nesium has been substituted for two of the four iron atoms.[16,50-52] Gray and co-workers have complexed pentaammineruthenium to the surface histidines of both myoglobin and cytochrome *c* to include a second electron-transfer site at a known distance.[47,48,53,54] A comparison of the electron-transfer reactions of these Ru-modified myoglobins shows the rate to decrease exponentially as distance increases. The electron-transfer reactions in the present work occur over long distances, distances comparable to those just described. However, we suggest that the differences in the rates of electron transfer for the myoglobin complexes studied in this work, 7×10^{-6} cm s^{-1} for myoglobin and 5.4 (±0.9) $\times 10^{-4}$ cm s^{-1} for cyanomyoglobin, cannot be explained by distance, electron path, extent of heme exposure, orientation of the heme, or solvent effects.[55] As it is probable that any six-coordinate ferromyoglobin is low-spin due to the ligand field strength of imidazole coordinated at the fifth position,[46] then the electron-transfer reaction of Mb(III)CN$^-$ to Mb(II)CN$^-$ is low-spin to low-spin but the electron-transfer reaction of Mb(III)H$_2$O to Mb(II)H$_2$O is high-spin to low-spin.

The rates for electron transfer for heme iron redox couples generally follow the order low-spin/low-spin > high-spin/high-spin ≫ high-spin/low-spin or low-spin/high-spin due to the reorganizational energy accompanying changes in spin state.[56,57] It is known that the iron in the heme of low-spin cyanometmyoglobin lies in the heme plane and that the porphyrin ring is flat.[58,59] Reduction to low-spin cyanomyoglobin results only in a slight increase in the iron radius. High-spin metmyoglobin with water as the sixth ligand has the iron out of the heme plane due to longer bonds between the iron and the nitrogens of the porphyrin ring. The ring is described as domed or puckered. (In any of the four combinations of spin state and oxidation number, the porphyrin ring "nitrogen-to-center" distance remains approximately the same or close to 2.01 Å.[59]) Reduction from high-spin metmyoglobin to low-spin aquomyoglobin should result in the shortening of the Fe–N bonds as the iron is pulled into the porphyrin plane. The reorganizational energy change for these electron-transfer reactions should exceed that for the analogous electron-transfer reactions between low-spin states. This energy difference appears to cause the decrease in the electron-transfer rate that is observed here. These results also agree with those of Tsukahara for electron transfer between two high-spin five-coordinate species.[12]

Further work will involve examining the effects described above for myoglobin complexes that incorporate ligand-binding features such as size, charge, and the spin state of the heme iron in the complexed state.

Acknowledgment. The authors wish to acknowledge beneficial discussions with Professor Isao Taniguchi and the financial support of the NSF (Grant CHE-9111786; F.M.H.) and NIH (Grant HL-13531 and HL-40453; B.M.H.).

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A Magnetic Resonance Study of the Inclusion Compounds of Sodium in Zeolites: Beyond the Metal Particles Model

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Abstract: The reaction between sodium vapor and three different zeolites—Na-X, Na-Y, and Na-A—has been studied quantitatively, as a function of the concentration of metal. Its efficacy in introducing sodium into the zeolite pores, selectively and on a large scale, is demonstrated through ^{23}Na solid-state NMR measurements. The ESR singlet lines, previously thought to originate from metallic clusters within the zeolite pores, have been closely examined to test in some detail the properties of sodium in zeolites against those expected of the smallest metal particles. Although they exhibit *g* values characteristic of sodium metal, it is clear that these ESR spectra are not consistent with a simple metal particles model, and that talk of quantum size effects in such systems is premature. An alternative conceptual framework for the study of this class of compounds is developed, which focuses on the interaction of (ionized) sodium valence electrons with the zeolite cations, and with each other. The model described is consistent with many aspects of the experimental observations and suggests that such compounds may contribute to our understanding of the metal–nonmetal transition.

Introduction

The well-defined class of crystalline aluminosilicates known as zeolites, many of which are naturally occurring minerals, are composed of corner sharing SiO$_4$ and AlO$_4$ tetrahedra, arranged into three-dimensional frameworks in such a manner that they contain regular channels and cavities of molecular dimensions (see Figure 1). The presence of aluminum (formally Al^{3+}) in such a framework, in place of silicon (Si^{4+}), produces a net negative charge, which is balanced by cations resident in the cavities. These cations are usually coordinated to water molecules and often have a high degree of mobility, readily exchanging with others in aqueous solution. The water molecules can be removed by heating, leaving the zeolite cations imperfectly coordinated to the anionic framework, a situation which can result in the generation of considerable electric fields within the zeolite;[1] other molecules of suitable size can then be absorbed by the dehydrated zeolite.

Perhaps the first to anticipate that, through the filling of their pore space with other solid materials, zeolites might be used as templates for a new kind of solid-state chemistry was Barrer,[2] who spoke of forming "structures heterogeneous on the molecular scale with oxide threads and clusters having the pattern of the channel

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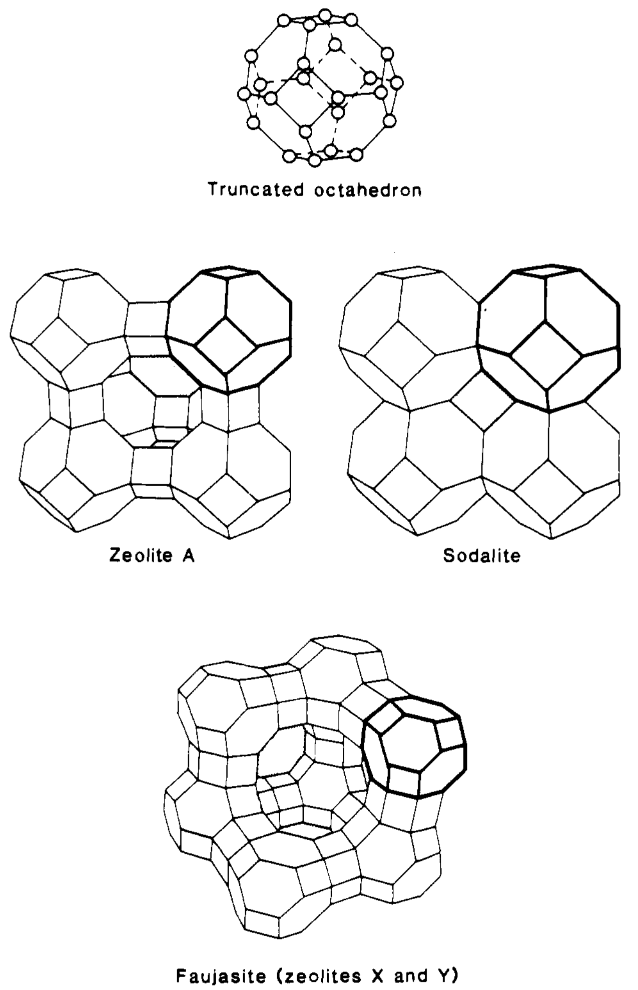

Figure 1. The structures of the zeolites used in this work are shown along with those of the related mineral sodalite and the sodalite cage structural unit. The vertices of the polyhedra are occupied by silicon or aluminum atoms; the framework oxygens and exchangeable cations are omitted for clarity.

and cavity systems and supported by the aluminosilicate framework of the zeolite". He noted three ways in which the zeolites might be filled: from the vapor phase, from salt melts, or through heating the zeolite with salt powders. Subsequent workers were quick to appreciate that the zeolite system of regular intracrystalline voids might play host to a well-defined array of discrete, uniform metal particles, of not greater than the cavity size, which would be ideal for the study of quantum size effects (QSE).[3-6]

The reaction of alkali metals with zeolites is not new. As long ago as 1966, Rabo et al.[7] reported that when sodium zeolite Y (Na-Y) was exposed to sodium vapor under vacuum, a bright red color developed. This was attributed to the formation of Na_4^{3+} color centers, which had first been observed the previous year by Kasai,[8] on irradiation of the same zeolite. When exposed to sodium vapor under similar conditions, Na-X exhibited a blue color, which was interpreted in terms of Na_6^{5+} centers; the existence of four further centers—K_4^{3+},[9] K_3^{2+},[10] Na_5^{4+},[11] and Na_3^{2+} [12]—has has subsequently been demonstrated in zeolites X, Y, and A. Barrer and Cole[13] showed that Na_4^{3+} centers could also be produced when dehydrated synthetic sodalite (Figure 1) was allowed to react with a controlled amount of sodium vapor, and that the mineral was capable of sorbing sodium atoms in excess of the amount required to form a center in each sodalite cage. Later, Edwards et al.[3,9] found that zeolite Y reacted with higher concentrations of sodium, potassium, or rubidium vapor to form dark solids, whose single-line ESR spectra were ascribed to the presence of metallic clusters within the zeolite pores.

Partly in anticipation of novel catalytic properties and partly in the hope of observing QSE, this work was gradually extended and an alternative preparative route developed.[4-6,14,15] These efforts were rewarded with the discovery that, as is predicted for very small particles,[16] the intensity of the singlet ESR lines exhibited by a number of such compounds increased as the temperature was lowered.[3-6] It was with the purpose of comparing in detail the properties of sodium in zeolites against those expected of small metal particles that this work was carried out.

