JOURNAL OF SOLID STATE CHEMISTRY **44**, 245–253 (1982)

The Structure of Dehydrated Na Zeolite A (Si/Al = 1.09) by Neutron Profile Refinement

J. M. ADAMS AND D. A. HASELDEN

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE, Wales

AND A. W. HEWAT

Institut-Laue-Langevin, 156X, 38042 Grenoble Cedex, France

Received December 23, 1981; in final form April 30, 1982

Contrary to the recent work of J. M. Thomas *et al.* (*J. Chem. Soc. Chem. Commun.*, 678, 1981), it was found that a high-resolution neutron powder diffraction pattern of a sample of dehydrated Na zeolite A (with Si/Al ratio 1.09) can be indexed and refined in the cubic space groups $Pm\bar{3}m$ (R_{pw} = 11.0%) (A. K. Cheetham and J. C. Taylor, *J. Solid State Chem.* **21**, 253, 1977) and $Fm\bar{3}c$ (R_{pw} = 10.3%), whereas in the rhombohedral space group $R\bar{3}$ refinement was unsuccessful. For two other samples having Si/Al ratios of 1.03 and 1.12 the diffraction patterns again showed no evidence of rhombohedral distortion and can be indexed using a cubic unit cell. It appears that the Si, Al ordering of zeolite A, and hence the crystal symmetry, must depend upon the conditions of preparation of the zeolite.

Introduction

The crystal structure of zeolite A was first determined by Reed and Breck (*3*), who found a 12.3-Å cubic cell. Later more accurate X-ray studies were made of the hydrated zeolite by Gramlich and Meier (*4*), who showed that the true cell had a 24.6-Å repeat and conformed to space group $Fm\bar{3}c$; they also located the water molecules in the zeolite cavities. Subramanian and Seff (*5*) later made a claim for a "near-zero coordination sodium ion" in the dehydrated structure. Their study used the 12.3-Å pseudocell with space group $Pm\bar{3}m$. Pluth and Smith (*6*) carefully reexamined this dehydrated structure and refined it successfully, using single-crystal X-ray data, in $Fm\bar{3}c$, although they noted a few weak reflections which were not in agreement with this space group. They found that although the sodium atoms have unusual coordinations, the Na–O distances do not satisfy the concept of near-zero coordination.

Recently there has been an upsurge of interest in the structure of dehydrated Na-zeolite A, which started with a solid-state ^{29}Si nuclear magnetic resonance (NMR) study (*7*) which demonstrated that each SiO_4 tetrahedron is connected to three Al atoms and one Si atom (3 : 1 ordering). This contravenes Loewenstein's rule and, furthermore, is not consistent with the space group $Fm\bar{3}c$ used in the previous accurate X-ray structural investigations (*4, 6*). Trimethylsilylation studies of zeolites (*9*) also suggested that between one-third and one-half of the AlO_4 tetrahedra in zeolite A were

0022-4596/82/110245-09$02.00/0

linked in pairs. Lodge *et al.* (*10*) argued that the space group should be $Pm\bar{3}$ when Si/Al was unity and $Fm\bar{3}$ when the ratio deviated from this value. In addition, Thomas *et al.* (*11*) stated that although the method of preparation of the zeolites sodalite and cancrinite can apparently affect the short-range Si, Al ordering, this does not appear to be the case for zeolite A. Their samples were prepared either by the method of Charnell (*12*) or from kaolinite (*13*) and in both cases 3 : 1 ordering was apparent from NMR measurements.

More recently Thomas *et al.* (*11*) reported that the true space group is $R\bar{3}$ rather than $Pm\bar{3}$ or $Fm\bar{3}$ (*11*). Bursill *et al.* (*14*) demonstrated that powder neutron diffraction measurements made with 2.96-Å radiation show certain peaks to be split while others are not; the conclusion was that the samples used were not polyphasic and although they were unable to index the reflections in $Fm\bar{3}c$, they could do so in $R\bar{3}$.

We collected a high-resolution neutron diffraction data set and report here attempts to refine the structure in several of the possible space groups suggested above.

