The Structure of Iron Oxide Implanted Zeolite Y, Determined by High-Resolution Electron Microscopy and Refined with Selected Area Electron Diffraction Amplitudes

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Abstract: It has been shown for the first time that iron atom positions can be determined inside the framework of zeolite crystals, such as the FAU structure of zeolite Y $[Na_{48}(Fe_2O_3)_{38}][Al_{48}Si_{144}O_{384}]$, by means of electron crystallographic methods for three-dimensional reconstruction from high-resolution electron micrographs and selected area electron diffraction. The iron-containing zeolite with the FAU structure type was refined in the space group $Fd3m$ ($a = 24.7$ Å) with 42 unique reflection amplitudes from electron diffraction. The Fe_6O_n molecule is situated in the sodalite cage with the iron atoms facing the square windows of the cage. The Fe–Fe distance is 3.6 Å and the Fe–O distances to the nearest oxygen atoms in the sodalite cage are close to 2.2 Å. As a verification and a comparison, the structure of $[Na_{48}][Al_{48}Si_{144}O_{384}]$ without iron was also determined by the same method, and the atom positions of the Si/Al network were found to coincide with those of the structure determined from single-crystal X-ray diffraction methods.

Keywords: clusters · electron diffraction · electron microscopy · iron · structure elucidation · ultramicrotomy · zeolites

Introduction

Zeolites are framework aluminosilicate materials with well-defined channels and cavities that are of a suitable size for incorporation of small molecules and clusters. Iron-containing zeolite crystals of the FAU type are of great interest, because they show interesting catalytic properties. The process for the catalytic reduction of NO_x in exhaust gases involves, for example, the use of iron-containing zeolite Y (FAU).[1] Catalytic synthesis of carbon nanotubes, with a fullerene-like structure, has been reported with the use of a zeolite Y catalyst which contains iron or cobalt.[2]

In order to understand the properties of zeolites with incorporated molecules or clusters, the location of these must be determined. Often, single-crystal X-ray diffraction, the most common technique for structure determination, cannot be employed because of the small crystal size of the zeolites. A combination of high-resolution transmission electron microscopy (HRTEM), image processing, and selected area electron diffraction (SAED) is more suitable for small crystals. Recent developments in image recording, such as slow-scan CCD cameras and imaging plates suitable for low dose imaging and linear recording of diffraction patterns, have made it possible to use these techniques for beam-sensitive materials, such as zeolites. Ultramicrotomy of embedded crystalline samples provides large, even and thin (less than 200 Å) areas suitable for SAED. Most structure determinations by HRTEM have been derived from two-dimensional data recorded along a short unit cell axis.[3, 4] The atom positions along the short axis were then deduced from geometrical and chemical considerations. This method is not suited for most zeolites, which have three long unit cell axes. Instead a full three-dimensional reconstruction,[5] combining HRTEM data from several crystallographic directions, is preferable.

In this work HRTEM images and SAED amplitudes have been used to determine the positions of small iron oxide clusters in a zeolite Y with the formula $[Na_{48}(Fe_2O_3)_{38}][Al_{48}$-

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$Si_{144}O_{384}$] (in the following text called (Na,Fe)Y). The same compound without implanted iron oxide, $[Na_{48}][Al_{48}Si_{144}O_{384}]$ (in the following text called NaY) was subjected to the same procedures and the structure was determined as a control experiment. A three-dimensional least-square structural refinement was performed with the observed diffraction amplitudes.

Results and Discussion

For the first time, a crystal structure determination of a partly unknown zeolite structure has been performed with HRTEM images and SAED data to evaluate the amplitude and phases. The preliminary atom positions determined from the inverse Fourier transform were then used in a three-dimensional least-squares refinement of F_o^2 from the diffraction intensities. The results from the two steps of the structure determination are given here.