Experimental Section

The compounds were prepared in sealed, evacuated quartz reaction tubes, in a manner similar to that described by Harrison et al.[3] Three zeolites were used—sodium X and sodium Y (Laporte Inorganics) and sodium A (BDH)—whose unit-cell compositions were $Na_{87}Al_{87}Si_{105}O_{384}$ (Na_{87}-X), $Na_{55}Al_{55}Si_{137}O_{384}$ (Na_{55}-Y), and $Na_{11.5}Al_{11.5}Si_{12.5}O_{48}$ (Na_{12}-A). The structures of these zeolites are illustrated in Figure 1, along with that of the related mineral sodalite and the so-called sodalite cage, which is the principal building block of the other structures shown. Zeolites X and Y share the faujasite structure, differing principally in the silicon to aluminum ratio, which for zeolite X is 1.1 ± 0.1, and for zeolite Y can be anything greater than about 1.5. The crystallinity of these three starting materials was checked by powder X-ray diffraction (XRD). The reaction tube, consisting of a central chamber to which were attached both an access arm and a length of Spectrosil ESR tube, was soaked in strong detergent, rinsed thoroughly with tap and distilled water, and fired overnight at 500 °C. A suitable amount of zeolite (typically 1 g) was added and the tube was then connected to a vacuum line, heated gradually to between 400 and 600 °C, and evacuated overnight to better than 10^{-5} mbar.

Sodium metal of the highest purity available (Aldrich 99.95%) was purchased in a sealed ampoule and distilled into calibrated capillary tubes without exposure to the atmosphere. This was achieved with techniques and apparatus which were developed for the study of alkali metal solutions in ammonia and other solvents, and which have been described in detail by Dye.[17] In this form, the required amount of alkali metal could be selected by measuring a suitable length of capillary. The reaction tube was taken into a high-quality argon glovebox where the metal was introduced, and returned to the vacuum line to be evacuated and sealed with a gas torch. At no stage did the metal come into contact with the atmosphere. When the sealed tube was later heated, the alkali metal vapor filled the reaction chamber and spontaneous coloration of the zeolite occurred. In most cases the initial reaction was not uniform, the lower parts of the zeolite being less exposed to the sodium vapor. Subsequent annealing of the zeolite, with frequent rotation of the reaction tube, was required to produce a visibly homogeneous sample. A portion of each sample was sealed in the Spectrosil section of the reaction tube so that conjoint ESR and NMR measurements could be made without exposing the product to air.

In this work we have chosen to perform our reactions at temperatures considerably lower than those often favored by previous workers.[3,7] High temperatures were found to produce samples of poor crystallinity and reproducibility; to avoid these problems we have endeavored to keep the temperature of reaction as low as possible. One limit to this policy is

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defined by the need to evaporate the metal for reaction to occur, a requirement which can easily be met if a good vacuum is obtained within the sealed reaction tube. More critical in this case is the requirement for a sufficiently high rate of diffusion within the zeolite that sample homogeneity is not compromised. Temperatures in the region of 250 °C, together with relatively long annealing times (several days in some cases), produced optimum results. It is worth noting that these temperatures are well below that at which sodium azide decomposes, as many workers have used the azide as a convenient source of sodium metal.[14,15,18]

The compounds were all found to be unstable in air, some extremely sensitive, others taking several weeks to react completely. In water, they produced hydrogen gas and a basic solution, but none reacted violently in the manner of the parent alkali metals. This inhibition of reactivity is probably kinetic in origin, the diffusion of reacting molecules into filled zeolite pores occurring only slowly. Titration of the alkaline solutions enabled an estimate of the concentration of metal in the sample to be obtained. The concentration of metal could also be estimated from the length and bore of the capillary tube, and, knowing the mass of the zeolite (measured in the glovebox after dehydration), the approximate stoichiometry of the samples could be calculated. For a number of reasons this second method always produced a higher value: some metal is used up in the "threshold effect";[19] a certain amount of metal may react with the zeolite to form insoluble silicate or aluminate species; a certain amount may react with the silica vessel itself. In short, the first method gave a lower limit and the second an upper limit to the actual concentration, and it is the latter, available without sacrifice of the sample, which is quoted in this work. The average discrepancy was less than 30%, and this may be taken as an indication of the accuracy of the values, but it is important to remember that the numbers given are likely to represent overestimates of the actual concentrations. The notation Na_x/Na_{55}–Y is used to designate Na_{55}–Y containing an amount of sodium metal equivalent to x sodium atoms per unit cell (p.u.c.); Na/Na–Y refers to the *class* of sodium inclusion compounds in zeolite Na–Y. The crystallinity of representative samples was examined by powder XRD.

First- and second-derivative ESR spectra of the colored powders were recorded on a Varian E-109 spectrometer operating at X-band frequencies (9.3 GHz) with 100-kHz field modulation. Microwave power up to 200 mW was provided by a Varian E-102 microwave bridge but most spectra were recorded at much lower power (<1 mW). The microwave frequency was measured with a Hewlett-Packard 5342A frequency counter to an accuracy of ±1 kHz, and g values were determined through comparison of the resonant field with that of the 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical at $g = 2.0036 \pm 0.0001$.[20] Perhaps one of the most surprising aspects of the work reported here is that almost all the ESR spectra were both readily observable, and indeed recorded, at room temperature. On the occasions where lower temperatures were employed, these were maintained with the help of an Oxford Instruments ESR-900 continuous flow cryostat.

The ^{23}Na NMR spectra were recorded, at room temperature and 106 MHz, on a Bruker MSL-400 pulsed FT spectrometer, with static powder samples. Each spectrum represents the accumulation of several thousand transients collected with a recycle delay of 10 s.

Results

A. NMR. The ^{23}Na NMR spectrum of dehydrated Na_{55}–Y before and after exposure of the zeolite to small and large amounts of sodium vapor is shown in Figure 2. The spectra consisted of one or more features close to 0 ppm; in the case of dehydrated Na_{55}–Y and Na_3/Na_{55}–Y, the main peak at around −10 ppm was accompanied by two further components, but in Na_{50}/Na_{55}–Y these had all but disappeared. Perhaps the most interesting difference, however, between the spectrum of white dehydrated Na_{55}–Y and that of colored Na_{50}/Na_{55}–Y was intensity, the latter being many times weaker, despite the fact that extra sodium was present. A weak signal was observed at the position of the sodium Knight shift (+1130 ppm) in only one case (Figure 2d), when the sample Na_{50}/Na_{55}–Y was deliberately heated with a microtorch to drive a small proportion of the included sodium from the zeolite and produce a thin mirror of sodium metal on the inside of the sealed quartz sample container; no signal was observed between 0 and +1500 ppm on any other occasion. To check that the observed spectrum emanated solely from the zeolite cations and not the included sodium, ^{23}Na NMR spectra of Na/K–Y were recorded under similar conditions; no signal was detected.

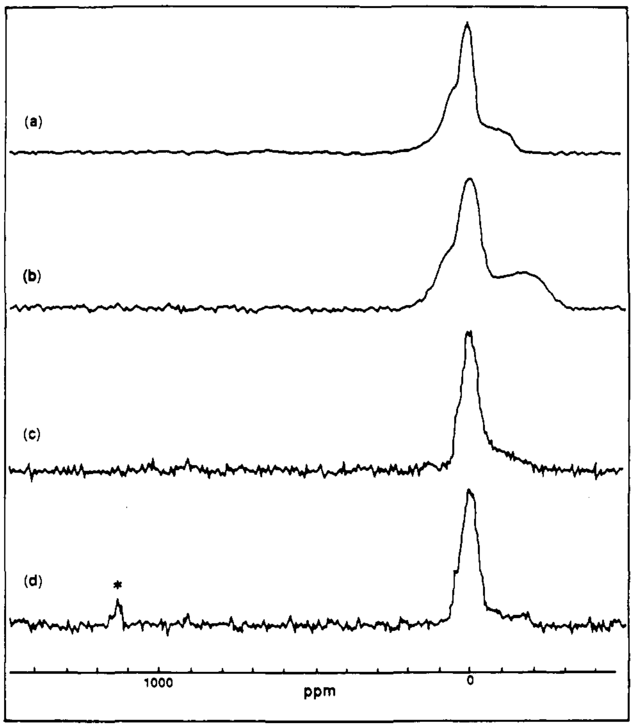

Figure 2. The ^{23}Na NMR spectrum of (a) dehydrated Na_{55}–Y, (b) Na_3/Na_{55}–Y, (c) Na_{50}/Na_{55}–Y, and (d) Na_{50}/Na_{55}–Y with sodium mirror. The asterisk in part d marks a weak resonance at the position of the sodium Knight shift.

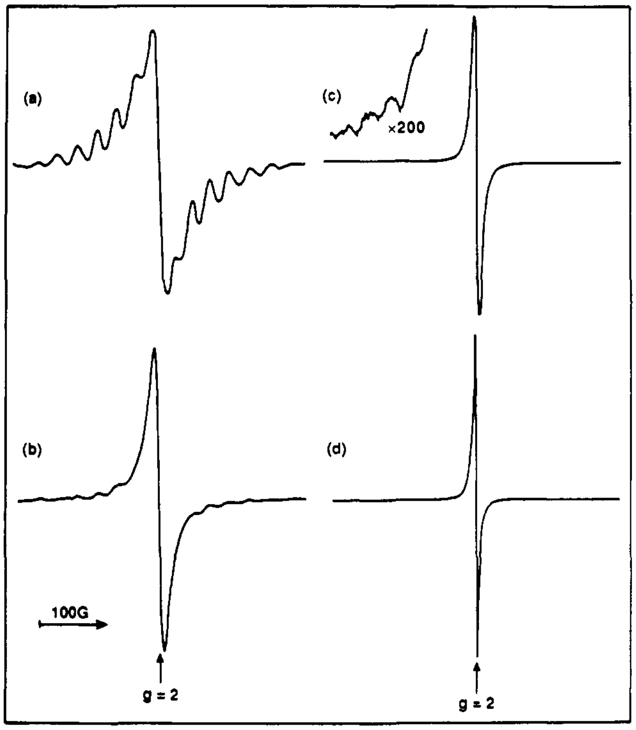

Figure 3. The ESR spectrum of Na_{55}–Y containing (a) 3, (b) 8, (c) 13, and (d) 32 included sodium atoms per unit cell.

