Neighbour and next-nearest neighbour tetrahedral site determinations in framework materials by EXAFS

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Gallium K-edge EXAFS is used to investigate the local geometry in a framework material and the nature of the nearest- and second nearest-neighbour tetrahedral sites determined.

The majority of framework structures formed from linked tetrahedral units are aluminosilicates with an upper limit on the Al to Si ratio of 1 : 1. The replacement of aluminium by gallium in such frameworks has recently been of interest due to improved catalytic activity.[1,2] In both silicon-rich aluminosilicates and gallium containing structures the distribution of the tetrahedral species is of great interest particularly as this influences the active-site distribution and pore sizes in the catalytic forms of the framework material. The main techniques used for determining site distributions in these materials have been neutron diffraction, for long-range order, and ^{29}Si solid-state MAS NMR. MAS NMR is routinely used to probe the local silicon and aluminium environments through measurements of the chemical shift which depends markedly on the nature of the four neighbouring tetrahedral atoms.[3] Newsam[4] has attempted to extend the analysis of chemical shifts to the determination of the second-nearest tetrahedral neighbour but the important effects of the changing framework geometry, *e.g.* Al–O–Si bond angle, as aluminium locally replaces silicon cannot be integrated.

Gallium K-edge EXAFS[5] has been used to probe whether gallium was incorporated into framework tetrahedral sites but this work provided no information on the nature of the neighbouring tetrahedral atoms. As a quadrupolar nucleus ^{71}Ga produces broad MAS NMR peak widths and chemical shift ranges for different local environments are not easily resolved. In this paper we have, for the first time, used EXAFS to probe both the nearest-neighbour and next-nearest-neighbour identities in a framework which is long-range disordered but where local ordering occurs.

Gallobicchulite, $Ca_8(Ga_2SiO_6)_4(OH)_8$, was prepared hydrothermally as described previously.[6] Gallium K-edge absorption data were collected on station 7.1 at the SRS Daresbury operating in transmission mode. Background subtraction was undertaken using PAXAS[7] and data analysis carried out using EXCURV92.[8]

$Ca_8(Ga_2SiO_6)_4(OH)_8$ has a sodalite type framework with long-range disorder of the gallium and silicon atoms as shown by neutron diffraction.[6] However, ^{29}Si MAS NMR data from this material, consisting of a single resonance, demonstrated that each silicon was surrounded by four GaO_4 tetrahedra. This contrasts markedly with the spectrum that would be expected from a disordered framework. The sodalite framework topology is shown in Fig. 1; only one crystallographically distinct tetrahedral site is present. The immediate coordination environment of a tetrahedral species (T; T = Ga in this study) consists of four $T'O_4$ groups with a T to T′ distance of 3.2 Å. In a fully disordered framework the composition at this site would reflect the overall stoichiometry of the material; for gallobicchulite $2\frac{2}{3} : 1\frac{1}{3}$ Ga : Si. However, the ^{29}Si MAS NMR data show that Ga–O–Ga linkages are avoided as far as possible[6] and therefore this nearest-neighbour site composition is unlikely to reflect the compound stoichiometry.

The initial stage of the EXAFS analysis involved refinement of the first three coordination shells to probe the composition of this site. The backscattering from gallium and silicon are sufficiently different that the composition of the nearest tetrahedral site should be readily apparent. The EXAFS data were fitted initially using three shells, oxygen at approximately 1.8 Å, silicon/gallium at 3.2 Å and calcium at 3.6 Å. As coordination numbers are highly correlated with Debye–Waller factors in EXAFS the values for the Si/Ga shell were initially fixed at a reasonable value, $A = 0.01$ Å^2. Various Ga/Si ratios were input into the refinement in order to obtain the best fit to the data. Fig. 2 shows the variation of the fit factor, R_f, as a function of this Si/Ga ratio, with refinement of the oxygen distance/temperature factor, calcium distance/temperature factor and the Si/Ga shell distance. The shape of this curve changed

Table 1 Structural model used in the final fit to the Ga K-edge EXAFS data. e.s.d.s for refined parameters are given in parentheses; CN = coordination number, r = distance, A = Debye–Waller factor

Shell	Atom	CN	r/Å	A/Å^2
1	O	4	1.828(1)	0.006(0)
2	Si	3	3.198(11)	0.027(4)
3	Ga	1	3.215(3)	0.004(1)
4	Ca	4	3.643(8)	0.017(2)
5	O	12	3.77(1)	0.027(3)
6	Ga	1	4.46	0.027(17)
7	Si	1	4.46	0.027(17)
8	O	4	4.75(7)	0.020(13)
9	O	4	4.85	0.024(33)
10	Ca	4	4.895	0.026(9)
11	O	8	5.224(14)	0.012(6)
12	Si	2	5.47	0.040(11)
13	Ga	6	5.47	0.040(11)
14	O	8	5.873	0.007
15	Ca	4	5.95	0.051
16	O	8	6.02	0.004

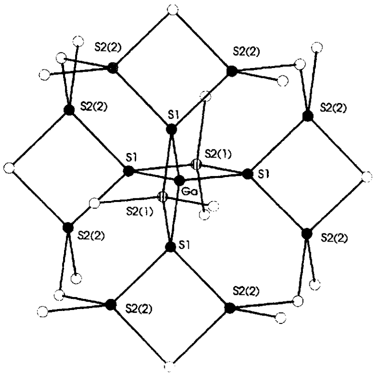

Fig. 1 The framework topology of the sodalite structure. The central black atom represents Ga. The first coordination shell of tetrahedral atoms is shown in dark grey and is labelled S1. The second tetrahedral shell is shown in pale grey and the two distinct distances labelled S2(1) (hatched) and S2(2) (solid). The empty circles are the third tetrahedral shell.

