

Structure of Na_4^{3+} in Sodium Zeolite YA. R. Armstrong,[†] P. A. Anderson,[‡] L. J. Woodall,[‡] and P. P. Edwards[‡]School of Chemistry, University of Birmingham
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The growing interest in the inclusion compounds of the alkali metals in zeolites stems from their potential use as basic catalysts¹ and increasingly from a rich variety of observations relating to their electronic, magnetic and optical properties.^{2–8} A considerable volume of electron spin resonance (ESR) investigations has demonstrated the existence of a range of brightly colored paramagnetic centers— $\text{K}_m^{(m-1)+}$ and $\text{Na}_n^{(n-1)+}$ ($m = 3, 4; n = 3–6$)—in zeolites X, Y, and A.^{9–15} Structures of zeolites containing cesium, rubidium, potassium, and sodium clusters have been reported by Seff and co-workers^{16–19} and by Armstrong et al.,^{20–22} but the location of the single-electron ionic cluster Na_4^{3+} continues to be the subject of debate.^{10,11,23,24} The incorporation of larger amounts of alkali metal results in dark solids with single-line ESR spectra, widely attributed to the formation of metallic clusters within the zeolite pores.²⁵ More recent work has cast doubt on this interpretation,²⁵ and it has been proposed that in sodium-loaded sodium zeolite Y (Na/Na-Y), for example, the ESR line results from the interaction

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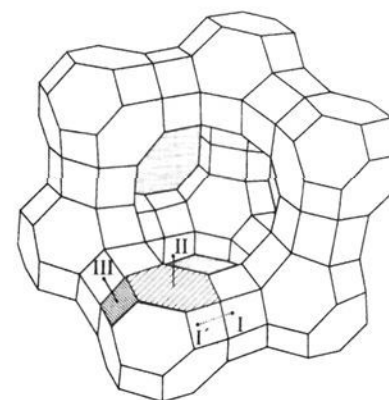


Figure 1. Framework structure of faujasite (zeolites X and Y), showing the four cation sites occupied in $\text{Na}_7/\text{Na}_{56}\text{-Y}$. The vertices of the polyhedra are occupied by silicon or aluminum atoms; the framework oxygens and exchangeable cations are omitted for clarity.

of localized unpaired electrons in neighboring Na_4^{3+} centers.² Although structural studies^{8,16–22} on alkali metal/zeolite inclusion compounds now encompass a number of metal–zeolite combinations, there have been no structural investigations to date involving either sodium-loaded zeolites or zeolite Y. In this Communication, we return to the original system discovered by Rabo and co-workers⁹ and report the structure of an inclusion compound of sodium in sodium zeolite Y, which clearly identifies an ordered three-dimensional array of interacting Na_4^{3+} centers, located in the sodalite cages, as the source of the controversial ESR line.

The deep red solid $\text{Na}_u/\text{Na}_{56}\text{-Y}$ was prepared through the reaction, in a sealed evacuated quartz tube, of dehydrated $\text{Na}_{56}\text{-Y}$ ($\text{Na}_{56}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$), with a controlled amount of sodium vapor (equivalent to $u = 8$ atoms/unit cell) at 200 °C.² Time-of-flight neutron powder diffraction data were collected at room temperature on HRPD, the high-resolution powder diffractometer at the ISIS pulsed source at the Rutherford Appleton Laboratory. The initial model for the structure refinement used the space group $Fd\bar{3}m$ and included all the framework atoms and the principal sodium sites I at (0,0,0), I' at (x,x,x) ($x \approx 0.06$), and II at (x,x,x) ($x \approx 0.23$), as shown in Figure 1. Isotropic temperature factors were assigned to all atoms.

Rietveld refinement of the framework atom positions, and those of Na I' and Na II, converged smoothly to values close to those previously reported for dehydrated Na-Y.²⁶ Na I showed a large reduction in occupancy compared with those observed in previous studies of the host zeolite, such that the occupancy and thermal parameter could not be refined simultaneously. Consequently, the thermal parameter was fixed at an appropriate value and the occupancy allowed to vary. In addition to the three principal sodium sites, difference Fourier methods led to the identification of an additional sodium site (Na III) in the supercage at around (0.40,0.15,0.10). Inclusion of these four sodium positions in the structure refinement led to the final values shown in Table 1.

