2)	286.3(15)	K(2)–O(4)	291.0(10)
K(1)–OW(1)	285.1(16)	K(2)–OW(1)	249.1(14)
		K(2)–OW(2)	300.0(17)
OW(1)–OW(2)	144.3(15)	Cl(1)–K(2)	307.89(23) (× 4)
OW(2)–OW(2)	161.6(30)	Cl(1)–K(1)	327.35(33) (× 2)

Angles (in °) in the ClK₆ polyhedra

K(1)–Cl–K(2)	74.35(4)	
K(1) ⁱ –Cl–K(2)	105.65(4)	<i>i</i> = <i>x</i> , <i>y</i> , 1 – <i>z</i>
K(2)–Cl–K(2) ⁱ	93.87(19)	<i>i</i> = – <i>x</i> , – <i>y</i> , <i>z</i>
K(2)–Cl–K(2) ⁱ	94.48(19)	<i>i</i> = <i>x</i> , – <i>y</i> , 1 – <i>z</i>

rhombic deformation of the unit cell is very small; nevertheless, it is observable as a line broadening for certain reflections in the high-resolution powder diffractograms (Fig. 1). The refined distances were in the following ranges: Al–O 170.4–175.5 pm and Si–O 158.4–164.0 pm.

The distribution of the non-framework atoms is very interesting. The Cl[–] ion is coordinated by six K⁺ ions in a distorted octahedral arrangement, Cl–K(1)=327.4(3) pm (2 ×) and Cl–K(2)=307.9(2) pm (4 ×). The

average value of 314.4 pm is very close to the K–Cl distance found in the perfect octahedra in KCl,¹¹ 314.6 pm. The ClK₆ octahedra fill voids in the channels running along [001] (Fig. 4). The potassium atoms are bonded to one chlorine and several framework and non-framework oxygen atoms (Table 2). In the refinements the displacement parameters of the non-framework atoms were kept at identical values, 3.30(8) Å². The displacement parameters and occupancy factors are strongly correlated, and the charge unbalance calculated

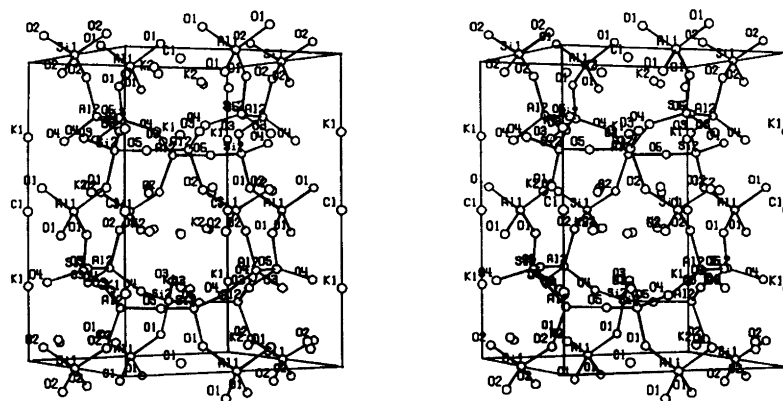
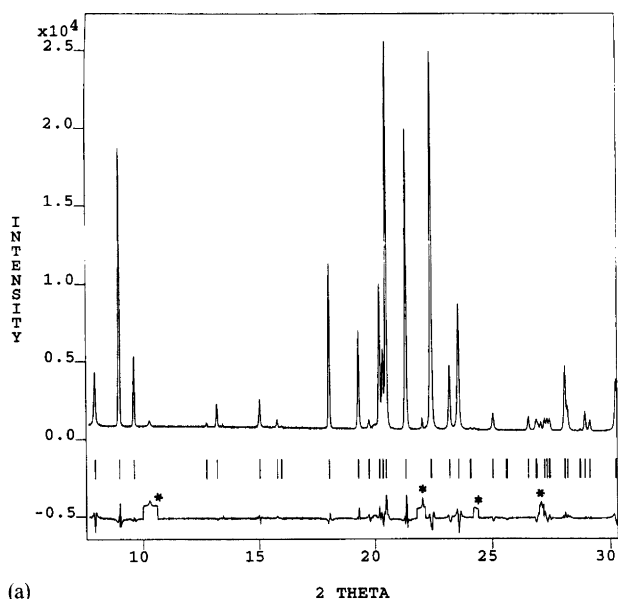
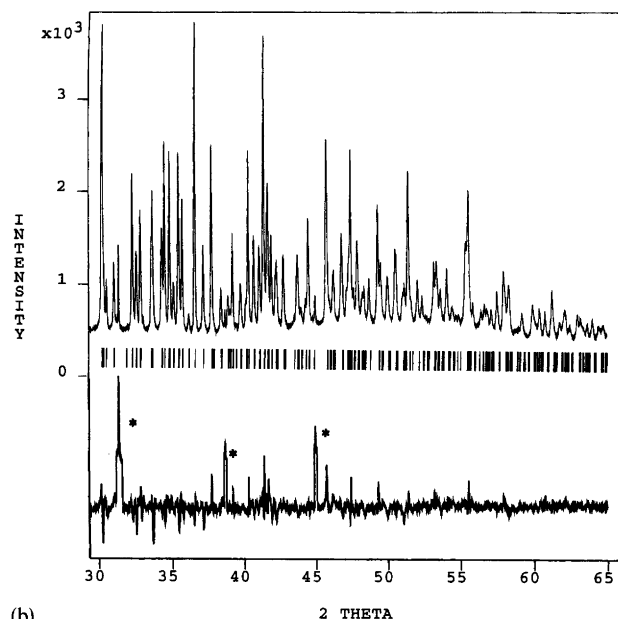