little as a function of the thermal factor applied to the Ga/Si site though the absolute values of R_f were modified. The best fit is clearly seen with a Ga/Si ratio close to 1:3 significantly different from that expected from a completely disordered model ($2\frac{2}{3}:1\frac{1}{3}$ Ga:Si). The distribution of gallium and silicon in this structure is not random and this refined stoichiometry probably reflects the minimisation of the number of Ga–O–Ga linkages. With a 2:1 Ga:Si ratio Ga–O–Ga links are unavoidable; however, these may be minimised by surrounding each silicon by four galliums, maximising the number of Si–O–Ga links and consequently reducing the occurrence of Ga–O–Ga units as far as possible. One model for calculating the likely number of silicate tetrahedra surrounding each gallium would be to start from a perfectly ordered 1:1 Si:Ga array and replace of the silicon atoms by gallium. This would produce an array with no Si–O–Si links. The resultant average gallium coordination would be $Ga(-OSi)_{2\frac{2}{3}}(-OGa)_{1\frac{1}{3}}$ in close agreement with the experimentally determined value. An additional point is that the first shell around gallium, the four oxygens forming the GaO_4 tetrahedron, refined at a distance of 1.83 Å; this value is markedly different from the averaged T–O distance found previously (1.77 Å) but as expected for a Ga–O bond.[6]

Further analysis of the data included more shells with the object of obtaining information on more distant tetrahedral sites. Addition of all these shells produced significant improvement in the fit to the data (typically R_f decreased by 1–2% per shell), greater than that expected using Joyner's tests[9] though such tests are not really applicable to this system where the parameters defining a shell are already known largely from the crystallographic data. The Ga:Si ratio on the nearest-neighbour site was held at that corresponding to the best fit to the first three shells at Ga:Si = 1:3, though a better fit to the data was obtained by allowing this site to become two shells with a slightly more distant gallium, reflecting the expectation that Ga–O–Ga links are longer than Ga–O–Si. The thermal factors for these two sites diverged producing a high value for the silicon shell, though this value was strongly correlated with that of the gallium and these values are probably not physically significant.

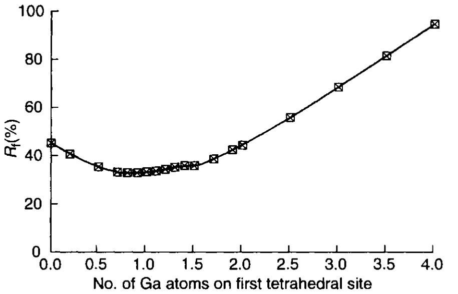

Fig. 2 Variation of R_f as a function of the number of gallium atoms on the nearest tetrahedral site

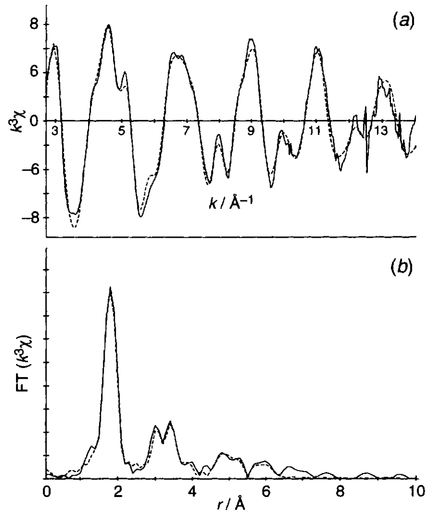

Fig. 3 (a) Fit to the k^3 weighted Ga K-edge EXAFS; (b) Fourier transform. In both plots the experimental data are shown as a complete line and the theoretical fit as the broken line.

Further shells were introduced at distances derived from the refined structure, in most cases the shell distance was fixed at the value obtained from the crystallographic data though for some framework oxygen atoms it was necessary to permit refinement probably a consequence of the local framework geometry around gallium being relaxed and extended from that of the 'average' Si/Ga site.

In the sodalite structure the next-nearest tetrahedral neighbours are at two distances. One distance, 4.46 Å, corresponds to the distance across a four-ring and there are two such sites; the second distance, 5.47 Å, corresponds to T–O–T–O–T distances across part of the six-ring with eight such sites, Fig. 1.

Attempts to refine the stoichiometry of the 4.46 Å shell were unsuccessful presumably due to the low coordination number and proximity of two other shells (calcium and oxygen) and the composition of this site fixed at Si:Ga = 1:1. However, the 5.47 Å shell refined clearly (R_f 1–2% below pure gallium or pure silicon on this site) to a stoichiometry close to 6Ga:2Si. This value would seem reasonable given the stoichiometry of the first tetrahedral sites (3Si:1Ga) and the avoidance of Si–O–Si links.

This is the first determination of next-nearest neighbour sites in a framework material. The best fit achieved to the Fourier transformed Ga K-edge EXAFS data is shown in Fig. 3, R_f = 16.84% and this was obtained by fitting shells out to 6.1 Å. Note that additional features in this spectrum are apparent out to 8 Å, in some cases corresponding to more distant tetrahedral sites and it may be possible to obtain information, but less reliably, on the gallium and silicon distributions at these distances. The local gallium environment determined for this long-range disordered material is that of an uncompressed GaO_4 tetrahedron surrounded by the maximum level of silicon achievable for the compound stoichiometry; this model for the gallium site could be used in the interpretation of enhanced catalytic activity in gallium doped zeolites.

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