Experimental

The sample of zeolite 4A, prepared by Charnell's method (*12*) (particle size ~20 μm), was dissolved in dilute HCl and analyzed for sodium by flame photometry and for silicon and aluminum by gravimetric procedures (*15*); the composition was found to be $Na_{92}Al_{92}Si_{100}O_{348} \cdot 216H_2O$, i.e., the Si/Al ratio was found to be 1.09 ± 0.02. The data were collected using the high-resolution powder diffractometer D1A at the Institut Laue-Langevin, Grenoble (*16*). A 5-g sample was loaded into a 16-mm-diameter vanadium can and dehydrated *in situ* on D1A at 300°C and 5×10^{-3} mm Hg for 1 hr, after which the sample was allowed to cool to 300K. Throughout the data collection the pumping was maintained to avoid any possibility of rehydration. Data ranging from 2.04 to 161.04° (2θ) were collected in 22 hr at a wavelength of 1.909 Å. The background was estimated by linear interpolation from regions where no Bragg peaks occurred. The refinement of the structure was made using the Rietveld technique of profile refinement (*17, 18*) with the programs of Hewat (*19, 20*). The scattering lengths used were from the "International Tables for X-Ray Crystallography" (*21*).

Structure Refinement

In all of the structure refinements discussed below the $Fm\bar{3}c$ atomic coordinates of Pluth and Smith (*6*) were taken as a basis. In those cases where refinement was attempted using space groups of lower inherent symmetry than $Fm\bar{3}c$ the approach of Katz and Megaw (*22*) was followed to obtain the initial shifts in atomic coordinates.

At the time that this work was undertaken, Lodge *et al.* (*10*) had argued that for a sample of zeolite A with Si/Al ≠ 1.0 the space group should be $Fm\bar{3}$. A full refinement was attempted in that space group, but large shifts were observed in the atomic positions and, in addition, the refinement was unsatisfactory in that an R_{pw}[1] of only 26% could be obtained even with anisotropic thermal parameters for all atoms.

At this point it was suggested (*1*) that the true space group of zeolite A was $R\bar{3}$, although since the rhombohedral cell angle was close to 60° there was a pseudocubic symmetry. Consequently a refinement was attempted in $R\bar{3}$. The positions of all the atoms in the cubic cell were generated from the $Fm\bar{3}c$ coordinates (*6*), the origin was

---

[1] $R_{pw} = 100\left[\Sigma w(y(\mathrm{obs}) - \frac{1}{c}\,y(\mathrm{calc}))^2/\Sigma w(y(\mathrm{obs}))^2\right]^{1/2}$, where w is the weight at each 2θ step and y(obs) and y(calc) are the observed and calculated intensities at that point.

shifted to the center of the α-cage, and then the coordinates were transformed to $R\bar{3}$. All of the atomic positions were therefore known approximately before the beginning of the refinement, but the identity of the atom at each Si,Al site was unknown. An average scattering length was employed at each position. Refinement of the cell constants and half-width of the peaks led to $R_{pw} = 22.7\%$. However, any further refinement in which atomic positions were allowed to vary gave large parameter shifts without any associated refinement. It was noted that the rhombohedral cell angle α was 59.998(2)°, which suggested that in the case of this sample of zeolite A either the true cell was cubic or the pseudocubic symmetry was very marked. At this stage neutron diffraction traces taken with 2.98-Å neutrons were obtained for dehydrated Na zeolite A samples having Si/Al ratios of 1.03 and 1.12 (Fig. 1). The observed peaks could be indexed using a cubic cell, and attempts to refine a rhombohedral cell unit using the Rietveld program (*17*) gave rhombohedral cell angles within one esd of 60°, again showing that the samples were cubic.

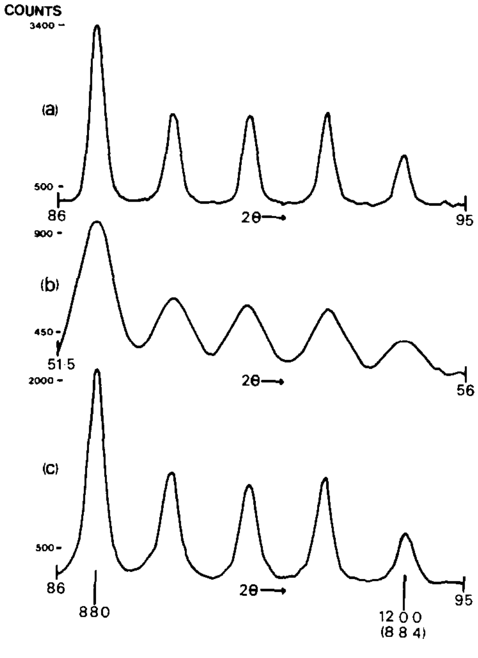

FIG. 1. Observed neutron diffraction profiles (at 300K) for selected 2θ regions for dehydrated Na zeolite A samples with (a) Si/Al = 1.03, (b) Si/Al = 1.09, (c) Si/Al = 1.12. Traces (a) and (c) were obtained with 2.98-Å radiation, whereas (b) used 1.909-Å neutrons.