The structures from inverse Fourier synthesis: In the inverse Fourier determination of the structure of NaY, the silicon (aluminium) atoms were placed on the 192(*i*) position at $x = 0.310$, $y = 0.125$, $z = 0.036$, which deviated only about 0.16 Å from the position at $x = 0.3034$, $y = 0.1254$, $z = 0.0363$ from the X-ray structure determination.[6] The two shortest Si–Si distances were 2.9 and 3.1 Å, which can be compared with 3.1 Å in the X-ray structure determination, and 3.1 Å in quartz.[7] The Si–Si distance of 2.9 Å was unusually short, and indicated a larger uncertainty in the position determination than in the X-ray case. The resolution of the images was not high enough to give clear oxygen positions, even if there was some weak electron density at the expected positions.

For the (Na,Fe)Y structure, the silicon (aluminium) atoms were located on the same position, 192(*i*), with $x = 0.318$, $y = 0.130$, $z = 0.033$; a deviation of 0.39 Å from the X-ray structure of NaY. The two shortest Si–Si distances here were 2.4 and 3.0 Å, which again indicated the larger uncertainty in the determination of the silicon position. The iron atoms were located on the position 48(*f*) at $x = 0.125$, $y = 0.125$, $z = 0.021$, and thus formed an octahedron in the sodalite cage (Figure 1). The Fe–Fe distances within the octahedron were close to 3.6 Å, in reasonable agreement with the value of 2.8–3.3 Å obtained by EXAFS before phase shift,[8] but considerably longer than 2.7–3.1 Å present in bulk iron oxides.[9–12] The oxygen positions within the cluster could not be determined from the inverse Fourier transform. If the framework oxygen atoms were assumed to be in the same position as for NaY, the closest iron-framework oxygen distance would be 2.2 Å. The ionic radius of eight-coordinated Fe^{3+} in a perovskite type structure has been calculated to be 0.90 Å,[13, 14] which gives an Fe–O distance of 2.3 Å, in good agreement with the 2.2 Å obtained above.

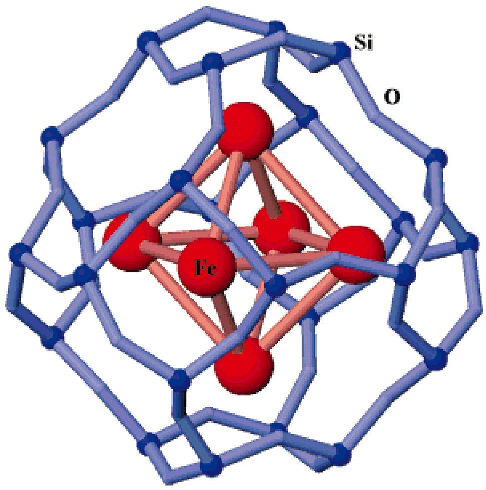

Figure 1. The location of the Fe_6O_n clusters inside a sodalite cage. Perspective view close to [100].

Refinement of the structures NaY and (Na,Fe)Y: The refinement converged for a silicon atom position (Table 1) in NaY, which was 0.16 Å from the position obtained from the inverse Fourier transform (used as the starting point in the refinement) and 0.12 Å from the refined X-ray position. The oxygen atom positions differed by between 0.18 and 1.2 Å from the X-ray positions. The large deviations for the oxygen atoms can be explained by the low resolution and the perturbation in the diffraction amplitudes caused by multiple diffraction as discussed in the Experimental Section.

For the (Na,Fe)Y structure, the refined silicon atom position (Table 1) deviated by 0.29 Å from the position determined from the inverse Fourier transform, and 0.45 Å from the positions determined by X-ray diffraction in NaY. The oxygen atoms deviated by between 0.21 and 1.40 Å from the X-ray coordinates for NaY. The iron atom position (Table 1) refined to a value of 0.25 Å away from the starting point taken from the inverse Fourier transform. The location of the remaining iron atoms (28, when full occupancy at the 48(*f*) position is assumed) in the unit cell could not be determined.

