On the Possibility of an Insulator–Metal Transition in Alkali Metal-Doped Zeolites

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1 Introduction

Conventionally a metal may be viewed through the notional separation of its constituent atoms into a regular array of ions and a gas of itinerant electrons.[1,2] Although neither exists in practice, a close approximation to the former is a dehydrated zeolite, where cations connected on only one side to an anionic framework line the inside of a series of regular, interconnected cavities (Figure 1).[3] These white solids are, of course, insulators. The most effective route for the controlled and continuous doping of 'excess electrons' – possibly localized, possibly itinerant – into these pristine solids is through their reaction with alkali metal vapour.[4–6]

We will illustrate here that where the incursive atoms of the vapour of, for example, Na, K, Rb, or Cs, enter a dehydrated zeolite containing a large number of framework cations (generally Na^+ or K^+), they are spontaneously ionized by the intense electric fields within the host matrix.[7] The incoming metal atoms (M^0) are to all intents and purposes 'dissolved' and the resultant entities M^+ and e^- are totally integrated into the solid host structure in a manner reminiscent of the spontaneous dissolution of these same alkali metals in liquid ammonia.[8,9] At low doping levels of alkali metal vapour, the released excess electrons are then at liberty to interact with a number of framework cations leading to the formation of well defined, and spatially localized paramagnetic clusters of the former $M'^{(n-1)+}_n$, where M' is the framework alkali cation and n = 2,3,4,5,6. The introduction, of alkali atoms into the receptive host zeolite can therefore be considered both to increase the cation density and to 'titrate' excess electrons into the structure.

At some critical stage of metal loading, one expects enhanced electron–electron interactions and one may further envisage the possibility of a 'matrix-bound' Insulator–Metal Transition[10,11] within the zeolite host. The possibility of such an intriguing 'metallization' transition occurring within the intracrystalline

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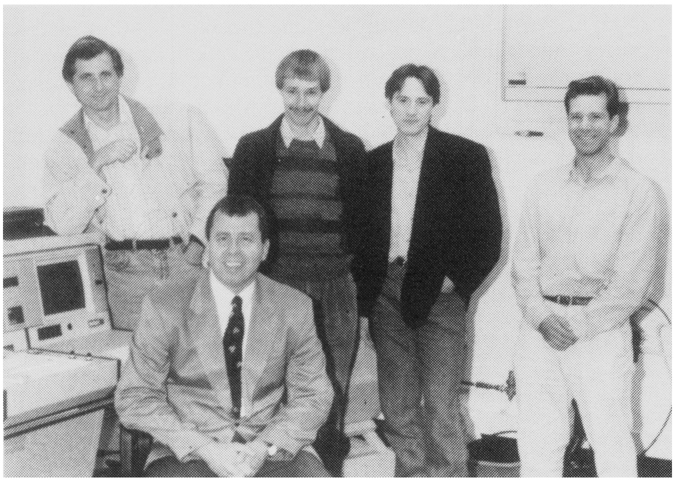

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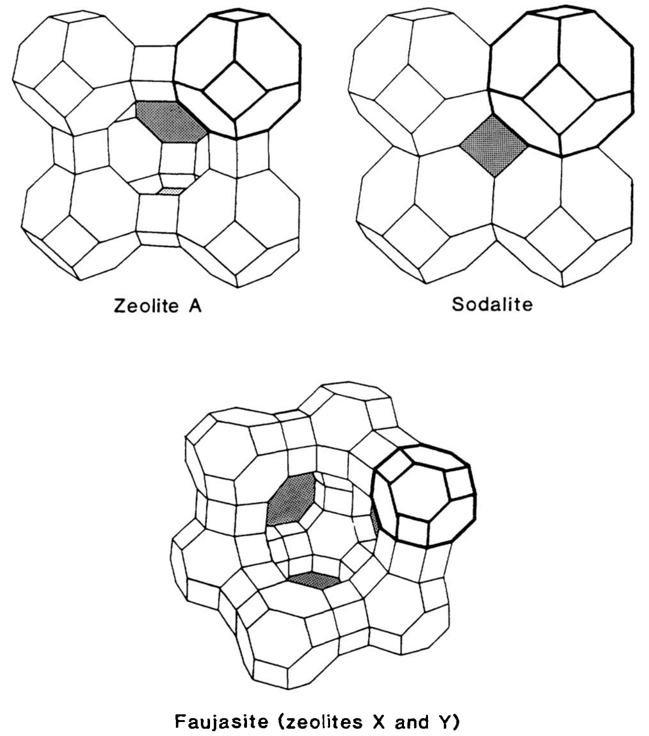

Figure 1 The structures of the zeolites discussed in this work are shown along with those of the related mineral sodalite. The vertices of the polyhedra are occupied by silicon or aluminium atoms: the framework oxygens and exchangeable cations are omitted for clarity.

