Zeolite-directed Growth of a Potassium Superlattice

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A potassium superlattice has been observed in zeolite A in which growth is dictated by the intrinsic topological constraints of the host zeolite.

The possibility of engineering filamentary networks and cluster arrays in the intracrystalline channels and cavities of nanoporous zeolites was highlighted by Barrer.[1] Among the oldest examples of such materials are the inclusion compounds of alkali metals in zeolites,[2–4] whose geometric and electronic structures remain largely unexplored. Here we describe the preparation and characterization of potassium zeolite A saturated with potassium metal, and find a zeolite-directed potassium superlattice having fewer than five potassium valence electrons for every 17 cations. Spontaneous segregation into electron-rich and predominantly cationic zones may also reflect an incipient insulator-to-metal transition within the zeolite host.

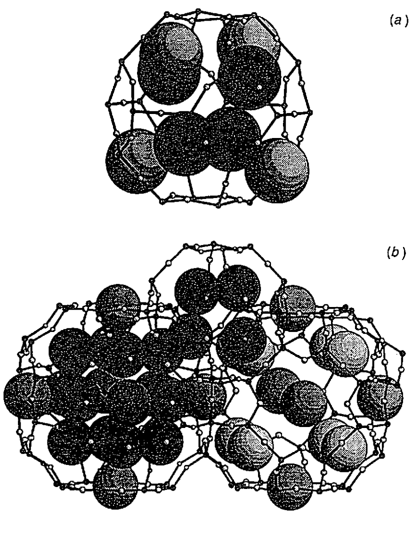

Fig. 1 Structure of K_5/K_{12}-A. (*a*) Sodalite cage in K_5/K_{12}-A, showing a tetrahedron of K(3) ions inside the cage (dark circles) with faces capped by a tetrahedron of K(1) ions outside the cage (pale circles). (*b*) Fragment of the structure showing neighbouring α-cages and a sodalite cage (different shadings represent the different ionic sites). The much less open structure of the left-hand cage containing K(4) is readily apparent.

The green–brown solid K_5/K_{12}-A was prepared through the reaction, in a sealed evacuated quartz tube, of dehydrated potassium LTA (K_{12}-A) with a calibrated amount of potassium vapour (equivalent to five potassium atoms per primitive unit cell) at temperatures between 200 and 250 °C.[3,5] A small amount of unreacted potassium forming a mirror on the surface of the tube indicated that the product was saturated with metal. Time-of-flight neutron powder diffraction data were collected at room temp. on the POLARIS diffractometer at the ISIS pulsed source at the Rutherford Appleton Laboratory.

The starting model for the structure refinement used the primitive cubic space group $Pm\bar{3}m$, and included framework atoms and the principal potassium sites K(1) at (0.23, 0.23, 0.23) and K(2) at (0, x,x)($x \approx 0.5$).[6] Difference Fourier methods were used to locate further potassium sites in the sodalite cage around (0.13, 0.13, 0.13) [K(3)], and in the α-cage at approximately (0.25, 0.25, 0.5) [K(4)]. All four potassium sites are known in dehydrated K_{12}-A,[6,7] and may be regarded as primarily ionic in character. Importantly, no distinction can be drawn between potassium originally present in the zeolite and that absorbed from the vapour phase. Presumably in return for a framework coordination site, the incoming 'guest' potassium atoms give up their valence electrons which then interact with the framework cations. The profile fit in this model contains a significant number of supercell reflections. The standard supercell in zeolite A involves Si and Al ordering (space group $Fm\bar{3}c$);[8] this gives an improved refinement but, importantly, the prominent supercell reflections are not fitted by this model.