Fig. 2. Stereoscopic view of the structure of zeolite N. The *c*-axis is vertical.



(a)



(b)

Fig. 3. Observed and difference X-ray powder diffraction pattern, $\lambda=109.81$ pm. Excluded regions are marked by a star.

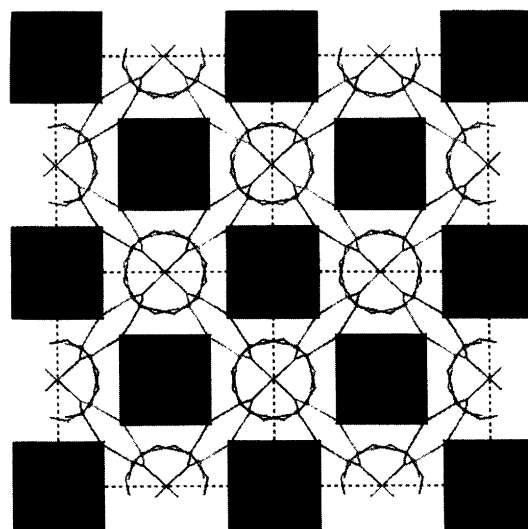


Fig. 4. Distribution of non-framework potassium and chlorine atoms shown as ClK₆ octahedra. Framework bonds are shown as thin lines. Projection on the *ab*-plane.

from the occupancy factors, where 1.8 Cl⁻ must balance 1.6 K⁺, may be less pronounced if the displacement parameters of the potassium and chlorine atoms were refined without any restraints.

The 8*k* positions used for describing the non-framework oxygen atoms OW(1) are pairwise rather close, i.e. at a separation of 162 pm. The refined occupancy for OW(1) is 0.59(1); however, since such short O–O distances are improbable the occupancy was fixed to 0.5 in the final refinements. The distribution of the OW(1) atoms is shown together with the OW(2) atoms and the ClK₆ octahedra in Fig. 5.

The difference Fourier maps showed, furthermore, a significant remaining electron density in the position (8*k*) 0.40, 0.34, 0.425. From distance considerations it is likely that this corresponds to a second water molecule, OW(2). This eight-fold site is half occupied, and the OW(1) and OW(2) atoms are so close (144 pm) that the occupancy of water in the two half-filled sites must be quite systematic in order to avoid neighbours that are too close.