The structure of the lead/lead oxide implanted NaX, $[(Pb^{4+})_{14}(Pb^{2+})_{18}(Pb_4O_4)_8][Si_{100}Al_{92}O_{384}]$, was recently determined by X-ray analysis.[15] In this case the lead oxide cluster Pb_4O_4 was located inside the sodalite cage (with the lead on the 32(*e*) position), with the remaining lead ions distributed over the normal cation positions with low occupancies. It is

Table 1. Positions and isotropic temperature factors for NaY and (Na,Fe)Y as determined by the refinement.

Atom	Wyckoff position	*x*	*y*	*z*	*U* [Å^2]
NaY					
Si	192(i)	0.3055(7)	0.1296(9)	0.0365(9)	0.33(5)
O(1)	96(g)	0.173(8)	0.173(8)	0.975(9)	0.8(2)
O(2)	96(g)	0.201(7)	0.201(7)	0.356(9)	0.6(1)
O(3)	96(g)	0.259(12)	0.259(12)	0.153(13)	1.0(2)
O(4)	96(h)	0.095(5)	0.905(5)	0	0.6(1)
(Na,Fe)Y					
Si	192(i)	0.3125(4)	0.1368(4)	0.0252(4)	0.44(8)
O(1)	96(g)	0.180(9)	0.180(9)	0.971(13)	0.7(2)
O(2)	96(g)	0.186(7)	0.186(7)	0.268(9)	0.6(1)
O(3)	96(g)	0.274(12)	0.274(12)	0.129(15)	0.7(3)
O(4)	96(h)	0.134(21)	0.866(21)	0	0.8(3)
Fe	48(f)	0.125	0.125	0.011(9)	1.2(5)

possible that the remaining iron in the structure studied here was similarly distributed, with occupancies too low to show up in the electron microscopy images or the limited electron diffraction data recorded here.

Conclusions

The iron oxide cluster is hexanuclear, with the iron atoms in an octahedron located inside the sodalite cage. The position of the framework silicon atoms is consistent with the known X-ray structure of NaY, and thus supported the results for the unknown location of the Fe_6O_n clusters. The distances within the cluster are in reasonable agreement with EXAFS measurements published previously.[8] The refined oxygen positions are very uncertain, despite the low standard deviations in the refinement.

Ultrathin sectioning of zeolite crystals gives large areas of even thickness, which is important both for recording the HRTEM images and electron diffraction of beam-sensitive materials, where a large number of unit cells from areas of comparable thickness are required to give a high signal-to-noise ratio. The ultrathin sections can be made sufficiently thin to avoid severe multiple scattering, and enable electron crystallography of materials with low or medium atomic weight.

Combination of HRTEM and SAED is a possible way to determine the structure of small crystals of inorganic materials.[4, 16] The accuracy is not as good as in single crystal X-ray structure refinement and care must be taken with the evaluation of the results, especially for bond lengths and angles. This paper shows that it is possible to obtain atomic positions from electron microscopy, even for zeolites which are very sensitive to electron beams.