The refined occupancies of sites K(1), K(3) and K(4) were all close to 0.5. An impossibly short K(1)–K(3) separation of 2.1 Å across the six-rings of the sodalite cage prevents occupation of adjacent sites and this intrinsic topological constraint leads to cation ordering. The most energetically favourable arrangement is a tetrahedron of K(3) ions with faces capped by a further tetrahedron of K(1) as illustrated in

Table 1 Final crystallographic data for K_5/K_{12}-A at room temp.[a]

Atom	Wyckoff symbol	x/a	y/b	z/c	B_{11}/Å^2	B_{22}/Å^2	B_{33}/Å^2	B_{23}/Å^2	B_{13}/Å^2	B_{12}/Å^2	B_{iso}/Å
Si/Al	192l	0.75	0.8430(2)	0.9389(1)	0.4(1)	0.7(1)	0.6(1)	0.1(1)	0.1(2)	0.1(2)	
O(1)	96j	0.0	0.8731(2)	0.7450(2)	1.8(2)	1.0(1)	1.5(2)	0.9(2)			
O(2)	96k	0.8915(1)	0.8915(1)	0.7539(3)	0.8(1)	0.8(1)	1.5(2)	−0.5(1)	0.5(1)	1.0(1)	
O(3)	96k	0.8053(2)	0.8053(2)	0.9327(2)	2.3(2)	2.3(2)	1.1(2)	−0.3(1)	−0.3(1)	−0.1(3)	
O(4)	96k	0.3070(2)	0.3070(2)	0.4280(3)	1.3(1)	1.3(1)	1.8(2)	0.4(1)	0.4(1)	0.1(2)	
K(1)	32f	0.8676(4)	0.8676(4)	0.8676(4)	2.1(3)	2.1(3)	2.1(3)	0.5(3)	0.5(3)	0.5(3)	
K(2)	96k	0.0069(10)	0.0069(10)	0.75							0.0(7)
K(3)	32f	0.3177(3)	0.3177(3)	0.3177(3)	2.0(2)	2.0(2)	2.0(2)	1.4(3)	1.4(3)	1.4(3)	
K(4)	48i	0.5	0.3727(3)	0.3727(3)	0.3(6)	2.6(4)	2.6(4)	−0.4(4)			

[a] Cubic: space group $Fm\bar{3}m$ (no. 225); a = 24.6324(2) Å; R_{wP} = 2.9%; R_E = 2.3% R_I = 6.2%. All sites fully occupied except for K(2) with an occupancy of 0.140(10). An Si : Al ratio of 1 : 1 was assumed.

$$R_{wP} = \left[\frac{\sum_i w_i[|y_i(\mathrm{obs.}) - y_i(\mathrm{calc.})|]^2}{\sum_i w_i y_i^2(\mathrm{obs.})}\right]^{\frac{1}{2}}; \quad R_E = \left[\frac{N - P + C}{\sum_i w_i y_i^2(\mathrm{obs.})}\right]^{\frac{1}{2}}; \quad R_I = \left[\frac{\sum_k |I_k(\mathrm{obs.}) - \frac{1}{c} I_k(\mathrm{calc.})|}{\sum_k I_k(\mathrm{obs.})}\right]$$

where N, P and C are the number of observations, parameters and constraints, respectively.