B. ESR. (i) Na_x/Na_{55}–Y. The exposure of dehydrated Na_{55}–Y to sodium vapor, caused the white solid first to turn pink, then bright red, deep red, and eventually black. If the amount of sodium vapor available for reaction was limited, homogeneous samples of the various colored solids could be obtained and examined. Examples of the ESR spectra of such products are given in Figure 3. The pink to bright red solids, obtained by the

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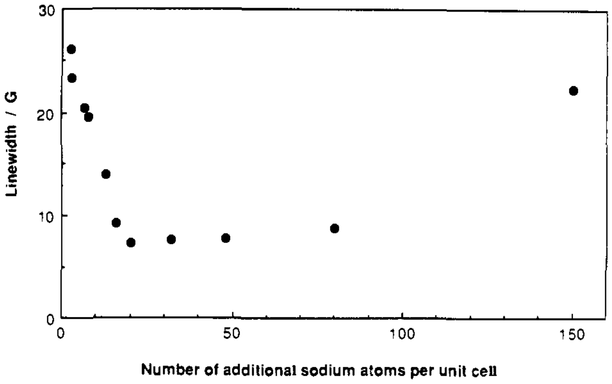

Figure 4. The minimum line width (ΔH_{pp}) of the singlet component in the ESR spectrum of Na_x/Na_{55}–Y, as a function of the concentration of included sodium (x).

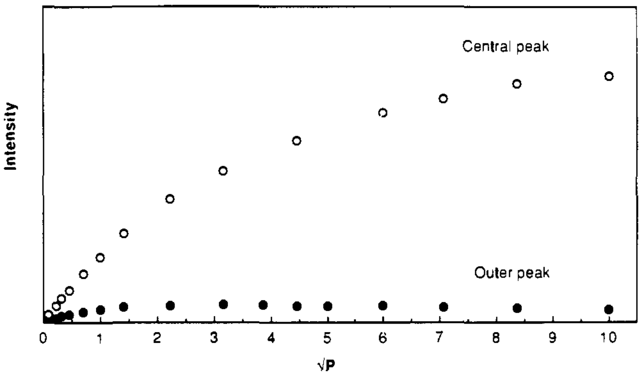

Figure 5. The ESR intensity at 4 K of the central, and fourth from central, lines in the spectrum of Na_3/Na_{55}–Y as a function of the square root of the microwave power (P).

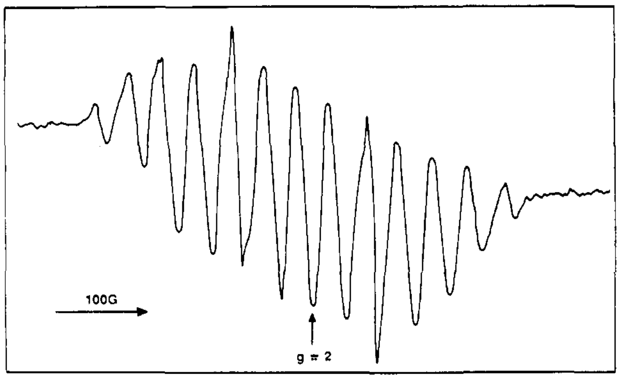

Figure 6. The ESR spectrum of Rb_1/Na_{55}–Y.

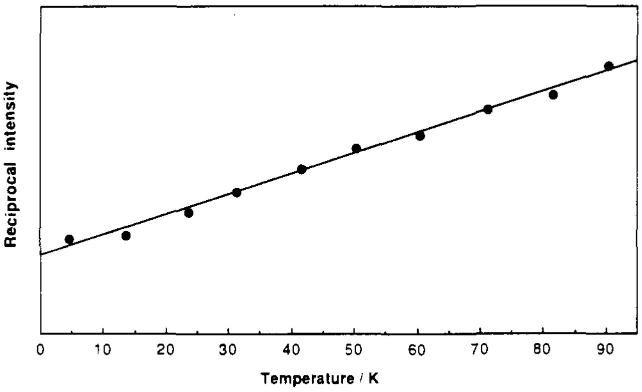

Figure 7. The reciprocal intensity of the ESR spectrum of Na_4^{3+} (recorded from Rb_1/Na_{55}–Y) as a function of temperature.

treatment of the zeolite with relatively low concentrations of metal ($x < 4$), exhibited the characteristic ESR spectrum of Na_4^{3+},[8] consisting of 13 equally spaced lines with hyperfine splitting $a = 32.9 \pm 0.2$ G and $g = 2.0023 \pm 0.0001$ (Figure 3a). At higher metal concentrations a singlet resonance at $g = 2.0014 \pm 0.0001$ was visible, whose relative intensity grew with increasing x, eventually to eclipse the spectrum of 13 lines (Figure 3, b, c, and d). The peak-to-peak line width (ΔH_{pp}) of this singlet was dependent both on x and, to a lesser extent, the stage of reaction (see Figure 9); the minimum line widths recorded for given samples are plotted as a function of concentration in Figure 4. Though symmetric, the signal generally exhibited more intensity in the wings than a true Lorentzian line, and it could not be saturated with the microwave power available even at 4 K. ESR spectra recorded at temperatures below ambient were similar to those obtained at room temperature. On cooling to 77 K, the hyperfine splitting of the signal due to Na_4^{3+} fell, typically from 32.9 to 32.1 G, and the line width of the singlet resonance was reduced in all cases by ~1 G.

Although the zeolite would consume concentrations of metal as high $x = 150$, the crystallinity of the zeolite was almost completely destroyed. Some damage to the zeolite framework was found to be unavoidable at concentrations above 50 to 60 atoms p.u.c. In Figure 5, the intensity of the spectrum of Na_3/Na_{55}–Y is plotted as a function of the square root of the microwave power (P) at 4 K. Two lines of the hyperfine pattern were used to measure the intensity of the signal: the central and the fourth from central. Although neither could be saturated at room temperature with the microwave power available, the latter became saturable at lower temperatures. This clear difference in behavior of the two lines confirms the important contribution of the singlet resonance to the spectrum, even at concentrations of metal as low as 3 atoms p.u.c.

Within our experimental setup, the reaction with only small amounts of metal was found to be rather difficult to control, and, despite numerous attempts, we were not able to prepare satisfactory samples of Na_x/Na_{55}–Y with $x \leq 2$. On account of the lower temperatures required, the reaction with rubidium vapor presents less of a problem in this respect, and we succeeded in producing a compound Rb_1/Na_{55}–Y, which exhibited a particularly good spectrum of Na_4^{3+}, without interference from other resonances (Figure 6). Figure 7 shows a plot of the reciprocal intensity of the ESR signal versus temperature.

On heating at 250 °C for prolonged periods (several days), samples of all concentrations became somewhat browner in color. The same effect could be achieved in a much shorter time by heating at higher temperatures. The effect of heating was also manifest in the ESR spectrum of a typical sample and the line width of the singlet resonance of a typical sample (Na_{32}/Na_{55}–Y), shown in Figures 8 and 9 as a function of reaction time at 300 °C. After about 90 h, the sample tube started to go brown, a visible sign that sodium was beginning to react with the quartz.[21] The reaction was continued at 300 °C for 195 h; then the temperature was raised to 400 °C for a further 33 h, after which the color of the solid had changed from its previous rusty brown to dull orange. The ESR spectrum of the solid after this final heating contained no trace of the singlet resonance, but although the crystallinity of the zeolite was found to be seriously damaged, the spectrum of 13 lines ($a = 33.7 \pm 0.3$ G) was clearly visible (Figure 8d). Despite the variations in line width as a function of both concentration and reaction time, the g value of the ESR singlet was found to deviate significantly from $g = 2.0014$ in only one circumstance: values as low as 1.9997 ± 0.0003 were recorded in some samples with $x > 100$ which had been heated at temperatures over 350 °C. The crystallinity of such samples was found to be poor.

(ii) Na_x/Na_{87}–X. The exposure of dehydrated zeolite Na_{87}–X to sodium vapor under vacuum caused the white solid to turn purple and then black, depending on the concentration of metal; again there was a tendency for the more concentrated samples to go brown if heated at or above 250 °C for too long. Na_{87}–X appeared to be saturated with metal at concentrations in the region

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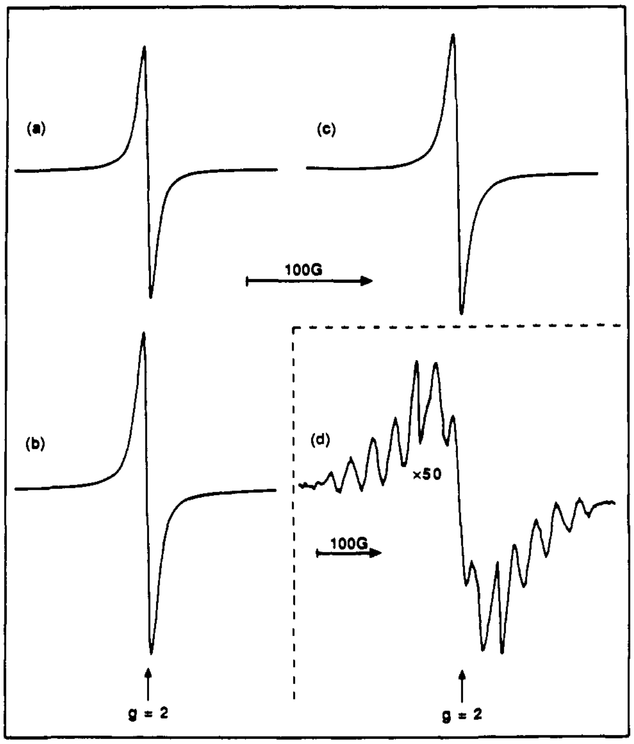

Figure 8. The ESR spectrum of Na_{32}/Na_{55}–Y after (a) 18 h, (b) 85 h, and (c) 195 h at 300 °C, and (d) after a further 33 h at 400 °C.