The positions of the atoms in the framework of the

Table 3. Comparison of the non-framework atomic positions in zeolite N and in Rb-D.⁵

This investigation						Ref. 5					
Atom	Site	Occupancy factor	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	Site	Occupancy factor	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
K1	4 <i>i</i>	0.970	0	0	0.2499	Rb(1a)	4 <i>i</i>	0.49	0	0	0.205
K2	8 <i>k</i>	0.970	0.2115	0.2121	0.4363	Rb(1b)	4 <i>i</i>	0.26	0	0	0.331
OW1	8 <i>k</i>	0.500	0.424	0.346	0.425	Rb(2b)	8 <i>k</i>	0.34	0.219	0.225	0.433
OW2	8 <i>k</i>	0.500	0.361	0.476	0.441	Rb(2c)	8 <i>k</i>	0.33	0.323	0.319	0.428
Cl	2 <i>c</i>	0.914	0	0	1/2	Rb(2a)	8 <i>k</i>	0.18	0.378	0.335	0.945
						H ₂ O(1)	8 <i>k</i>	0.38	0.353	0.402	0.511
						H ₂ O(2)	8 <i>k</i>	0.30	0.93	0.96	0.54

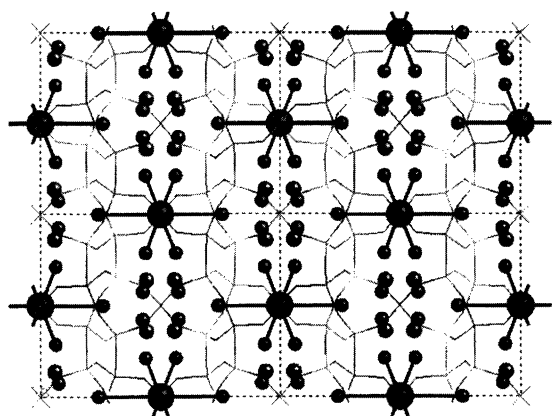


Fig. 5. Non-framework atoms shown in projection on the *ac*-plane. The ClK₆ octahedra and the OW atoms (50% filled sites) are shown.

zeolite N structure resembles the framework atom positions reported for Rb-D.⁵ However, the positions of the non-framework atoms found in this investigation are somewhat different from those reported by Baerlocher and Barrer.⁵ Table 3 shows a comparison of the two sets of atomic positions for the two investigations. The electron density interpreted as Cl⁻ ions is in this work at the 2*c* site, whereas for Rb-D⁵ a water molecule, H₂O(2), is sited close to this position in site 8*k*. The remaining electron densities interpreted as non-framework atom positions coincide in the two investigations but are in some cases interpreted differently. The positions in this work of the atoms K1, K2, OW1 and OW2 are indicated in Ref. 5 as the positions of Rb(1a) and Rb(1b), Rb(2b) and Rb(2c), Rb(2a) and H₂O(1), respectively.

The refined chemical content of the unit cell is K_{11.6}Al₁₀Si₁₀O₄₀Cl_{1.83}·8H₂O, which fits well the chem-

ical formula deduced from chemical analysis, K₁₂Al₁₀Si₁₀O₄₀Cl₂·5H₂O.

Acknowledgements. The Danish Natural Science Research Council has supported this investigation with grants. Carlsbergfondet is acknowledged for the TG-TGA thermal analyzer. The possibility of collecting data at the Swiss-Norwegian beam line, BM1, at the European Synchrotron Radiation Facility is gratefully acknowledged; this is contribution no. 02.97 from the Swiss-Norwegian Beam Line at ESRF. Mrs. M. A. Chevallier, Mrs. C. Secher, Mr. A. Lindahl and Mr. N. J. Hansen are acknowledged for valuable assistance.

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Received November 28, 1996.