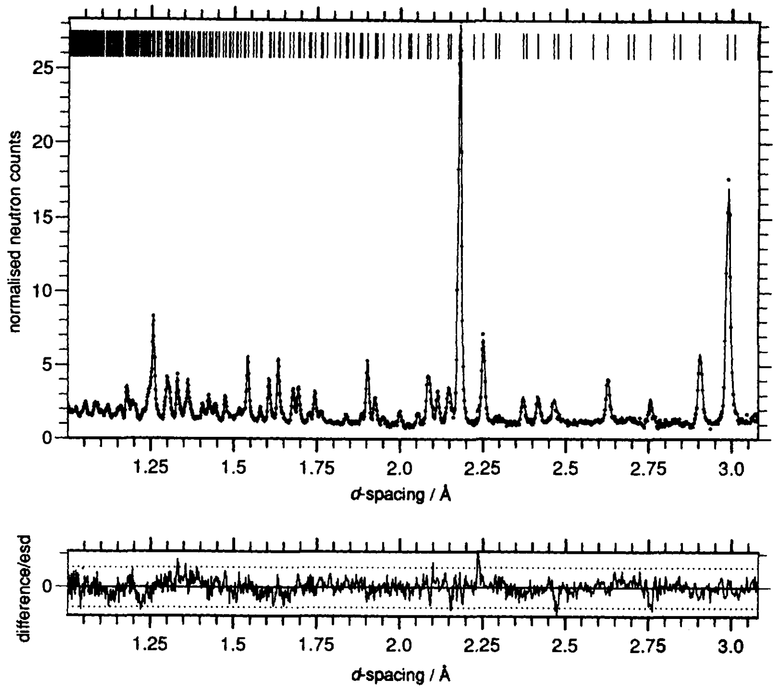

Fig. 2 Observed and calculated diffraction profiles for K_5/K_{12}-A in space group $Fm\bar{3}m$

Fig. 1. On average each α-cage contains four K(1) and six K(4), which would require short K(1)–K(4) interactions of 3.3 Å. Further ordering with alternate α-cages containing either eight K(1) or 12 K(4), was accommodated in space group $Fm\bar{3}m$, (assuming Si/Al disorder) and gave a significantly improved refinement, successfully fitting all superlattice reflections as shown in Fig. 2. Final crystallographic data are shown in Table 1.

The observation that included potassium in K_5/K_{12}-A is found in ionic sites is consistent with previous EPR results which reflect the spontaneous ionization of alkali-metal atoms on entering potassium zeolites.[3,9] The cations of dehydrated K_{12}-A represent a more or less regular array into which precise numbers of electrons may be injected through reaction with controlled amounts of potassium vapour.[5] In zeolites X, Y and A excess electrons are often trapped in paramagnetic centres (directly analogous to crystalline F-centres) located in the sodalite cages.[2,3,9–11] In K_5K_{12}-A the single-line EPR spectrum (g = 1.9978, ΔH_{pp} = 21.6 G) testifies to a high degree of delocalization of the excess electron spins over large areas of the potassium lattice. It is important to stress that only five valence electrons for 17 potassium ions leads to a net charge in excess of +0.7 per cation.

However, the distribution of potassium in K_5/K_{12}-A is inhomogeneous: the α-cages containing eight K(1) retain the structure of the parent zeolite, whilst those containing 12 K(4) are much more densely packed [Fig. 1(*b*)]. Both the EPR *g*-value and the K–K nearest-neighbour distances in the denser region of the structure are comparable to those observed in the bulk metal.[12,13] These K–K distances fall in the range 4.238(3)–4.884(3) Å compared with a value of 4.54 Å for potassium metal.[13] Bond valence sums (BVS) for potassium have been calculated using the method of Brown.[14] Whilst these should be treated with some caution,[14] K(1) and K(3) are directly comparable since both coordinate to the 6-rings of the sodalite cage. Interestingly, whereas K(1) (BVS = 1.00) behaves as K^+, the value for the tetrahedron of K(3) (0.78) is close to that expected for K_4^{3+} (0.75). Although the low value for K(4) (0.50) in part reflects its lower coordination number, these ions appear electron-rich compared with K(1). Apparently both electronic and structural segregation has occurred in K_5/K_{12}-A, with half the α-cages remaining as pristine pockets of dehydrated zeolite with the excess electrons confined to a cationic network located in the sodalite cages and the more densely occupied α-cages.

As structural instability and phase separation are frequent harbingers of an incipient metal–insulator transition[15] the potassium ordering observed in K_5/K_{12}-A may be electronically as well as structurally driven. EPR,[5] NMR[16] and preliminary magnetic susceptibility measurements already demonstrate the importance of antiferromagnetic ordering, with few (<1%) unpaired electron spins contributing to the observed paramagnetism.[17]

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