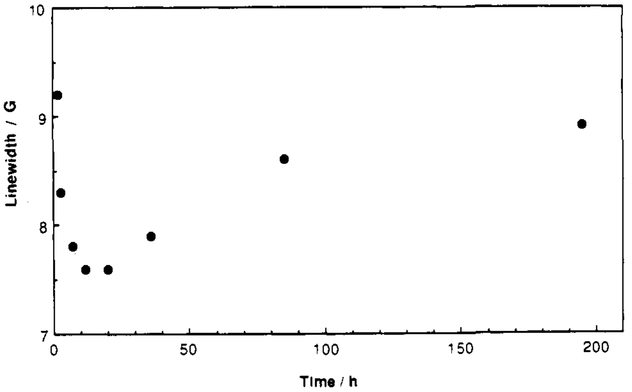

Figure 9. The ESR line width (ΔH_{pp}) for Na_{32}/Na_{55}–Y as a function of the reaction time at 300 °C.

of 40 to 50 atoms p.u.c., much less than Na_{55}–Y, and some damage to the zeolite framework was found to have occurred at this level.

In some ways the ESR spectra (Figure 10) of this series of compounds were very similar to their counterparts in zeolite Y. At low concentrations of metal there was a symmetric hyperfine splitting pattern centered on $g = 2.0022 \pm 0.0001$ due to the presence of Na_5^{4+} and Na_6^{5+} centers.[11] This was eventually eclipsed at higher metal concentrations by a singlet line, also symmetric but again with more intensity in the wings than a Lorentzian line. The singlet occurred at $g = 2.0012 \pm 0.0002$, and a reduction in its g value, this time as low as 1.9982 ± 0.0003, was observed only under the same extreme conditions as in Na_x/Na_{55}–Y; it could not be saturated with the microwave power available. For samples with $x > 20$, ΔH_{pp} was typically in the region of 4 to 5 G at 298 K, greater, as before, for those most concentrated or, in particular, those severely heated. At lesser concentrations, lines up to 80 G broad were recorded, but, since the line width in such cases decreased rapidly with reaction time, the relationship between line width and concentration was difficult to quantify. Line widths recorded below ambient temperature were marginally (up to 4%) greater than those at room temperature.

(iii) Na_x/Na_{12}–A. The reaction of sodium vapor with dehydrated Na_{12}–A occurred much less readily than with zeolites X and Y. At 250 °C, the zeolite developed pale blue, green, brown, and black patches, but a visibly homogeneous sample could only be obtained (in reasonable time) at temperatures of 300 °C or above. The final color of samples ranged from blue-gray at the lowest concentrations through black, to greenish brown for those containing most metal. Unfortunately, some damage to the crystallinity of the zeolite was observed in virtually all cases, usually heralded by the reaction of sodium with the quartz of the reaction tube. In an attempt to circumvent this, an alternative preparation involving the reduction of the zeolite cations by solvated electrons[12] was also tried.

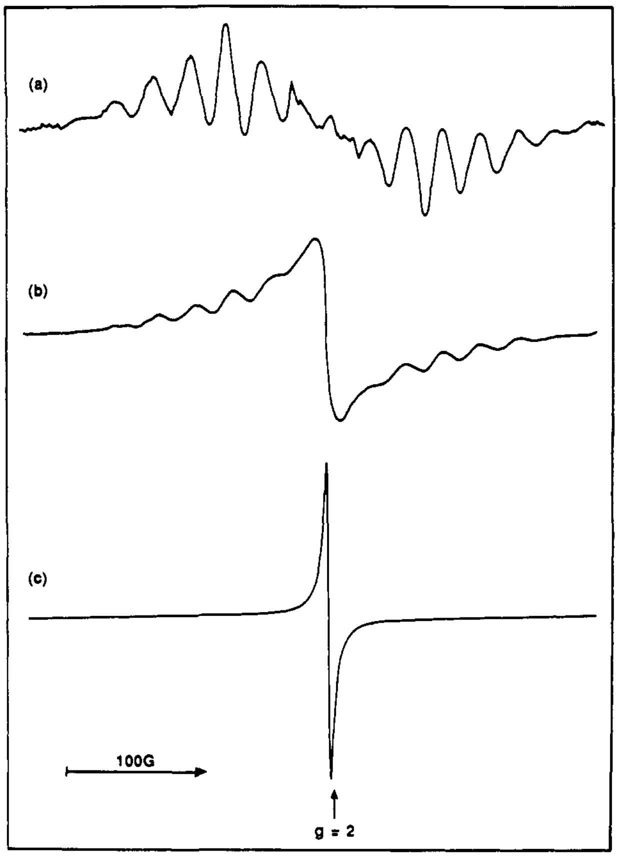

Figure 10. The ESR spectrum of Na_{87}–X containing (a) 3, (b) 12, and (c) 38 included sodium atoms per unit cell.

The ESR spectra of the products (Figure 11) were weaker and less consistent than those obtained from samples of sodium in zeolites X and Y. Although the line shapes were complex, two main components can be distinguished. At low concentrations the spectrum consisted of a resonance at $g = 2.0014 \pm 0.0001$, symmetric as before, with ΔH_{pp} between 10 and 18 G, and with more intensity in the wings than a Lorentzian line; at higher concentrations this was joined by a narrower signal with $\Delta H_{pp} \approx 5$ G at $g = 2.0005 \pm 0.0003$. On cooling to 120 K, the latter narrowed to ~3 G, but no significant change in the line width of the broader signal was observed. Neither signal could be saturated with the microwave power available. The spectrum obtained from the less concentrated compounds showed signs of hyperfine structure in the wings of the main signal. The average splitting was ~32.5 G, but at room temperature the pattern was in all cases too weak to count the number of lines. At 120 K, with the help of the second derivative signal, it can be seen that the familiar spectrum of Na_4^{3+} was responsible (Figure 12).

Discussion

A. Critique of the Metal Particles Model. (i) NMR Results. When Grobet et al.[22] measured the ^{23}Na spectrum of sodium deposited on Na–Y by the thermal decomposition of sodium azide,

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[22] Grobet, P. J.; Van Gorp, G.; Martens, L. R. M.; Jacobs, P. A. *Proc. 23rd Congress Ampère (Rome)* **1986**, 356–357.

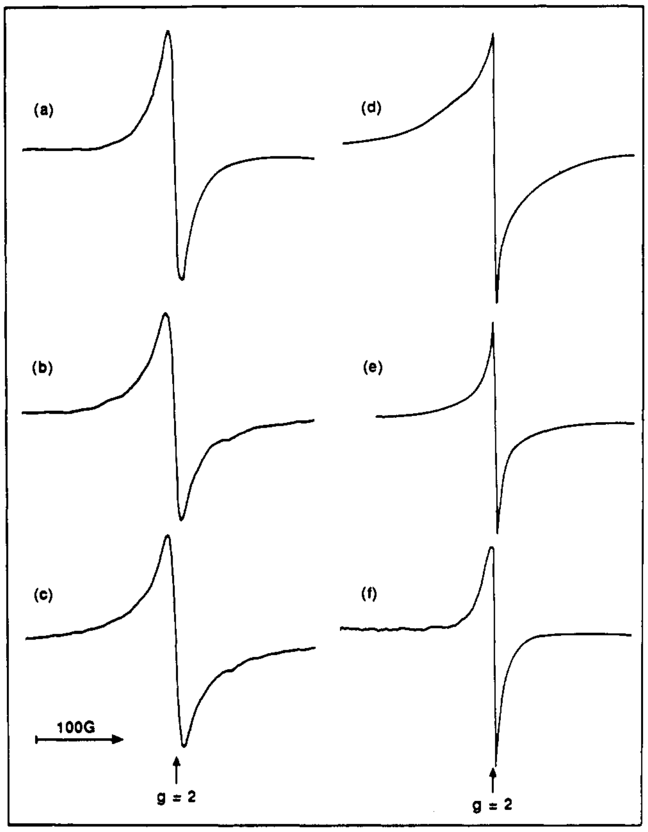

Figure 11. The ESR spectrum of Na_{12}–A containing (a) 1, (b) 2, (c) 3, (d) 4, and (e) 6 included sodium atoms p.u.c., and (f) after reduction by a solution of lithium metal in butylamine.

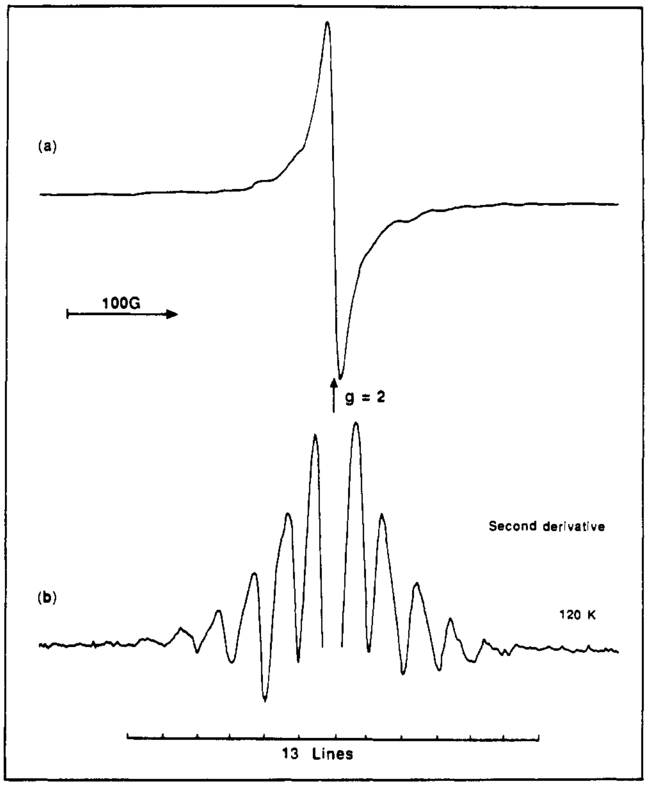

Figure 12. The ESR spectrum of a sample of Na_2/Na_{12}–A illustrating the presence of Na_4^{3+}: (a) first derivative at room temperature, and (b) second derivative at 120 K.