Experimental Section

After they were degassed at 673 K, crystals of zeolite NaY were exposed at room temperature to $Fe(CO)_5$ vapour at 273 K, followed by evacuation at room temperature for 10 min. The oxidation of $Fe(CO)_5$ encaged in NaY was carried out at 10 Torr of oxygen in a circulation system (200 cm^3).[8] The oxidation temperature was 258 K initially and was increased at a rate of 0.3 $K\,min^{-1}$. The gas phase was frequently analysed by gas chromatography. After consumption of the gas phase oxygen, the gas phase was evacuated and the temperature was decreased to 258 K again, followed by introduction of oxygen. These procedures were repeated several times until no oxygen consumption was observed at 270 K. Finally the oxidation temperature was raised to 358 K and maintained for 12 h to ensure complete oxidation of iron. The $Fe(CO)_5$ adsorption and oxygen treatment was repeated in order to achieve a high concentration of iron inside the crystals. The maximum concentration reached was about 76 $FeO_{1.5}$ per unit cell, according to energy dispersive X-ray spectroscopy (EDX) analysis of several crystals. Crystals of (Na,Fe)Y and NaY were dried at 300 °C for 24 h and embedded in an epoxy resin (Spurr).[17] Polymerisation was performed at 343 K for 16 h followed by room temperature curing for at least one week. Ultrathin sections, less than 200 Å, were prepared with an ultramicrotome (Leica Ultracut UCT) equipped with a diamond knife and the sections were supported on lacy carbon film on copper grids. The ultrathin sectioned samples were investigated in a JEM-4000EX electron microscope which operated at 400 kV with a structural resolution of about 1.6 Å ($Cs = 1.0$ mm, $Cc = 2.7$ mm, spread of focus about 60 Å and semi convergence angle 0.50 mrad). Structure images were recorded (two examples are shown in Figure 2) at 250000 times magnification (3.3 pixels/2 Å) with a slow-scan CCD camera (Gatan 694). The slow-scan CCD camera was also used for focusing, which allowed very low electron doses. Diffraction patterns from the same crystals used for the HRTEM images were also recorded on the slow-scan CCD camera, with the smallest condenser aperture and the smallest spot size of the microscope (Figure 3). Care was exercised to avoid saturation of the CCD camera. Some diffraction patterns of the NaY sample were recorded on imaging plates in a JEM-1250 HVEM electron microscope (Tohoku University, Japan) which operated at 1250 kV with a structural resolution of 1.0 Å.

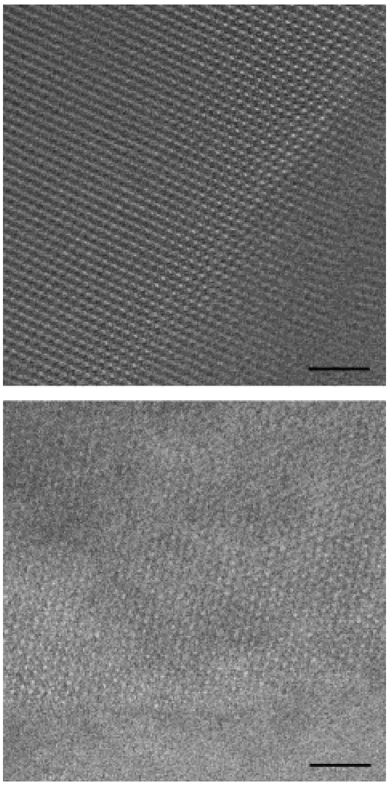

Figure 2. HRTEM images of NaY (top) and (Na,Fe)Y (bottom) along [110] recorded close to Scherzer defocus with a slow-scan CCD camera. The bar represents 100 Å

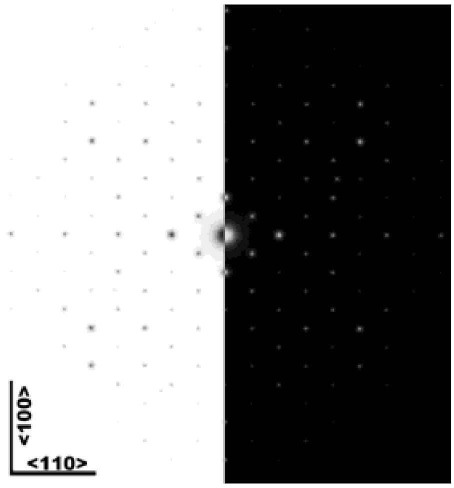

Figure 3. SAED pattern of NaY along [110] recorded with a slow-scan CCD camera. The logarithm of the original intensity is shown and the centre spot is attenuated, and half the image has inverted contrast, in order to show the weak spots.

Structure determination: NaY is cubic, space group *Fd3m* ($a = 24.7$ Å) if no Si/Al ordering is assumed.[6] The iron-containing zeolite was assumed to have the same space group, which was consistent with the symmetry of the images and recorded diffraction patterns. For NaY crystals, two different directions, [110] and [111], were imaged, which resulted in 57 reflections out of 101 unique reflections and extended to a resolution of 1.7 Å. For crystals of (Na,Fe)Y only the [110] direction was recorded, to give 38 reflections out of 67 unique reflections and extended to a resolution of 2 Å. The lower resolution in the latter case is due to the higher sensitivity of (Na,Fe)Y to the electron beam, which gave a lower signal-to-noise ratio in the images, and thus fewer of the weak reflections could be extracted from the slow-scan CCD-recordings.