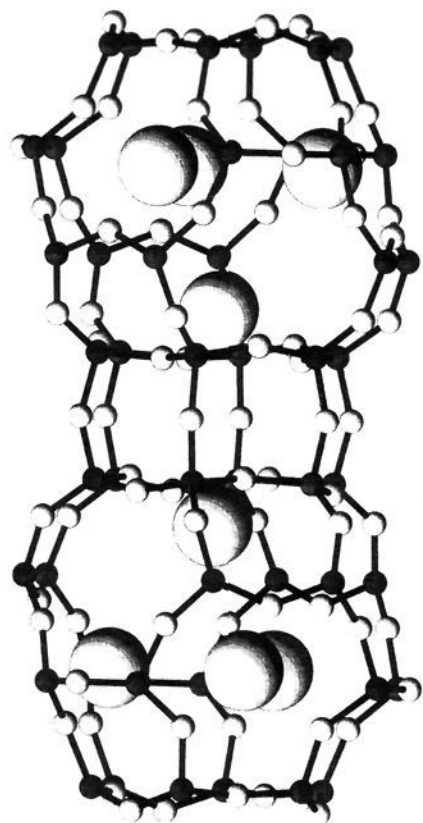
Comparison of the sodium site occupancies with values previously reported²⁶ for dehydrated sodium zeolite Y reveals substantial changes in the distribution of sodium cations caused by the inclusion of extra sodium atoms. Much of the additional sodium appears to occupy the four-coordinate site III in the supercage, which is found to contain around 12 Na. A slight reduction is observed in the population of the main supercage site, the six-coordinate site II, from 29(2) to 26(2). The most remarkable change, however, involves the occupancies of sites I and I': whereas site I is severely depopulated as a result of sodium inclusion, with the number of sodium ions dropping from 7(1) to 1.9(3), the occupancy of site I' shows a marked increase from 14(2) to 23(2) sodium ions/unit cell.

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Table 1. Structural Parameters for Na₇/Na₅₆-Y^a

atom	Wyckoff symbol	<i>x/a</i>	<i>y/a</i>	<i>z/a</i>	<i>B</i> _{iso}	site
Si	192i	0.125 19(13)	0.946 06(12)	0.036 41(16)	0.87(6)	0.71
Al	192i	0.125 19(13)	0.946 06(12)	0.036 41(16)	0.87(6)	0.29
O1	96h	0.104 21(11)	0.895 79(11)	0.0	2.01(12)	1
O2	96g	0.252 12(11)	0.252 12(11)	0.142 88(14)	1.90(10)	1
O3	96g	0.174 58(12)	0.174 58(12)	0.968 48(16)	1.88(9)	1
O4	96g	0.180 25(11)	0.180 25(11)	0.318 04(15)	1.61(10)	1
Na I	16c	0.0	0.0	0.0	0.5 (fix)	0.13(3)
Na I'	32e	0.062 3(3)	0.062 3(3)	0.062 3(3)	2.9(7)	0.73(5)
Na II	32e	0.234 0(2)	0.234 0(2)	0.234 0(2)	1.4(5)	0.81(5)
Na III		0.403 5(16)	0.154 6(10)	0.095 4(10)	0.1(14)	0.12(2)

^a Cubic, space group $Fd\bar{3}m$; $a = 24.830\ 62(9)$ Å. $R_{wp} = 7.9\%$; $R_E = 6.5\%$; $R_I = 7.7\%$. $R_{wp} = [\sum_i w_i |y_i(\text{obs}) - y_i(\text{calc})|^2 / \sum_i w_i y_i^2(\text{obs})]^{1/2}$, $R_E = [(N - P + C) / \sum_i w_i y_i^2(\text{obs})]^{1/2}$, and $R_I = [(\sum_k |I_k(\text{obs}) - (1/c)I_k(\text{calc})|) / \sum_k I_k(\text{obs})]$, where N , P , and C are the numbers of observations, parameters, and constraints, respectively.