A return was then made to the space group $Fm\bar{3}c$ which has been used successfully both for hydrated and dehydrated Na zeolite A (*4*, *6*). The Si(1) site was fully occupied by Si, whereas the Al(1) site was constrained to have 92 Al and 4 Si (labeled Si(2)) to agree with the chemical analysis. In addition, the total number of sodium ions was constrained to 92. When using isotropic temperature factors and fixing the population of the sodium ions approximately to values given by the previous X-ray refinement (*6*), convergence was noted at $R_{pw} = 13.2\%$. After refinement of the site populations of sodium at sites Na(1), Na(2), and Na(3), the population parameters remained close to those of Pluth and Smith (*6*). An anisotropic refinement then proved possible for all atoms except Na(3), which had a very small occupancy factor. The reasonable agreement between the anisotropic thermal parameters here and those of Pluth and Smith (*6*) (Table I) was considered heartening as it is well known that anisotropic thermal parameters are the least reliable data from the Rietveld refinement. The final R_{pw} was 10.3%, corresponding to a conventional R[2] of 7.2%. The unit cell constant was 24.5920(2) Å (the esd in cell parameter does not include a contribution from the uncertainty in the neutron wavelength: for comparison, the cell constants for the two samples having Si/Al ratios 1.03 and 1.12 were 24.5982(4) and 24.5996(2) Å,

---

[2] The program (*19*, *20*) divides the observed counts between overlapping reflections according to the relative contributions of the calculated reflections, applies a Lorentz correction, and then calculated F^2_{obs} and F^2_{calc}. The values of F^2_{obs} and F^2_{calc} were square-rooted and used to calculate the conventional R factor according to $R = \Sigma||F_{obs}| - |F_{calc}||/\Sigma|F_{obs}|$.

TABLE I

Comparison of Refinement in Space Group $Fm\bar{3}c$ with Previous Work

				Pluth and Smith (6)	
	Si(1)	Si(2)	Al(1)	Si(1)	Al(1)
Position	96(*i*)	96(*i*)	96(*i*)	96(*i*)	96(*i*)
Pop.	96	4	92	96	96
x	0.0		0.0	0	0
y	0.09352(29)		0.18665(43)	0.09316(5)	0.18715(7)
z	0.18558(33)		0.08921(38)	0.18499(6)	0.69042(6)
β_{11}	5(1)		16(2)	9.7(3)	9.4(3)
β_{22}	12(1)		8(2)	7.9(3)	6.5(3)
β_{33}	10(1)		7(1)	5.9(3)	8.7(3)
β_{12}, β_{13}	0		0	0	0
β_{23}	−6(1)		9(1)	0.6(1)	1.0(1)
		Na(1)		Na(1)	
Position		64(*g*)		64(*g*)	
Pop.		64.0		62.2	
x		0.10066(12)		0.09960(4)	
y		0.10066(12)		0.09960(4)	
z		0.10066(12)		0.09960(4)	
β_{11}, β_{12}, β_{22}		16(1)		15.7(2)	
β_{12}, β_{13}, β_{23}		5(1)		2.7(1)	
		Na(2)		Na(2)	
Position		96(*i*)		96(*i*)	
Pop.		23.62		23.2(4)	
x		0.0		0	
y		0.21580(94)		0.2165(6)	
z		0.22604(91)		0.2111(6)	
β_{11}		36(6)		23(2)	
β_{22}		5(3)		32(4)	
β_{33}		19(6)		19(3)	
β_{12}, β_{13}		0		0	
β_{23}		27(3)		−5(6)	
		Na(3)		Na(3)	
Position		96(*h*)		96(*h*)	
Pop.		4.38		6.3(4)	
x		0.25		0.25	
y,z		0.11550(156)		0.1060(7)	
β_{11}				24(7)	
β_{23}, β_{33}				15(4)	
β_{12}, β_{23}				−1(2)	
β_{13}				−2(7)	
B		0.42(1.16)			
		O(1)		O(1)	
Position		96(*i*)		96(*i*)	
Pop.		96		96	
x		0		0	