The image processing was performed with the Semper software (Synoptics, Ltd.). The images were Fourier transformed in each case and corrected for the effect of the contrast transfer function (CTF) of the objective lens. The focus was estimated from the Fourier transform of the amorphous material present on the surface of the zeolites. Both the amplitudes and the phases of the diffraction peaks were affected by the CTF. In areas where the CTF was positive, atoms were imaged as white, and in areas where the CTF was negative, atoms were imaged as black. Amplitudes were dampened by multiplication with the value of the CTF. Only the position of the zeros in the CTF, and not its actual shape influenced the final result in this case, since the image amplitudes were replaced with measured diffraction amplitudes in the reconstruction and only the phases of the reflections were extracted from the images. Nevertheless, full correction with a Wiener filter[18] was performed to check that all images gave comparable results. Amplitudes and phases of the diffraction peaks with a signal-to-noise ratio of more than three were extracted from the focus-corrected Fourier transform. The origin was shifted to the correct phase-origin of the projection and the symmetry of the projection was imposed on the amplitudes and phases, and the phases (0 or π) extracted. Amplitudes were then measured from the SAED patterns. The background was subtracted from the recorded patterns, the integrated intensities in the whole diffraction spots were measured, the amplitudes (square root of intensity) calculated and the correct space group symmetry imposed. The amplitudes from different SAED patterns were scaled to each other by use of common reflections and the average was calculated. The extracted diffraction amplitudes were combined with image phases (Table 2).

Simulations[19] performed for NaY and (Na,Fe)Y showed that multiple diffraction in these zeolites starts to alter the relative amplitudes of the reflections at thicknesses above 200–300 Å for 400 kV accelerating voltage. Calculations for the zeolite mordenite give comparable values for thickness.[20] The section thickness was estimated to be around 150 Å for the samples used in the structure determination, based on the settings of the ultramicrotome and the relative intensities of the reflections in the diffraction patterns. Diffraction patterns recorded at 400 kV and 1250 kV, where multiple diffraction should be less noticeable, showed a similar intensity distribution with around 30 % difference after scaling between the most affected diffraction peaks, which further supports the observation that the influence of multiple diffraction is small. Images of several crystals

Table 2. Observed and calculated structure factors for NaY and (Na,Fe)Y.