channels and cavities of nanoporous zeolites is the focus of this present report. Its experimental verification is, as yet, unproven, although there are very strong precedents for this proposal.[12] Just what degree of metal loading is required – and indeed what type of 'metal' ensues – is currently unknown. Obviously, this is not a report of completed work on a well developed subject. It cannot be, for many of the key experiments (most notably electrical transport measurements) are yet to be undertaken. However, we can report recent and substantial advances not only in the determination of the crystal structure of these intriguing solids, but also in the nature of the electronic properties conferred upon the zeolite system through the controlled doping with alkali metals. For the latter, we review ESR, NMR and magnetic susceptibility studies which, in combination, directly probe the electronic nature of the excess electrons.[13] These magnetic and resonance measurements also have a fundamental advantage in that they are non-intrusive/non-destructive interrogators of the electronic structure of solids – a major consideration in the study of these highly reactive, moisture-, and air-sensitive materials. The experiments are difficult, but one feels that the reward will be new contributions to our understanding of the Insulator–Metal Transition and, indeed, to the very nature of the metallic state itself. Thus, instead of providing definitive answers we can, at this juncture, outline the current emerging views. Before reviewing our current knowledge of the title systems, it is appropriate to set comparisons with other, perhaps more established systems which undergo Insulator–Metal Transitions.[10,11]

2 Matrix-Bound Insulator–Metal Transitions

In a 'pure', one-component vapour (*e.g.* Na or Cs metals under supercritical conditions) very high densities are generally required to effect the transition from insulating to metallic behaviour.[14] The particular examples of expanded Cs and Hg are included in Figure 2 which illustrates the Insulator–Metal Transition for a range of systems as detected by the concentration dependence of the electrical conductivity.[15] As one can see from this figure, transitions from insulating to metallic behaviour occur as some parameter of the system, or some external variable, is continuously changed. Of particular concern to us will be the precise location of this electronic phase transition, as well as the temperatures generally used in probing such a transition to – and from – the metallic state. Importantly, all of these parameters are intrinsically system-dependent and derive from subtle differences in the physics and chemistry of the problem. We will amplify these comments in the paragraphs below.

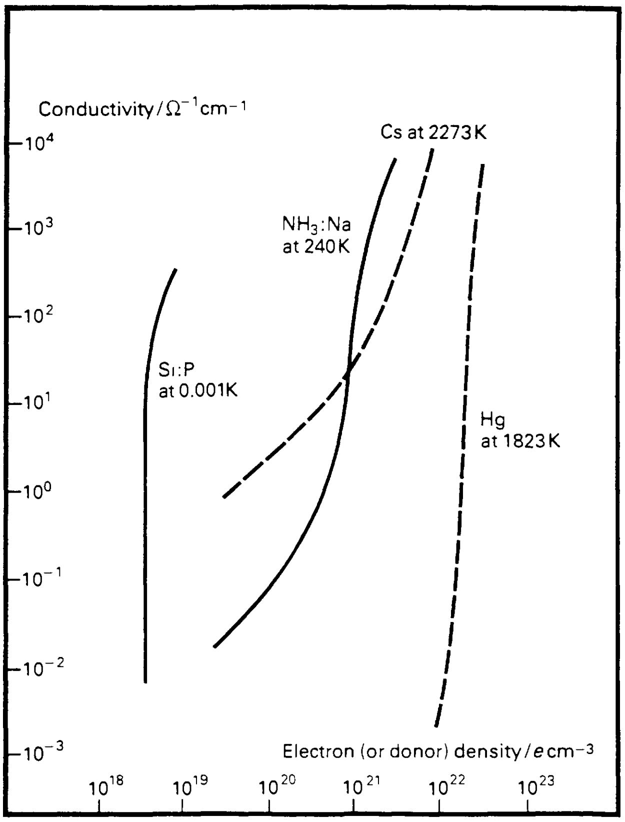

Figure 2 The Insulator–Metal Transition, showing the concentration dependence of the electrical conductivity for the expanded metals Hg and Cs, and the matrix-bound transitions in Si:P and NH_3:Na. The appropriate observation temperatures are also given (from ref. 15).

The vast majority of such experimental systems (Figure 2) are best described as 'matrix-bound' in that they comprise an assembly of, for example, one-electron impurity or donor centres embedded in a host material (*e.g.* elemental Si, liquid NH_3).[13] Within this description, one encompasses the examples of expanded (supercritical) alkali metals, alkali metal–ammonia solutions, and doped group 14 semiconductors.[11] A prototype example of a matrix-bound Insulator–Metal transition is seen in the metallic condensation of the lattice of hydrogen-like impurity centres (*e.g.* P, As, Sb) in the hosts silicon and germanium.[16,17] In all of these systems, the chemical nature of the host matrix is of paramount importance from two counts.[18] First, it dictates the precise form of the (localized) excess electron wavefunction at low doping levels. Secondly, and at higher densities, it influences (part through the preceding effect) the critical conditions for the transition to the metallic state.