TABLE I—*Continued*

		Pluth and Smith (*6*)
y	0.11377(11)	0.11367(10)
z	0.24695(33)	0.24663(17)
β_{11}	19(1)	15.5(5)
β_{22}	18(1)	18.4(6)
β_{33}	6(1)	5.5(5)
β_{12}, β_{13}	0	0
β_{23}	−3(1)	0.0(4)
	O(2)	O(2)
Position	96(*i*)	96(*i*)
Pop.	96	96
x	0	0
y	0.14493(21)	0.14459(14)
z	0.14583(20)	0.14591(14)
β_{11}	25(1)	23.9(6)
β_{22}	13(1)	11.1(1.0)
β_{33}	5(1)	10.8(1.0)
β_{12}, β_{13}	0	0
β_{23}	7(1)	?
	O(3)	O(3)
Position	192(*j*)	192(*j*)
Pop.	192	192
x	0.05480(18)	0.05379(9)
y	0.05785(19)	0.05865(9)
z	0.17104(7)	0.17152(6)
β_{11}	9(1)	11.6(6)
β_{22}	17(1)	11.9(5)
β_{33}	13(1)	13.6(3)
β_{12}	2(1)	1.8(2)
β_{13}	2(1)	0.6(2)
β_{23}	3(1)	0.1(2)

Note. Anisotropic displacement factor given as $10^4 \exp - h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}$. β_{23} omitted for O(2) in Ref. (*6*).

respectively). Structural parameters are given in Table II.

Because of the success of the refinement in the cubic cell a refinement was attempted in the space group $Pm\bar{3}m$. It is known that this 12.3-Å cell is only a pseudocell since X-ray data (*4, 6*) and electron microscopy (e.g., *23, 24*) often show a 24.6-Å cell. However, Yanagida *et al.* (*25*) stated that their samples of zeolite A showed a 12.3-Å cell and must therefore not have any long-range Si, Al ordering. In addition, Seff and co-workers have had some success in refinement of zeolite A complexes in this pseudocell (e.g., *26–29*).

For the Si, Al scattering length an average value was computed for Si/Al = 1.09 from data in the "International Tables for X-Ray Crystallography" (*21*). Again the total number of sodium ions was constrained to fit the chemical analysis, but the distribution between sites was initially allowed to vary.

Refinement of the zero point on the 2θ scale, cell constant, and half-widths of the diffraction peaks gave $R_{\text{pw}} = 14.8\%$. An

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLE (°) FOR REFINEMENT IN *Fm*$\bar{3}$*c* (esd IN LAST FIGURE IS GIVEN IN PARENTHESES)

Si(1) –O(1)	1.589(11)	O(1) –Si(1)–O(2)	109.5(5)
Si(1) –O(2)	1.598(9)	O(1) –Si(1)–O(3)	111.9(3)
Si(1) –O(3), O(3$^{\mathrm{i}}$)	1.647(6)	O(2) –Si(1)–O(3)	106.8(4)
Al(1) –O(1$^{\mathrm{vi}}$)	1.741(13)	O(3) –Si(1)–O(3$^{\mathrm{i}}$)	109.8(5)
Al(1) –O(2)	1.729(11)	O(1$^{\mathrm{vi}}$)–Al(1)–O(2)	106.1(5)
Al(1) –O(3$^{\mathrm{vii}}$), O(3$^{\mathrm{viii}}$)	1.699(7)	O(1$^{\mathrm{vi}}$)–Al(1)–O(3$^{\mathrm{vii}}$)	112.6(4)
Na(1)–O(3), O(3$^{\mathrm{v}}$), O(3$^{\mathrm{vii}}$)	2.319(4)	O(2) –Al(1)–O(3$^{\mathrm{viii}}$)	105.6(4)
Na(1)–O(2), O(2$^{\mathrm{v}}$), O(2$^{\mathrm{vii}}$)	2.923(4)	O(3$^{\mathrm{vii}}$)–Al(1)–O(3$^{\mathrm{viii}}$)	113.7(6)
Na(2)–O(2)	2.632(24)	Si(1) –O(1)–Al(1$^{\mathrm{xii}}$)	141.4(4)
Na(2)–O(1)	2.561(23)	Si(1) –O(2)–Al(1)	164.1(5)
Na(2)–O(1$^{\mathrm{vi}}$)	2.909(23)	Si(1) –O(3)–Al(1$^{\mathrm{v}}$)	143.5(5)
Na(3)–O(3$^{\mathrm{x}}$)	2.830(28)		
Na(3)–O(1$^{\mathrm{xi}}$), O(1$^{\mathrm{x}}$)	2.842(38)		

isotropic refinement lowered R_{pw} to 13.2%, but it was found that the occupancies of the sodium ions were highly correlated with their temperature factors; consequently their occupancies were fixed at values deduced from the *Fm*$\bar{3}$*c* refinement. Anisotropic refinement converged at R_{pw} = 11.0%, which was equivalent to a conventional *R* of 6.4%. The cell parameter was 12.2966(1) Å. Atomic positions are given in Table III and bonding information in Table IV.