Table I. Reported *g* Values for Sodium Metal

sample	*g* value	ref
fine particles in paraffin wax	2.001 ± 0.003	26
colloidal suspensions in paraffin wax	2.0014 ± 0.0002	27
metal sheets; particles in paraffin wax	2.0015 ± 0.0002	28
particles in sodium azide	2.0017 ± 0.0002	29
particles in sodium hydride	2.0015 ± 0.0002	30
bulk metal solid and liquid	2.00134 ± 0.00003	31
particles in sodium chloride	2.00130 ± 0.00005	32
particles in frozen HMPA[a]	2.0012 ± 0.0002	33
included in zeolite Y	1.9997 ± 0.0005	3, 9
included in Vycor porous glass	1.996 ± 0.001	34
included in zeolite X	2.0011 ± 0.0005	14
included in zeolite Y	2.0014 ± 0.0001	this work
included in zeolite X	2.0012 ± 0.0001	this work
included in zeolite A	2.0014 ± 0.0001 2.0005 ± 0.0003	this work

[a] Hexamethylphosphoric triamide.

they found a spectrum consisting of an intense line at 0 ppm, a medium line at 673 ppm, and a weak line at 1132 ppm, which were assigned to zeolite cations, metal particles within the zeolite, and metal particles on the surface of the zeolite, respectively. In contrast, the lack of a peak at the metallic Knight shift (~1130 ppm) in our spectra (except from an extraneous sodium mirror) precludes the presence of large metal particles, even in samples containing copious amounts of sodium, and is the best evidence to date that sodium is not just simply deposited on the solid from the vapor phase as it would be on supports such as silica or alumina. For the sodium to remain in a finely divided state at such high concentrations must mean that it is, after all, located within the zeolite pores, and implies that the direct reaction between vapor and solid was more effective in incorporating metal atoms *into* the zeolite pores.

It is interesting that the peak at 673 ppm ascribed by Grobet et al.[22] to particles within the zeolite was also missing from our spectra. The experimental parameters employed for the measurements reported set a maximum detectable line width of 100 kHz, but weak lines narrower than this might still not be visible above the noise. The peak at 673 ppm in the spectrum of samples prepared by the metal vapor route may therefore either be too broad to be observed or absent altogether. The cause of this difference must be traced to the chemistry employed in the two preparations. For a given concentration of sodium, the distribution and chemical environment of the incorporated sodium atoms may be different in samples prepared by the decomposition of azide; the maximum obtainable concentration may itself be different. Significantly, a subsequent paper from Grobet and co-workers[23] talks in terms of neutral sodium clusters anchored to the zeolite through an interaction between residual nitrogen atoms and the oxygen atoms of the zeolite framework. Nevertheless, it is clear that ^{23}Na NMR studies provide no evidence for the presence of metal particles or metal clusters in our compounds.

(ii) ESR Results. Although the ESR signal observed from the conduction electrons (CESR) of bulk metal samples is anticipated to be asymmetric,[24] the possibility of observing symmetric lines from small metal particles is equally well established.[25] It was this expectation that underpinned the proposal that the singlet resonance in Na/Na–Y might be due to metallic sodium clusters within the zeolite pores.[3,9] Although the *g* value reported then was at variance with values recorded for either bulk metal or

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(23) Martens, L. R. M.; Vermeiren, W. J. M.; Grobet, P. J.; Jacobs, P. A. *Stud. Surf. Sci. Catal.* **1987**, *31*, 531–542.

(24) Dyson, F. J. *Phys. Rev.* **1955**, *98*, 349–359.

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(33) Edmonds, R. N.; Edwards, P. P.; Guy, S. C.; Johnson, D. C. *J. Phys. Chem.* **1984**, *88*, 3764–3771.

(34) Edmonds, R. N.; Harrison, M. R.; Edwards, P. P. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2515–2519.

particles in a variety of media (Table I), the current work establishes that the earlier value was perhaps misleading. The vast majority of samples we prepared exhibited signals whose *g* values did not deviate significantly from that of sodium in bulk or particulate form. Lower values appear to be strongly associated with damage to the aluminosilicate framework.

The assumption of intracrystalline metallic clusters enables the rationalization of a number of experimental observations relating to the ESR spectrum of sodium in zeolites to be attempted. In all three zeolites the main singlet resonance was symmetric, but with more intensity in the wings than a true Lorentzian line. Such a line shape has been observed previously from sodium colloids in irradiated sodium azide and was explained as a composite line comprising contributions from particles of various sizes, whose Lorentzian lines had different widths but the same *g* value.[35] For both bulk metals and small particles, the CESR line width has been found to be proportional to temperature from less than 60 K to the melting point (371 K),[36] but the same cannot be said for the signals in zeolites. In Na_x/Na_{55}–Y the consistent reduction in line width of ~1 G observed on cooling from room temperature to 77 K represents a change of about 15% for high *x* samples, and much less than that for the rest. In Na_x/Na_{87}–X the line width, if anything, *increased* on cooling. Possible explanations for the relative constancy of the line widths include the suggestion that the particles in zeolites are so small that electron spin relaxation is dominated by the surface relaxation term, which is to a first approximation independent of temperature.[33,35]

In Na_x/Na_{55}–Y the measured width of the singlet resonance was strongly dependent on *x* (Figure 4). From a value of over 25 G at the lowest concentrations of metal, ΔH_{pp} at room temperature dropped to less than 7 G at $x \approx 20$ atoms p.u.c. In the range $x = 20$ to $x = 80$ atoms p.u.c., the width remained below 10 G, but at concentrations above this the rapid collapse of the zeolite structure was accompanied by greater line widths. These large variations with concentration were mirrored in much smaller changes which took place during the annealing of a given sample (Figure 9). Such observations might be accounted for by the suggestion that the size of the clusters increases with the concentration of sodium: in the absence of quantum size effects, smaller particles are expected to give broader lines due to an increased contribution from surface relaxation,[37] a relation which has been verified for particles of sodium as small as 10 Å.[35,38] The eventual increase in line width, under conditions where the crystallinity of the framework was deteriorating, could then be attributed to a reduction in cluster size as sodium atoms were incorporated into decomposition products.

The narrowest lines of less than 7 G in Na_x/Na_{55}–Y are characteristic of relatively large particles (>1000 Å).[35,38] If one were observing CESR from particles of this size, one would anticipate the onset of asymmetry in the ESR line on cooling the sample, as the microwave skin depth became small relative to the diameter of the particles.[39] Unfortunately, the observation of a symmetric ESR line down to 4 K and the absence of any Knight-shifted ^{23}Na NMR signal preclude the presence of such particles. Measured line widths as low as 4 G (*less* than that of pure bulk sodium)[31] for sodium in zeolite X are equally difficult to explain. One possible explanation for the observation of anomalously narrow lines would be that the zeolites are host to metallic clusters so small that they exhibit the quantum size effects predicted of the smallest metal particles.[16] Particles with the dimensions of typical zeolite cavities would certainly be expected to exhibit QSE, but as yet there is no clear evidence for such behavior in sodium particles.[16] In any case the attempt to explain these observations as QSE in small metal particles is ultimately self-defeating. For if such particles were subject to QSE, the expected variation of their line width with particle size would be reversed, such that smaller particles would now be expected to produce *narrower* ESR lines.[16,39] It is clearly less reasonable to suppose that an increase in sodium concentration might result in smaller clusters within the zeolite, and so the explanation given above for the variation of the line width in Na_x/Na_{55}–Y is valid only if QSE are *not* in operation.

In contrast to those of Na_x/Na_{87}–X and Na_x/Na_{55}–Y, the ESR spectrum of Na_x/Na_{12}–A exhibited two singlet signals (Figure 11). The line width of the narrower contribution was close to values recorded in zeolite X. Its *g* value, significantly less than that of sodium metal, is indicative of relatively poor zeolite crystallinity, but implies that this signal, like those observed in zeolites X and Y, has its source within the zeolite pores. The line width and *g* value of the broader component are consistent with those of sodium particles in the size range 25–100 Å.[35,38] The structure of zeolite A is much less open than that of X and Y, and it is conceivable that the slower diffusion of sodium atoms into this zeolite, which made the preparation of homogeneous samples so difficult, may result in the formation of genuine particles at or near the surface of the zeolite crystallites.

Although our ^{23}Na NMR studies provided no evidence for the presence of metal particles or clusters in zeolite Y, following the practice of previous workers, we have first of all endeavored to interpret our ESR observations in terms of metallic sodium clusters located within the zeolite pores. We have found that this assumption does not provide an adequate explanation for the detailed ESR behavior of sodium in zeolites. One obvious potential source of deviation from the behavior expected of small metal particles lies in the possibility that metallic clusters in neighboring zeolite cavities might be in contact with, or at least close enough to interact with, each other. At this stage, it is important to realize that the singlet signal in Na_x/Na_{55}–Y, for example, first appeared (Figure 3) at concentrations of metal so low that, if evenly dispersed, the included sodium atoms would on average be very many interatomic distances apart, a fortiori, since it is established that the first atoms of an alkali metal entering a zeolite tend to lose their valence electrons to centers such as Na_4^{3+}.[3,9] Although we cannot exclude the possibility that metallic clusters form in these circumstances, the probability of finding two or more in neighboring cavities must be extremely low. For this reason possible alternative carriers for the singlet ESR lines in sodium zeolites will now be considered.