			(Na,Fe)Y						NaY		
h	*k*	*l*	F^2_{obs}	F^2_{calc}	P_{obs} [°]	*h*	*k*	*l*	F^2_{obs}	F^2_{calc}	P_{obs} [°]
1	1	1	342646	273413	180	1	1	1	209398	171719	180
1	1	3	39069.5	26163.1	180	0	2	2	159464	58704.4	0
1	3	3	24894.5	21438.8	180	2	2	2	902	883.278	180
3	3	3	19477	42308.4	0	1	1	3	15245	24749.6	0
0	0	4	2204.3	1843.84	0	1	3	3	14933	25201.6	180
2	2	4	11466.1	11255.1	180	3	3	3	2147	1525.68	180
0	4	4	82374.7	77095.1	180	0	0	4	1634	1356.45	180
2	4	4	5809.49	4135.78	180	2	2	4	2178	2090.32	0
4	4	4	3900	4719.69	180	0	4	4	48470	37353.3	180
1	1	5	14063.6	17849	180	2	4	4	14.8	18.0625	180
3	3	5	36637.8	9700.28	0	4	4	4	2666	1658.93	180
1	5	5	3103.6	7366.79	0	1	1	5	6969	1427.5	0
3	5	5	4208.12	1179.92	0	3	3	5	14047	1299.2	180
5	5	5	87302.5	57955.7	180	1	5	5	1964	479.62	0
2	2	6	6112.11	4202.93	180	3	5	5	466	68.632	180
4	4	6	176.093	224.101	0	5	5	5	43966	3358.8	180
0	6	6	61946.2	9759.46	0	2	2	6	1640	180.43	180
2	6	6	335.256	333.428	180	2	4	6	10747	353.56	180
4	6	6	4304.67	20494.8	180	4	4	6	340	407.636	0
6	6	6	1966.92	2095.81	0	0	6	6	7041	4116.51	0
3	3	7	4511.82	3374.45	0	2	6	6	135	110.04	0
5	5	7	4919.62	6098.05	0	4	6	6	4750	6689.6	180
1	7	7	512.117	834.054	0	6	6	6	794	536.386	0
3	7	7	5238.86	534.534		1	1	7	977	784.56	0
0	0	8	4120.36	5314.41	180	3	3	7	2832	3152.82	180
2	2	8	5345.07	8152.28	0	5	5	7	5256	2158.53	180
4	4	8	2907.37	5262.05	0	1	7	7	155	198.246	180
6	6	8	1565.78	1977.58		3	7	7	422	232.563	0
0	8	8	5563.67	1613.63		5	7	7	93.1	199.092	0
8	8	8	298.944	299.29		7	7	7	42.4	60.0625	0
1	1	9	82.81	77.44	0	0	0	8	515	371.333	180
3	3	9	843.902	842.322	0	2	2	8	1894	1863.65	0
5	5	9	324.72	223.802	0	4	4	8	1734	2439.37	0
3	9	9	469.156	425.597		2	6	8	746	1002.36	0
2	2	10	803.156	1551.57	0	6	6	8	385	37.21	0
1	1	11	894.608	1440.96	180	0	8	8	2517	1156	0
3	3	11	827.138	910.229	0	2	8	8	137	76.7376	
0	0	12	8952.94	5102.25	180	4	8	8	249	689.063	180
2	2	12	279.224	260.177		6	8	8	7.73	7.29	0
4	8	8	428.49	402.805		8	8	8	137	128.823	180

Table 2. Continued.

			NaY		
h	*k*	*l*	F^2_{obs}	F^2_{calc}	P_{obs} [°]
1	1	9	174	92.7369	0
3	3	9	413	628.505	180
5	5	9	61.8	47.4721	0
7	7	9	11.1	18.49	
1	9	9	63	211.412	0
3	9	9	93.9	25.5025	
5	9	9	71.7	105.473	
7	9	9	23.7	4.9729	
9	9	9	0.98	0.4356	
2	2	10	49.6	46.7856	180
4	4	10	134	198.528	0
4	6	10	22.1	29.2681	0
6	6	10	30.4	2.9584	0
2	8	10	122	176.093	0
8	8	10	5.9	0.16	
0	10	10	258	304.503	180
2	10	10	21	8.4681	
4	10	10	1.25	0.49	
6	10	10	5.81	0.5184	
1	1	11	443	1013.15	180
3	3	11	469	182.52	
5	5	11	114	142.803	180
7	7	11	22.7	11.6281	
9	9	11	11.4	6.8644	
1	11	11	70.1	121	
5	11	11	34.5	11.0889	
0	0	12	6300	4386.41	
2	2	12	126	258.245	0
4	4	12	15.5	42.25	0
6	6	12	38.3	20.6116	0
4	8	12	48	20.7025	180
8	8	12	28.4	13.9876	
2	10	12	4.33	0	0
0	12	12	50.1	55.6516	
1	1	13	5.34	27.8784	180
3	3	13	13.2	30.8025	
5	5	13	3.28	1.5129	
2	2	14	32.3	11.2896	
6	8	14	5.81	11.0889	
2	12	14	4.33	2.7556	
1	1	15	1.66	3.9204	
2	2	16	3.61	10.9561	
4	4	16	11	0.5041	
6	6	16	56.9	28.5156	
8	8	16	5.76	0.9025	
1	1	17	13	5.8564	
5	5	17	42.1	12.1104	