Discussion

From our refinements it is apparent that the sample of zeolite studied here is cubic. A Hamilton statistical test (*30*) was carried out on the hypothesis that the structure in *Pm*$\bar{3}$*m* was correct. The *R* factor used for comparison purposes was R_{pw} = 10.25% for *Fm*$\bar{3}$*c*, 11.03% for *Pm*$\bar{3}$*m*. The number of independent observations was 2804 (i.e., number of data points collected) and the dimension of the problem [15] was the number of parameters in the *Fm*$\bar{3}$*c* refinement [51] minus the number in the *Pm*$\bar{3}$*m* refinement [36]. The test shows that we can reject *Pm*$\bar{3}$*m* at the 95% significance level despite the lower conventional *R* factor for *Pm*$\bar{3}$*m*,

TABLE III

COMPARISON OF REFINEMENT IN SPACE GROUP *Pm*$\bar{3}$*m* WITH PREVIOUS WORK

		Pluth and Smith (*6*)	Subramanian and Seff (*5*)
	Si, Al	Si, Al	Si, Al
Position	24(*k*)	24(*k*)	24(*k*)
Pop.	24	24	24
x	0	0	0
y	0.18351(20)	0.1836(1)	0.1836(2)
z	0.37206(18)	0.3722(1)	0.3718(2)
β_{11}	40(2)	38(1)	32(2)
β_{22}	35(2)	35(1)	27(2)
β_{33}	27(2)	26(1)	17(2)
β_{12}, β_{13}	0	0	0
β_{23}	0.0(2)	3(1)	3(1)
	Na(1)	Na(1)	Na(1)
Position	8(*g*)	8(*g*)	8(*g*)
Pop.	8	7.30(7)	8
x	0.20136(25)	0.1991(2)	0.2014(3)
y	0.20136(25)	0.1991(2)	0.2014(3)
z	0.20136(25)	0.1991(2)	0.2014(3)
β_{11}, β_{22}, β_{33}	67(2)	55(2)	59(3)
β_{12}, β_{13}, β_{23}	21(2)	11(1)	8(2)
	Na(2)	Na(2)	Na(2)
Position	12(*i*)	12(*i*)	12(*i*)
Pop.	2.952	4.38(12)	3
x	0.0	0	0
y	0.44087(114)	0.4290(8)	0.4302(12)
z	0.44087(114)	0.4290(8)	0.4302(12)
β_{11}	194(29)	238(21)	141(27)
β_{22}	59(9)	177(12)	72(12)
	59(9)	177(12)	72(12)
β_{12}, β_{13}	0	0	0
β_{23}	79(13)	−32(7)	−10(9)

TABLE III—*Continued*

		Pluth and Smith (*6*)	Subramanian and Seff (*5*)
	Na(3)	Na(3)	Na(3)
Position	12(*j*)	12(*j*)	12(*j*)
Pop.	0.547	0.81(10)	1
x	0.5	0.5	0.5
y,z	0.23763(374)	0.2087(30)	0.2307(54)
β_{11}		10(56)	51(58)
β_{22}, β_{33}		74(35)	157(6)
β_{12}, β_{23}		0	0
β_{13}		−5(16)	37(41)
B	2.52(1.67)		
	O(1)	O(1)	O(1)
Position	12(*h*)	12(*h*)	12(*h*)
Pop.	12	12	12
x	0	0	0
y	0.22671(22)	0.2275(4)	0.2277(6)
z	0.5	0.5	0.5
β_{11}	69(2)	65(5)	52(7)
β_{22}	69(2)	76(5)	48(7)
β_{33}	37(2)	28(4)	31(6)
β_{12}, β_{13}	0	0	0
β_{23}	0	0	0
	O(2)	O(2)	O(2)
Position	12(*i*)	12(*i*)	12(*i*)
Pop.	12	12	12
x	0	0	0
y	0.29091(13)	0.2910(3)	0.2917(4)
z	0.29091(13)	0.2910(3)	0.2917(4)
β_{11}	93(3)	90(5)	77(8)
β_{22}	39(1)	48(3)	36(4)
β_{23}	39(1)	48(3)	36(4)
β_{12}, β_{13}	0	0	0
β_{23}	23(2)	11(2)	10(3)
	O(3)	O(3)	O(3)
Position	24(*m*)	24(*m*)	24(*m*)
Pop.	24	24	24
x	0.11258(12)	0.1119(2)	0.1123(3)
y	0.11258(12)	0.1119(2)	0.1123(3)
z	0.34226(14)	0.3437(3)	0.3418(4)
β_{11}	54(1)	52(2)	48(3)
β_{22}	54(1)	52(2)	48(3)
β_{37}	52(2)	56(3)	42(4)
β_{12}	8(1)	6(1)	5(2)
β_{13}	7(1)	2(1)	0(2)
β_{23}	7(1)	2(1)	0(2)