B. Single Electron Models. Consisting of a single valence electron held in the sodalite cage by a number of cations, species such as Na_4^{3+} are best regarded as single electron traps, akin to F-centers in ionic crystals.[10,11] Perhaps it is not unreasonable to speculate that when Na–Y, for example, is saturated with Na_4^{3+} centers, further excess electrons might end up in alternative traps. The irradiation of dehydrated Y zeolites under vacuum has been shown to result in various ESR signals in addition to that of Na_4^{3+}, but hyperfine coupling to the ^{27}Al nucleus is usually observed.[40] One exception is that of the so-called V_2 center thought to consist of an electron hole localized in a p orbital of an oxygen atom bonded to two silicon atoms.[41] Zeolites are largely composed of ^{28}Si and ^{16}O, neither of which possesses nuclear spin, but electron traps consisting of these two atoms are unknown in zeolites. An SiO_4^{5-} center has been observed in silica after bombardment with electrons,[42] but its ESR spectrum clearly contained satellites as a result of hyperfine coupling to ^{29}Si, which has a natural abundance of 4.7% and nuclear spin $I = {}^1/_2$. The clear observation of satellites and *g* values ranging from 2.0006 to 2.0009 mean that this center is unlikely to be responsible for the main singlet resonance in zeolites, but it is possible that traps of this sort contributed to the ESR spectra of those compounds exhibiting considerable framework damage, whose *g* values often fell in this range.

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(36) See, for example, refs 20, 28, 31–33, 35, and 38.

(37) See, for example, refs 16, 33, 35, and 39.

(38) Smithard, M. A. *Solid State Commun.* **1974**, *14*, 411–415.

(39) Edmonds, R. N.; Harrison, M. R.; Edwards, P. P. *Annu. Rep. Prog. Chem.* **1985**, *82C*, 265–308.

(40) See Kasai, P. H.; Bishop, R. J. In *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed.; ACS Monograph No. 171; American Chemical Society: Washington, DC, 1976; pp 350–391.

(41) Vedrine, J. C.; Naccache, C. *J. Phys. Chem.* **1973**, *77*, 1606–1610.

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A second possibility is that, in the absence of a suitable trap, the excess sodium atoms might retain their valence electrons. That on no occasion, in this or in previous work, was an ESR spectrum attributable to sodium *atoms* observed from a zeolite might be regarded as a serious flaw in this model. However, in the course of its random motion within the zeolite, an atom must collide many times with the walls of the cavities, which are only of molecular dimensions and lined with zeolite cations. Thus our incursive sodium *atom* is in almost constant collision with the sodium *ions* of the zeolite and, if even a small proportion of these encounters resulted in electron transfer from atom to ion, the hyperfine interaction would be averaged out on what is the relatively slow timescale of ESR. The *g* value of such a signal would not be expected to deviate from the atomic value, which in turn does not deviate from that of a free spin[43] and is unfortunately incompatible with the values observed. With no sign of atomic hyperfine splitting even at temperatures as low as 4 K, it is clear that there is little to support this idea.

In fact, the density of sodium cations in the three zeolites used is so high, and the zeolite cavities themselves are so small, that the possibility of finding atoms intact is perhaps somewhat remote. More likely is that an electron on an incoming sodium atom, subject to the intense electric fields generated by the sodium ions of the zeolite,[1] would effectively find itself under the influence of a group of ions rather than just a single one as is the case in an atom. This is, after all, the situation observed in the four known electron traps in sodium zeolites, $Na_m^{(m-1)+}$ ($m = 3, 4, 5, 6$).[11,12] Given the degree of vibrational and translational mobility which is well established for zeolite cations, we may conclude that, even at room temperature, the geometry of most of these groups of ions is unlikely to be fixed, and that the electron might well be able to "hop" from one to another throughout the zeolite crystal. If one believes that this, rather than atomic diffusion, is the process whereby electrons are ferried to the sodalite cages to form stable traps like Na_4^{3+}, then it follows that when all such cages are filled, the surplus electrons may be condemned to roam randomly in the intracrystalline channels, again producing an ESR signal with an averaged hyperfine interaction. In this case, the *g* value of the signal should also represent an average—of the values of the transient "traps" in which the electron at any point resides—and it is worth noting that the *g* value of none of the four stable sodium traps deviates significantly from free spin. The remarkable constancy of the various ESR spectra at temperatures between 4 and 300 K must also again cast some doubt on the validity of an explanation based entirely on motional averaging.

Although any one of the three models just described might plausibly account for the observation of a singlet resonance, in common with the metal particles model, none seems capable of accommodating the full and detailed range of experimental observations now available. We shall therefore explore one further possibility.

C. Interacting Electrons. (i) Low Concentrations of Metal: The Basic Model. Careful observation of the emergence of the ESR singlet resonance in Na_x/Na_{55}–Y, as x was increased, reveals that although the faujasite unit cell contains eight potential sites (sodalite cages) for Na_4^{3+}, the singlet was already important at nominal concentrations as low as $x = 3$ atoms p.u.c. and dominant at $x = 8$. Its first appearance in the spectrum came at between $x = 1$ and $x = 3$, when only about one-quarter of the sodalite cages should contain Na_4^{3+} centers. At $x = 13$ the spectrum of Na_4^{3+} had all but disappeared (Figure 3). These observations carry all the more force for the likelihood that these nominal values of concentration overestimate the true concentrations within the samples. Remarkably, it seems that the singlet appeared not at $x = 8$, when *all* the sodalite cages should be filled with Na_4^{3+}, but just at the stage where the probability that two Na_4^{3+} centers occupy *adjacent* sodalite cages becomes significant.

The clear implication of the preceding paragraph is that the change in ESR behavior, represented by the emergence of the singlet resonance, may be caused by the interaction of neighboring Na_4^{3+} centers. The proposal that Na_4^{3+} centers in adjacent sodalite cages might interact with each other is by no means without precedent. Herron et al.[44] have prepared cubic $(CdS)_4$ clusters located within the sodalite cages of zeolites X, Y, and A, whose optical properties were explained in terms of "superclusters"—groups of clusters bound together by the interaction between $(CdS)_4$ units in adjacent cages. Indeed it is already established that electrons in traps such as Na_4^{3+} may have a considerable range: in sodalites, the pulse-ENDOR and electron spin–echo envelope modulation (ESEEM) techniques have demonstrated an isotropic hyperfine interaction with sodium atoms located in neighboring cages.[18,45]

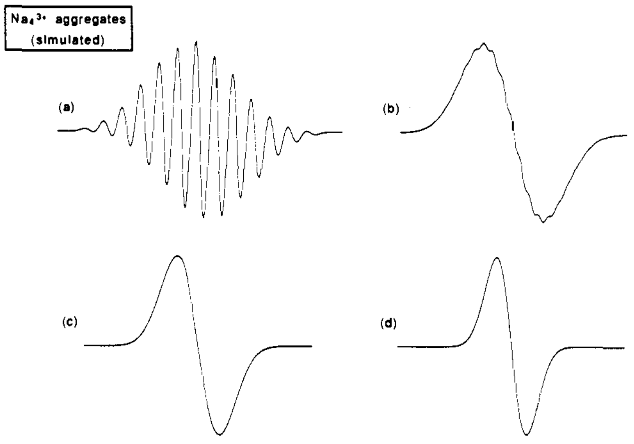

Figure 13. The simulated ESR spectrum (a) of the Na_4^{3+} center (a = 32 G, ΔH_{pp} = 20 G), and of (b) 2, (c) 4, and (d) 8 interacting centers.

Evidence that electrons in traps such as Na_4^{3+} do interact with each other, over relatively long distances, is provided by measurements on Rb_1/Na_{55}–Y. A plot of the reciprocal intensity of the signal (proportional to the inverse susceptibility $1/\chi$) versus temperature (Figure 7) has, when extrapolated, an intercept of ~25 K on the negative temperature axis, which is probably an indication of weak antiferromagnetic coupling between centers. The observation is remarkable because Na_4^{3+} centers in this compound can occupy no more than one-eighth of the sodalite cages, and are therefore on average at least 24 Å apart. Logically a much stronger interaction can be expected between centers in adjacent sodalite cages whose midpoints are a mere 12 Å, and whose sodium ions may be as little as 5 Å, apart.

It is our proposal that electrons in centers occupying adjacent sodalite cages are sufficiently close to one another that their wave functions overlap and they are coupled through quantum-mechanical exchange forces. What kind of ESR spectrum can be expected in this case? The problem has already been addressed by Slichter,[46] in relation to "impurity" centers in silicon located at donor atoms such as arsenic or phosphorus. In the case of strong coupling between centers, each electron spin effectively samples the nucleus not of one, but of all the coupled centers.[46,47] Applied to Na_4^{3+}, for instance, this means that if two neighboring centers are strongly coupled, each spin will effectively experience the hyperfine field of eight sodium nuclei instead of four, and the magnitude of the interaction with each nucleus will be reduced by the same factor of 2. The ESR spectrum expected in this instance has been simulated and is shown in Figure 13, along with those of Na_4^{3+} itself, and groups of four, and eight, interacting centers. It can be seen that the hyperfine splitting and line width of the spectrum of Na_4^{3+} are such that, even for two interacting

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(43) Catterall, R.; Edwards, P. P. *Adv. Mol. Relaxation Interaction Processes*, **1978**, *13*, 123–169.

(44) Herron, N.; Wang, Y.; Eddy, M. M.; Stucky, G. D.; Cox, D. E.; Moller, K.; Bein, T. *J. Am. Chem. Soc.* **1989**, *111*, 530–540.

(45) Smeulders, J. B. A. F.; Hefni, M. A.; Klaassen, A. A.; De Boer, E.; Westphal, U.; Geismar, G. *Zeolites* **1987**, *7*, 347–352.

(46) Slichter, C. P. *Phys. Rev.* **1955**, *99*, 479–480.