(eight different crystals for NaY and five for (Na,Fe)Y) from different sections and recorded at different defoci showed the same measured phases (0 or π since the structure is centrosymmetric) after focus correction. The only exceptions were four weak reflections for NaY, and two for (Na,Fe)Y. This consistency is important since a phase reversal for a single strong reflection can change the appearance of the calculated crystal structure completely. The maximum difference in diffraction intensities between crystals in different ultramicrotomy sections was 26% after scaling. The known structure of the zeolite framework for NaY also provides a method to determine the reliability of the structure analysis by comparison of the silicon atom positions from the inverse Fourier transform with those from the X-ray determination. The three-dimensional crystal potential (structure) was finally calculated by an inverse Fourier transform. The position of the atoms, both iron and silicon (aluminium and silicon are disordered and cannot be distinguished), were directly determined from the positions of the peak intensities in the three-dimensional images for both the structures NaY and (Na,Fe)Y (Figure 4). The resolution in the images is not good enough to show the oxygen positions.

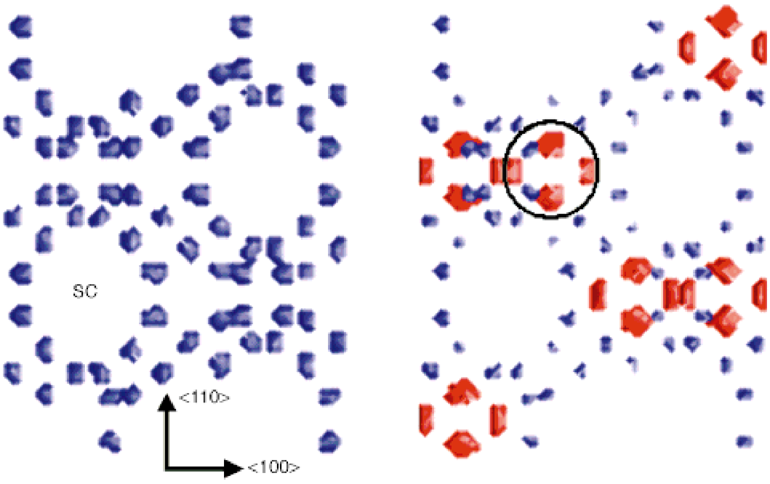

Figure 4. Three-dimensional reconstruction, inverse Fourier transform, of one unit cell of NaY (left) and (Na,Fe)Y (right) projected along [110]. SC denotes one super cage and the location of one Fe_6O_n cluster is marked with a circle in the right figure.

In an attempt to determine the oxygen positions, a least square refinement was initiated with the SAED intensities, with the SHELXTL crystallographic software system refining on F^2_o.[21] The SAED data extended out to a resolution of 1.3 Å for NaY (87 unique reflections) and 1.8 Å for (Na,Fe)Y (42 unique reflections). The atomic scattering factors for electrons[22] were used in the refinement. The atomic parameters for the framework (silicon and oxygen atoms) for NaY and for the framework and the iron atoms of the iron-containing (Na,Fe)Y were refined with isotropic temperature factors. The atomic positions from the inverse Fourier transform model were used as the starting coordinates for the silicon and iron atoms, and the X-ray coordinates were used for the oxygen atoms. Both the models converged with *R* values of 0.22 for NaY and 0.26 for (Na,Fe)Y. These *R* values are high compared with the values from the X-ray structure refinement, but quite typical of electron diffraction refinements.[23] Some attempts were made to refine the iron atom occupancy, but although a lower occupancy reduced the *R* value somewhat, the refinement was not stable. A subsequent difference Fourier synthesis revealed several residual peaks. Because only 60% of the iron atoms were found and no sodium positions were localised, several attempts to refine the residual positions were performed, but the refinements were unstable. The observed diffraction intensities were used without Lorentz correction (as indicated by Dorset[24]), and without correction for absorption, multiple scattering or the curvature of the Ewald sphere. The final structural parameters for NaY and (Na,Fe)Y are presented in Table 1. The observed and calculated squared structure factors together with the observed phases from the images are given in Table 2.

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