although the recent controversy concerning the statistical independence of the intensity data points (*31, 32*) suggests that this conclusion is not definitive. A search of the diffraction profile for reflections allowed in $Fm\bar{3}c$, but not in $Pm\bar{3}m$, disclosed the presence of the 21.9.7 reflexion at ~136° (2θ), and also the conspicuous peak in the difference intensity trace (Fig. 2) at ~27° (2θ) which may be due to the "diagnostic" 5.3.1 line present in $Fm\bar{3}c$ with its 24.6-Å cell, but absent in $Pm\bar{3}m$ (12.3-Å cell).

The only slightly controversial feature shown by the structural parameters is the length of the Na(3)–O bonds (Tables II and IV)—those quoted here are as long (2.9 Å) as those given by Subramanian and Seff (*5*). Pluth and Smith (*6*) have shown that Na(3)–O of about 2.5 Å can be observed in dehydrated Na zeolite A. Amaro and Seff (*29*) and Yanagida and Seff (*25*) pointed out that Na(3) is the least stable Na position and showed that on complexation with ethyne this Na(3) moves 0.9 Å away from the framework oxygen atoms. We propose that the long Na(3)–O distances found by ourselves and by Subramanian and Seff (*5*) are the result of bonding of Na(3) to a small residual amount of water in the α cage.

The successful refinement of the structure in $Pm\bar{3}m$ and $Fm\bar{3}c$ supports the previous conclusions of X-ray crystallographic studies of dehydrated Na zeolite A (*5, 6*) that the structure is cubic. This is contrary to the conclusions of Thomas *et al.* (*1*) and Bursill *et al.* (*14*), who also used powder neutron diffraction as a tool. They found that the diffraction pattern could not be indexed nor the structure refined in $Fm\bar{3}c$, whereas refinement was satisfactory in $R\bar{3}$. The only conclusion possible is that the Si, Al ordering in our sample was not the same as in that of these other workers (*1, 14*). It should also be emphasized here that the previous crystallographic studies which agree on cubic symmetry have disagreed on the Si, Al ordering and have shown either regular Si, Al alternation (*6*) or a complete lack of Si,Al ordering (*5*).

This assertion that the Si, Al ordering in zeolite A must depend upon its mode of preparation appears to contradict recent ^{29}Si nuclear magnetic resonance studies (*11*) which showed that samples of zeolite A prepared by Charnell's method (*12*) or

TABLE IV

INTERATOMIC DISTANCES (Å) AND ANGLE (°) FOR REFINEMENT IN *Pm*$\bar{3}$*m* (esd IN LAST FIGURE IS GIVEN IN PARENTHESES)

(Si, Al)–O(1)	1.660(2)	O(1) –(Si, Al)–O(2)	108.4(2)
(Si, Al)–O(2)	1.655(3)	O(1) –(Si, Al)–O(3)	111.9(1)
(Si, Al)–O(3)	1.677(2)	O(2) –(Si, Al)–O(3)	106.5(1)
Na(1) –O(3)	2.321(4)	O(3) –(Si, Al)–O(3^{i})	111.3(2)
Na(1) –O(2)	2.925(3)	(Si, Al)–O(1) –(Si, Al^{ii})	142.7(2)
Na(2) –O(2)	2.608(14)	(Si, Al)–O(2) –(Si, Al^{iii})	164.1(2)
Na(2) –O(1)	2.732(14)	(Si, Al)–O(3) –(Si, Al^{iv})	144.2(2)
Na(3) –O(1^{v})	2.925(45)		
Na(3) –O(3^{v})	2.914(34)		

Note. Symmetry code for tables: (i) $-x, y, z$; (ii) $-x, y, 1-z$; (iii) x, z, y; (iv) y, x, z; (v) z, x, y; (vi) $x, \frac{1}{2}-z, y$; (vii) y, z, x; (viii) $-y, z, x$; (ix) $z, y, \frac{1}{2}-x$; (x) $\frac{1}{2}-z, y, x^{rad}$; (xi) $z-x, y$; (xii) $-x, z, \frac{1}{2}-y$.