(47) Holcomb, D. F. In *The Metal-Nonmetal Transition in Disordered Systems*; Friedman, L. R., Tunstall, D. F., Eds.; Scottish Universities Summer School in Physics: St. Andrews, 1978; pp 251–333.

centers, individual hyperfine lines can barely be resolved; for four Na_4^{3+} centers all sign of hyperfine structure has vanished and the envelope has become a smooth, symmetric ESR line (Figure 13c).

In the faujasite structure possessed by zeolite Y the sodalite cages are linked to one another in the same way that the carbon atoms are joined in diamond (Figure 1). Each sodalite cage thus has four nearest neighbors from which it is separated only by a hexagonal prism. As more sodium atoms enter Na-Y and more sodalite cages are filled with Na_4^{3+} centers, gradually adjacent sodalite cages will become occupied, and we can expect that small groups of interacting centers will grow, giving rise to a singlet ESR line. For aggregates of exchange-coupled F-centers, Warren et al.[48] have shown that the ESR line width is proportional to $1/n^{1/2}$, where n is the number of interacting centers. Applying this relation to Na_4^{3+} centers, and with the help of simulations such as those in Figure 13, we find that the envelope line width expected for a group of n interacting centers is given by

$$\Delta H_{pp} \approx 140G/n^{1/2} \qquad (1)$$

It is reasonable to assume that as the concentration of Na_4^{3+} centers increases, the number with neighbors in adjacent sodalite cages will also increase, and that small groups will rapidly grow into extensive domains of coupled centers. Since the ESR envelope is predicted to narrow as n increases, this rather primitive model qualitatively predicts the observed rapid fall in the ESR singlet line width with increasing concentration of metal in Na_x/Na_{55}-Y (Figure 4). The characteristic observed line shape, with greater intensity in the wings than a Lorentzian line, is also readily explained: a distribution of line widths, due to the presence of groups and domains of various sizes, would result in a composite signal akin to that previously observed for metal particles.[35] Even the eventual slow increase in line width which accompanied decomposition of the zeolite framework at high concentrations of metal might be accounted for by a return to smaller groups as the structure collapsed, a process apparently resulting in the eventual reemergence of the spectrum of Na_4^{3+} (Figure 8).

According to eq 1, a group of four Na_4^{3+} centers should produce a line of width 70 G, but in practice the largest value recorded for Na/Na-Y is ~40 G.[3] As we have seen, each sample will actually contain a distribution of group sizes, but an envelope line width of 40 G yields a characteristic group size of $n \approx 12$. Power saturation studies on very dilute samples indicate that broader lines did occur in Na_x/Na_{55}-Y but were obscured by the spectrum of Na_4^{3+}; line widths as large as 80 G were observed in Na_x/Na_{87}-X. At the other extreme, a sample with $x = 8$ should have all its sodalite cages filled, and each zeolite crystallite should represent a single domain. The observed line width for Na_8/Na_{55}-Y was ~20 G, which implies a characteristic group size of $n \approx 50$, much less than the number of sodalite cages in an average crystallite. The narrowest line ($\Delta H_{pp} \approx 7$ G) recorded for the singlet in Na_x/Na_{55}-Y would correspond to domains of $n \approx 400$ centers.

Discrepancies between the observed line widths and the simple calculations of the preceding paragraph might be considered a consequence of inhomogeneity, or of crystalline imperfections in the zeolite, or indeed of the fact that nominal concentrations probably represent an overestimate of the amount of metal in the zeolites, but in any case the model is inadequate in at least one important respect: the form of an ESR spectrum observed from a group of exchange-coupled paramagnetic centers is likely to depend critically on the strength of the exchange interaction itself. In general this is primarily dependent on the average distance between the centers, and can be quantified by a characteristic frequency ω_E. Since the distance between adjacent sodalite cages is fixed, the strength of the interaction is roughly constant, a fact which goes some way toward explaining the partial success of the simple model: if the number of coupled centers is small and ω_E large, the ESR spectrum will indeed be primarily dependent on the number of centers in a domain, but as the number of interacting centers becomes large, there is imposed on the line width a lower limit, dependent on ω_E, which effectively represents the number of centers sampled by a spin on the timescale of the ESR measurement.

In the low-temperature limit one might expect a group containing an even number of centers to be diamagnetic with all spins paired.[46] In contrast, a group with an odd number of centers should retain at least one unpaired spin. In a real sample containing both "odd" and "even" groups, the overall effect is likely to be a residual Curie-like dependence of the susceptibility with temperature as previously observed in the ESR of both Na/Na-Y and other alkali metal/zeolite systems.[3-6] Furthermore, the model described in this section does not depend on atomic or electronic motion to effect spin delocalization, rather on overlap between the wave functions of electrons in neighboring Na_4^{3+} centers, and since this overlap evidently produces changes in the wave functions of those electrons, there is no reason to expect that the g value of the ESR signal should be the same as that of the isolated centers. That the observed value should be essentially the same as that of sodium metal suggests that the wave functions of electrons in our groups of coupled centers mirror some features of the bulk metal itself. Indeed, Slichter[46] regarded the growth of such groups in doped silicon as "simply the first step in the process of turning the sample into a metal".

(ii) Higher Concentrations of Metal: Approaching the Metal-Nonmetal Transition. In the preceding section the discussion was developed in some detail for the case of Na-Y, but as this point it is important to emphasize that the basic model could equally well apply to Na-A, where Na_4^{3+} centers are also found, or Na-X which plays host to analogous centers.[11] In any case the model is at best an incomplete description of the inclusion compounds of sodium in zeolites, for it does not take into account the fact that the uptake of sodium metal continued far in excess of the concentration ($x = 8$) at which Na-Y must be regarded as saturated with Na_4^{3+} centers. A sample such as Na_8/Na_{55}-Y is necessarily very different from Na_{50}/Na_{55}-Y, for example, where only a minority of sodium valence electrons might possibly reside in Na_4^{3+} traps, but remarkably, the ESR spectrum was found to change little as x was doubled once, twice, and even three times, from 8 atoms p.u.c.

The failure to observe a new component in the ESR spectrum of Na_x/Na_{55}-Y, as sodium atoms were introduced to the zeolite in excess of the number required to form an Na_4^{3+} center in each sodalite cage, might perhaps be taken as evidence that the additional sodium was being incorporated in a diamagnetic form, but in both this and previous work the intensity of the singlet line has been found to increase steadily up to concentrations of $x > 50$.[5] In any case, it is clear from ^{23}Na NMR results that the incorporation of sodium metal into dehydrated Na_{55}-Y caused a marked *decrease* in the amount of diamagnetic sodium detected in the zeolite. Recent double-rotation NMR studies on dehydrated Na-Y have shown that the relatively complex shape of the ^{23}Na NMR spectrum is partly due to the occupation of a number of different sites by the sodium cations within the zeolite structure, and that the main peak in the spectrum most probably emanates from ions in highly symmetric sites at the center of a hexagonal prism.[49] The intensity and line shape of the spectrum of Na_{50}/Na_{55}-Y suggest that not only did the resonance arise from sodium ions already present in the dehydrated zeolite, but also that it arose from only a small proportion of these, in only one of the possible cation sites.

A certain reduction in the number of sodium ions contributing to the NMR signal on the addition of sodium metal is not unexpected, as some must become incorporated into paramagnetic Na_4^{3+} centers, but it appears that most of the sodium ions originally present in dehydrated Na_{55}-Y do not, in fact, contribute to the spectrum of Na_{50}/Na_{55}-Y. If we exclude for a moment the possibility that this might be due to changes in cation sites or site symmetries,[50] we must conclude that many of the sodium

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valence electrons, introduced to the zeolite after it is saturated with Na_4^{3+} centers, also remain unpaired and associated with sodium ions, and that they interact with most of the sodium cations that were already present in the dehydrated zeolite. Further, the observation that the ESR singlet intensity continued to increase as the concentration of sodium exceeded 8 atoms p.u.c. indicates that these electrons may be able to participate in the complex of interacting centers. Since any unpaired electron within the zeolite structure, whatever its precise location, cannot be more than 6–7 Å from the nearest sodalite cage, this is entirely plausible. The characteristic g value of the singlet, unchanged at concentrations of metal far in excess of 8 atoms p.u.c., is fully consistent with the proposal that these surplus electrons both remain associated with sodium cations and are coupled to their neighbours.

One unfortunate consequence of the interaction between electrons, and the loss of hyperfine structure, is that it becomes rather more difficult to elicit precise information about their states and location, but the ESR experiment does provide us with some clues. Since an increase in the number of sodium valence electrons in the zeolite necessarily implies a decrease in the average distance between them and an increase in ω_E, the continuing fall in the observed ESR line width of Na_x/Na_{55}–Y, as x exceeded 8 atoms p.u.c., has a ready explanation. Borrowing once again from the work on F-centers,[51] we may obtain an estimate of the narrowing frequency through the relation

$$\omega_N = \gamma(\Delta H_{hfs})^2/\Delta H_{pp} \quad (2)$$

where γ is the electron gyromagnetic ratio, ΔH_{pp} the observed line width, and ΔH_{hfs} the "natural width" of the line. In F-centers, where hyperfine splittings are seldom resolved, this last parameter is simply the line width of an isolated center. Although such a line width cannot be measured directly for centers such as Na_4^{3+}, a value of ~140 G may be inferred from eq 1. Assuming that this is characteristic of the strength of the hyperfine field experienced by all the sodium valence electrons in the zeolite, we may calculate through eq 2 that, to produce the narrowest lines observed, the required narrowing frequency is in the range 10^{10} to 10^{11} Hz. This value is greater than ω_E quoted for crystalline F-centers,[52] but similar to that observed by Nicoloso and Freyland[51] for F-centers in molten halides, where motional averaging may also contribute to the narrowing.