**Figure 2.** Two sodalite cages in Na₇/Na₅₆-Y showing neighboring Na₄³⁺ centers, each composed of four site I' cations.

Two possible locations have been proposed for the Na₄³⁺ center in zeolite Y. The observation of nearly identical ESR spectra in sodium-loaded zeolites Y and A, and in the mineral sodalite, was regarded by Edwards and co-workers^{10,11} as strong evidence that Na₄³⁺ was located in the sodalite cage structural unit, common to all three hosts. More recently, Liu and Thomas,²⁴ on finding that the introduction of toluene—too large to enter the sodalite cage—to γ -irradiated zeolites X and Y caused the disappearance of the UV-visible absorption band attributed to Na₄³⁺, have argued that the center resides in the larger supercage, as originally proposed by Kasai.²³ The large observed increase in the occupancy of site I' in the sodalite cage and the matching decrease in those of site I (hexagonal prism) and site II (supercage) may be regarded as a direct observation of the movement of sodium cations through the six-ring windows into the sodalite cages to form Na₄³⁺. Accordingly, the Na—O bond lengths for site I' inside the sodalite cage are longer than those in dehydrated Na-Y and longer than those for site II, an equivalent site outside the sodalite cage. This is consistent with the extra electron density associated with the four site I' cations through their involvement in Na₄³⁺ centers.

The refined sodium content of Na_{*u*}/Na₅₆-Y corresponds to $u \approx 7$ sodium ions/unit cell, slightly less than the intended composition $u = 8$, enough to form an Na₄³⁺ center in every sodalite cage. The fractional occupancy of 0.73 for site I'

corresponds to 3 sodium ions/sodalite cage, enough in theory to place an Na₃²⁺ species in each sodalite cage; however, the observation of Na₃²⁺ only in sodium-poor zeolite Y,¹⁵ or at low temperatures,²⁴ renders this alternative interpretation implausible. Weak hyperfine splitting observed in the ESR spectrum of this compound is characteristic of Na₄³⁺ rather than Na₃²⁺, and if the observed paramagnetism is due only to Na₄³⁺, then SQUID magnetic susceptibility measurements indicate that $74 \pm 4\%$ of the sodalite cages contain Na₄³⁺ centers, a figure in excellent agreement with the crystallographic occupancy. The proximity of sites I and I' on either side of the six-ring window, between the hexagonal prism and the sodalite cage, is such that they are not occupied simultaneously. If one assumes that site I' contains only sodium ions involved in Na₄³⁺ species, then for every site I that is occupied, the two neighboring sodalite cages will be empty. This is consistent with observed fractional occupancies for sites I and I' of 0.13 and 0.73, respectively. It would appear, therefore, that Na₄³⁺ centers, whose distances from and orientations relative to each other are fixed by the zeolite host, form a three-dimensional network, whose order is broken only by the fact that a proportion of the cages remains empty.

Although the fingerprint hyperfine splitting pattern of Na₄³⁺ is weakly present in the ESR spectrum of Na₇/Na₅₆-Y, the dominant feature of the spectrum is the symmetric singlet line previously held to emanate from metallic sodium clusters. The structure of this compound provides no evidence for the presence of a second cluster, but significantly, it does lend support to the interacting electron model of Anderson and Edwards.² The Na₄³⁺ intracluster distance of 4.40(2) Å compares with an intercluster distance of only 5.36(3) Å through the hexagonal prisms (see Figure 2). This distance is certainly short enough to explain the loss of the ESR hyperfine structure at modest metal loadings. The strength of interactions between neighboring Na₄³⁺ centers is such that the hyperfine structure is observed only from isolated clusters. In the case of Na₇/Na₅₆-Y, the proportion of isolated Na₄³⁺ units will be very small; hence the weak contribution to the ESR signal. A much shorter distance, only 4.56(2) Å, between the sodalite cage ions (Na I') and ions in neighboring supercages (Na II) is less significant for the following reasons: first, the two sites in question are screened from each other by the zeolite framework, and second, the supercage site II is close only to site I' ions in one sodalite cage and therefore cannot mediate interactions between electrons trapped in different Na₄³⁺ centers. Nevertheless, it is likely that interactions with supercage ions are responsible for inhomogeneous broadening in the ESR spectrum of Na₄³⁺.

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