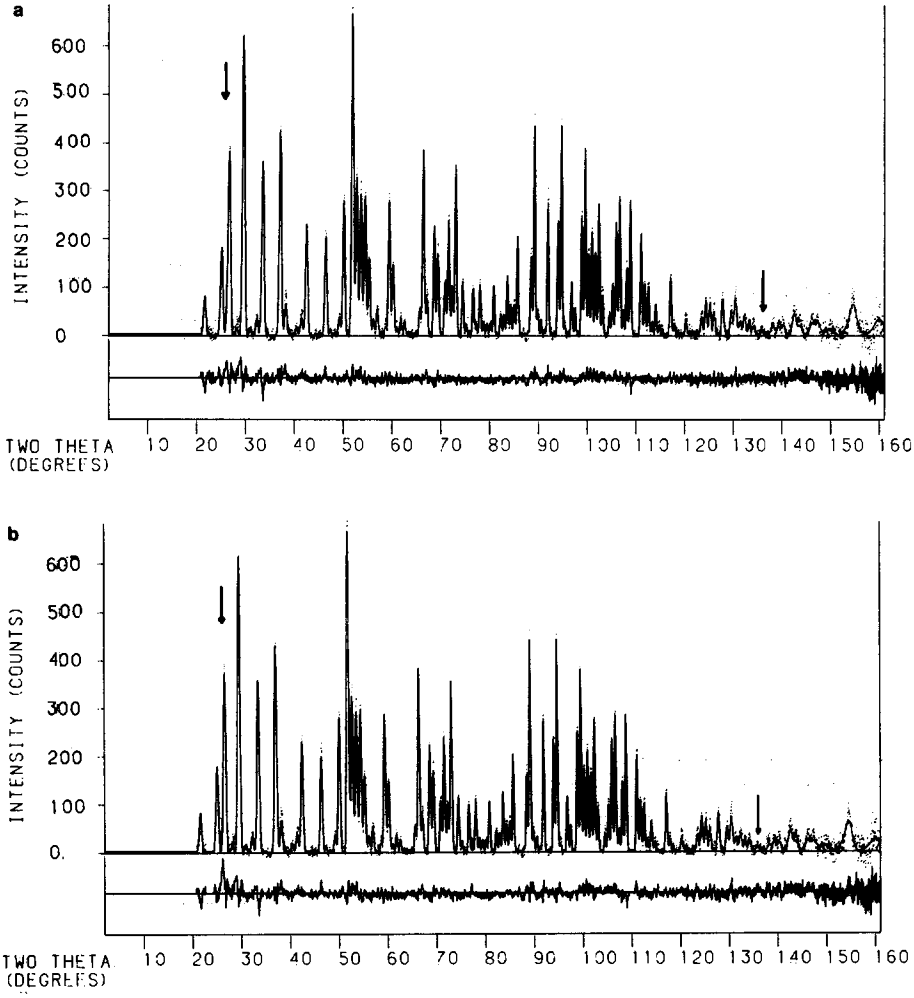

FIG. 2. Observed (· · · ·) and calculated (——) neutron diffraction profiles, together with difference plots, for the dehydrated zeolite at 300K (Si/Al = 1.09). The calculated profiles are those given by refinement in (a) space group *Fm*$\bar{3}$*c* and (b) space group *Pm*$\bar{3}$*m*. The arrow at ~27° (2*θ*) marks the position of the residual intensity peak that may correspond to the 531 reflection (24.6-Å cell). The second arrow at ~136° (2*θ*) on each diffraction trace marks the 21.9.7 reflection (24.6-Å cell). Both of these reflections are allowed in *Fm*$\bar{3}$*c*, but not in *Pm*$\bar{3}$*m* (12.3-Å cell).

from kaolin (*13*) had 3 : 1 Si, Al ordering, which is inconsistent with $Fm\bar{3}c$ or $Pm\bar{3}m$ space groups. However, it should be noted that in studies on the related zeolite sodalite, Englehardt is reported (Ref. *10* in (*11*)) to have *always* found 4 : 0 ordering, whereas Thomas *et al.* (*11*) *always* found 3 : 1 ordering. The conclusion was that for sodalite at least the type of ordering must depend upon the conditions under which it is formed. The neutron diffraction data presented here and by Thomas *et al.* (*1*) show that a similar conclusion must arise for zeolite A.