The assumption of a similar motional contribution to the line-narrowing in sodium zeolites enables the complicated and contradictory behavior as the temperature was reduced of the ESR singlet line width in the three zeolites to be blamed on the conflicting effects of an increase in T_2 (the electron spin–spin relaxation time) and a reduction in the narrowing frequency. It is also interesting that the line widths observed in samples of Na_x/Na_{55}–Y were in general greater than those of comparable compounds of Na_{87}–X and Na_{12}–A, both of which have a silicon to aluminum ratio of close to unity, and therefore have a higher cation density than Na_{55}–Y. This too is consistent with the idea that the line-narrowing process might be subject to a motional contribution; electron hopping, for instance, would be expected to occur more rapidly in zeolites whose cations were closer together.

How does one, then, best describe a compound like Na_{50}/Na_{55}–Y? We have seen evidence that, when sodium is introduced to the Na–Y, each valence electron interacts both with a number of sodium cations and with other unpaired electrons, regardless of whether it is located in a Na_4^{3+} center or not. Perhaps the most natural thing to imagine is that those electrons not in involved in Na_4^{3+} reside in similar but rather less stable traps elsewhere in the zeolite structure. As discussed earlier (section B), there is no direct evidence for the existence of such traps, which are at best likely to be only transient, with both ions and electrons enjoying a certain degree of mobility at normal temperatures. This at least is consistent with evidence for a motional contribution to line-narrowing. In fact, we cannot even tell if Na_4^{3+} centers persist in Na_{50}/Na_{55}–Y, but since they are not found in Na_{87}–X, it would seem unlikely that they are present in samples of Na_x/Na_{55}–Y with $x > 30$ included atoms p.u.c. In the absence of identifiable stable traps in concentrated samples, we are left simply with an ill-defined collection of electrons and ions all interacting together in a kind of "paramagnetic soup".

At this stage it seems appropriate to look at the experiment which is being performed from an entirely different point of view. Conventionally a metal is described by the notional separation of its constituent atoms into a "gas" of free electrons and a regular array of ions. Coordinated on only one side to the anionic framework, the "half-naked" cations of a dehydrated zeolite represent such an array, lining the inside of the zeolite channels and cavities. The reaction with metal can be considered both to increase the number of cations in the zeolite and to introduce valence electrons to the system. At first these electrons may occupy localized states in well-defined traps such as Na_4^{3+}, but at higher concentrations they show definite signs of delocalization.

In the case of silicon doped with phosphorus, an important distinction has been drawn between "spin delocalization"—the loss of hyperfine structure from the ESR spectrum—and "charge transport delocalization", which defines the compound as a genuine metal, able to conduct a current. As the concentration of phosphorus donors is increased, the former has been shown to occur well before the latter.[47] Edwards and Sienko[53] found that, in a wide variety of condensed systems, the transition from nonmetal to metal is successfully predicted by a scaled form of the Mott criterion,

$$n_c^{1/3}a_H^* = 0.26 \pm 0.05 \quad (3)$$

where n_c is the concentration of localized single-electron states, and a_H^* is an appropriate radius associated with the impurity wave function of the state in question. Applying this to the case of Na_4^{3+} centers in zeolites, and using the estimates of Xu et al.[54] for the radius of the valence electron in Na_4^{3+}, we can predict that a transition to metallic behavior should occur at concentrations of between 10^{21} and 10^{22} centers/cm^3.

The concentration of sodalite cages in the faujasite structure is about 5×10^{20} cm^{-3}, and so a sample of Na–Y containing a perfect array of sodalite cages each filled with an Na_4^{3+} center is not expected to be metallic. In samples containing more included metal, however, the concentration of sodium valence electrons introduced to the zeolite may well reach the values just mentioned. Although this analysis dovetails neatly with the earlier suggestion that electrons may have a certain degree of mobility in such compounds, so far we have collected no evidence to suggest that any compound of sodium metal in zeolites is indeed "metallic". This statement is not as conclusive as it may sound. If charge transport delocalization were to occur in such a compound, with its interpenetrating aluminosilicate lattice and less than one electron for every two cations, it would constitute a very peculiar metal indeed. Even if the channels and cavities of the zeolite were filled with a truly metallic phase, it is by no means clear what sort of physical properties would be expected of this porous and highly electron-deficient, diluted metallic state.

Summary and Conclusion

The results of this paper constitute the most detailed examination of the reaction between the alkali metals and zeolites yet undertaken. For the first time, the reaction between sodium vapor and three different zeolites—Na–X, Na–Y, and Na–A—has been studied quantitatively, as a function of the included metal, and its efficacy in introducing sodium into the zeolite pores on a large scale is demonstrated. In particular, ^{23}Na NMR results show that the direct reaction between vapor and solid achieves this more selectively than the alternative method involving the decomposition of sodium azide. For the first time the ESR singlet lines, previously attributed to small metal particles within the zeolite pores, have

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been studied in some detail. Although they exhibit g values characteristic of sodium metal, it is clear that these spectra are not consistent with a simple metal particles model, and that talk of quantum size effects in such systems is premature.

Initially when sodium atoms enter Na–Y, they are ionized, and the valence electrons thus released are trapped in the sodalite cages to form Na_4^{3+} centers. It is the cornerstone of our interpretation that centers located in adjacent sodalite cages are sufficiently close to one another that they are coupled strongly through the exchange interaction, resulting in the loss of hyperfine structure and a featureless singlet ESR line. The concept of domains of interacting paramagnetic centers enables many other features associated with the ESR of the inclusion compounds of sodium in zeolites X, Y, and A to be rationalized. The fall in line width of the ESR singlet in Na/Na–Y with increasing concentration of included metal may be ascribed to increasing domain size, and the eventual slow increase in line width which accompanied decomposition of the zeolite framework at high concentrations of metal may be accounted for by a return to smaller domains as the structure collapsed. The characteristic line shape, with more intensity in the wings than a Lorentzian line, can also be explained by the presence of a distribution of line widths due to different domain sizes. Lastly, the model is consistent with the important observation that the intensity of the singlet line increases at low temperature.

The emphasis of the basic model on the interaction between stable paramagnetic centers located in the sodalite cage limits its validity to relatively low concentrations of included metal, before the sodalite cages become saturated. In contrast, the ESR spectra are observed to evolve gradually as the zeolites accommodate sodium far in excess of this amount. Evidence from both ESR and ^{23}Na NMR suggests that, whatever their precise location, the surplus valence electrons are also able to interact with their neighbors and contribute to the singlet ESR line. The continued decrease in line width with increasing sodium concentration may thus be attributed to a decrease in the average distance between interacting electrons, as Na_4^{3+} becomes one of many possible paramagnetic centers all interacting together in a "paramagnetic soup". At high concentrations of included sodium there is some evidence of mobility, of either atoms, ions, or electrons, and a motional contribution to line-narrowing. A reason for the unusual nature of the variation of the singlet line width with temperature in the three zeolites considered may therefore be found in the conflicting effects of an increase in T_2 and a reduction in the narrowing frequency.

In the absence of framework degradation, the characteristic g values of the compounds we have studied are fully consistent with those recorded previously for sodium metal or metal particles (Table I). The fact that *liquid* sodium[31] exhibits the same g value is proof aplenty that the observation of this value is not indicative of the presence of the bulk lattice or, indeed, of any particular structure. The results presented here indicate that it may well be contingent only on the fact of interaction between sodium valence electrons. At any rate, it is abundantly clear that extreme caution must be exercised in the assignment of unexplained ESR lines to particulate or "colloidal" sodium.

In this paper we have developed a description of the inclusion compounds of sodium in zeolites which is consistent with a wide range of detailed experimental observations. Casting the incoming sodium atoms in the role of electron donors, and focusing on the interaction of the released electrons both with the sodium ions of the zeolite framework and with each other, it provides an entirely new conceptual framework for the study of this class of compounds and indicates that they will make an important contribution to our understanding of the metal–nonmetal transition.

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Structural Information of the Nitrogenase Metal Clusters Deduced from Paramagnetic Interactions

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Abstract: The MoFe-protein (component 1) of nitrogenase contains two major classes of metal clusters, called P and M. In the as-isolated form of the protein, the P-clusters are diamagnetic while the M-centers are paramagnetic, yielding an EPR spectrum of an $S = {}^3/_2$ species. This protein was titrated with thionin to oxidize the P-clusters, converting them into paramagnetic species while preserving the paramagnetism of the M-centers. During this titration, the relaxation properties of the protein's M-centers were monitored with an EPR spectrometer using the technique of progressive power saturation. The results obtained using this technique demonstrate the existence of a perturbation of the relaxation times (T_1T_2) of the M-centers induced by the presence of the paramagnetic P-clusters. The magnetic interaction that induces this perturbation depends on the orientation of the MoFe-protein in the spectrometer's magnetic field and, therefore, is probably dipolar in origin. Furthermore, the nonlinear relationship between the magnitude of this perturbation and the extent of oxidation of the P-clusters can be interpreted in terms of a semi-interactive model in which four P-clusters are grouped as two interactive pairs. In this model, the magnitude of the magnetic interaction between the P-cluster pairs and the M-centers is greater when one P-cluster is oxidized than when both clusters of the same interactive pair are oxidized. This model further shows that, while the P-clusters of the resting enzyme are diamagnetic, the 1- and 2-equiv oxidized forms of the P-cluster pairs can both be paramagnetic.

Nitrogenase catalyzes the biological reduction of dinitrogen to ammonia. The conventional form of the enzyme consists of two distinct proteins, both necessary for enzymatic activity. One of the proteins (called component 1 or the MoFe-protein) contains 30–33 Fe and 2 Mo atoms in various metal clusters and possesses the sites for substrate reduction.

Characterization of component 1 by EPR, Mössbauer, X-ray absorption, ESEEM,[1] MCD, and ENDOR spectroscopies has

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