Acknowledgments

We thank Laporte Industries for the gift of the zeolite sample and the SERC for support.

References

1. J. M. Thomas, L. A. Bursill, E. A. Lodge, A. K. Cheetham, and C. A. Fyfe, *J. Chem. Soc. Chem. Commun.*, 678 (1981).
2. A. K. Cheetham and J. C. Taylor, *J. Solid State Chem.* **21**, 253 (1977).
3. T. B. Reed and D. W. Breck, *J. Amer. Chem. Soc.* **78**, 5972 (1956).
4. V. Gramlich and W. M. Meier, *Z. Kristallogr.* **133**, 134 (1971).
5. V. Subramanian and K. Seff, *J. Phys. Chem.* **81**, 2249 (1977).
6. J. J. Pluth and J. V. Smith, *J. Amer. Chem. Soc.* **102**, 4704 (1980).
7. G. Engelhardt, D. Zeigan, E. Lipmaa, and M. Magi, *Z. Anorg. Allg. Chem.* **468**, 35 (1980).
8. W. Loewenstein, *Amer. Mineral.* **39**, 92 (1954).
9. N. H. Ray, R. J. Plaisted, and S. Johnson, *J. Chem. Soc. Dalton Trans.*, 1260 (1981).
10. E. A. Lodge, L. A. Bursill, and J. M. Thomas, *J. Chem. Soc. Chem. Commun.*, 875 (1980).
11. J. M. Thomas, J. Klinowski, C. A. Fyfe, J. S. Hartman, and L. A. Bursill, *J. Chem. Soc. Chem. Commun.*, 678 (1981).
12. J. F. Charnell, *J. Cryst. Growth* **8**, 291 (1971).
13. D. W. Breck, "Zeolite Molecular Sieves—Structure, Chemistry and Use," pp. 315–316, Wiley, New York (1974).
14. L. A. Bursill, E. A. Lodge, J. M. Thomas, and A. K. Cheetham, *J. Phys. Chem.* **85**, 2409 (1981).
15. H. Bennett and R. A. Reed, "Chemical Methods in Silicate Analysis—A Handbook," pp. 73–79, Academic Press, New York/London (1971).
16. A. W. Hewat and I. Bailey, *Nucl. Instrum. Methods* **137**, 463 (1976).
17. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
18. A. W. Hewat, "Accuracy in Powder Diffraction" (S. Block and C. R. Hubbard, Eds.), pp. 111–142, Natl. Bureau of Standards Spec. Publ. 567, Washington, D.C. (1980).
19. A. W. Hewat, *J. Phys. C.* **6**, 2559 (1973).
20. A. W. Hewat, "The Rietveld Computer Programme for the Profile Refinement of Neutron Diffraction Powder Patterns Modified for Anisotropic Thermal Vibrations," Harwell Report AERE R7350, AERE, Harwell (1973).
21. "International Tables for X-Ray Crystallography," Vol. IV., Kynoch Press, Birmingham, England (1974).
22. L. Katz and H. D. Megaw, *Acta Crystallogr.* **22**, 639 (1967).
23. J. A. Gard, *Proc. Eur. Reg. Conf. Electron Microsc. 2nd* **1**, 203 (1961).
24. L. A. Bursill, E. A. Lodge, and J. M. Thomas, *Nature (London)* **286**, 111 (1980).
25. R. Y. Yanagida, A. A. Amaro, and K. Seff, *J. Phys. Chem.* **77**, 805 (1973).
26. P. E. Riley and K. Seff, *Inorg. Chem.* **13**, 1355 (1974).
27. Y. Kim and K. Seff, *J. Phys. Chem.* **82**, 925 (1978).
28. K. Seff and D. P. Shoemaker, *Acta Crystallogr.* **22**, 162 (1967).
29. A. Amaro and K. Seff, *J. Chem. Soc. Chem. Commun.*, 1201 (1972).
30. W. C. Hamilton, *Acta Crystallgr.* **18**, 502 (1965).
31. A. W. Hewat, "Accuracy in Powder Diffraction," pp. 111–141, NBS Spec. Publ. 567, Washington, D.C. (1980).
32. M. J. Cooper, M. Sakata, and K. D. Roust, "Accuracy in Powder Diffraction," pp. 167–187, NBS Spec. Publ. 567, Washington, D.C. (1980).