Another venerable example is that of sodium–ammonia solutions.[8,9] Most chemists are aware that at low concentrations of sodium, these solutions are blue and electrolytic; at high concentrations they are bronze-coloured with a conductivity rivalling that of liquid mercury. As we hinted in Section 1, we believe there are strong links to the present example of alkali metal 'solutions' in zeolites. An appreciation of the semiconductor, or matrix-bound analogy for Na–NH_3 was given some 35 years ago.[19] In this view liquid NH_3 is viewed as a dielectric host matrix in which the alkali atom simply takes on the role of a donor or impurity state, this is a complementary description to the chemical 'dissolution' of the element in liquid ammonia.[9,20]

In the case of expanded metals, *e.g.* caesium and mercury (Figure 2) one can view the system as 'metal-doped vacuum' and this, once again, provides the direct semiconductor/matrix-bound analogy for which the 'host' dielectric constant now becomes unity.[13]

Returning to the case of the doped semiconductors, the ground state wavefunction for the localized (low density) impurity centre (*e.g.* Si:P) is characterized by an extremely diffuse, hydrogen-like function having a characteristic Bohr radius, a_H^*, of *ca.* 20 Å in Si and *ca.* 45 Å in Ge. A concomitant weak binding energy (typically < 0.005 eV) for the localized electron centre necessitates extremely low temperature measurements (typically 10 mK) to probe the natural evolution of the Insulator–Metal Transition within the silicon matrix (Figure 2).[21]

In the case of 'sodium-doped ammonia' (NH_3:Na) the excess or donor solvated-electron wavefunction at low doping levels is generally described as being strongly localized in a void or cavity in the host liquid, having a characteristic Bohr radius of *ca.* 2—3 Å.[8,9,20] Here typical binding energies would be in the region 1—3 eV. In the case of the solvated electron, the wavefunction is strongly localized on the highly polarized entourage of solvent molecules, the species can be written as $(NH_3)_x^-$. There are interesting comparisons to be made between, for example, Na_4^{3+} and $(NH_3)_x^-$.

These fundamental differences in the nature, extent and binding of the localized electron wavefunction in all of these systems has a profound bearing on the critical density (n_c) and location of the Insulator–Metal Transition at high densities.[18] Of course, the term 'high' is purely relative, samples of Si:P become metallic at densities above *ca.* 3×10^{18} elec cm^{-3}, NH_3:Na solutions attain metallic status at densities exceeding 10^{21} elec cm^{-3} (Figure 2).

It was Mott who first described a simple criterion linking a_H^* to the critical density, n_c, at the Insulator–Metal Transition, *viz.*[10,22]

$$n_c^{1/3} a_H^* \geq 0.2 \qquad (1)$$

Although more complicated theories have been developed,[11] Mott's view unquestionably describes the basic physics of the problem and at the same time it has the attraction of transparently describing/prescribing the transition in a wide variety of matrix-bound systems.[18]

The experimental data linking a_H^* and n_c (both determined experimentally) for the systems discussed above (and others) are shown in Figure 3. Edwards and Sienko[18] found that, for these wide variety of condensed phase systems, the transition from Insulator to Metal is successfully predicted by a scaled form of the Mott criterion,

$$n_c^{1/3} a_H^* = 0.26 \pm 0.05 \qquad (2)$$

This criterion appears to be upheld over almost eight orders of magnitude in n_c and three orders of magnitude in a_H^*. Such considerations will be important guides to our discussion of a possible metallization transition in alkali metal doped zeolites.

We now turn to the case in hand, and outline how alkali doping brings about changes in the electronic properties of the host system. Our aim will be to sharpen our emerging description of these new solids by comparison – and contrast – with the above, more-established systems.

3 The Electronic and Geometric Structure of Alkali Metals in Zeolites

3.1 Low Concentrations: Coordination and Ionization

The characteristic pink to red coloration and ESR spectrum of 13 lines characteristic of Na_4^{3+} were first observed by Kasai[4] upon irradiation (under vacuum) of dehydrated sodium-Y (Na–Y) with γ, or *X*-rays. Both the number of ESR lines and their intensities are in excellent agreement with those expected from a system of four equivalent nuclei with I = 3/2 (^{23}Na). In Na–Y this means that the ESR spectrum originates from an excess electron trapped between four equivalent sodium cations. Similar reasoning leads to the identification[5] of the corresponding potassium species, K_4^{3+} (Figure 4).

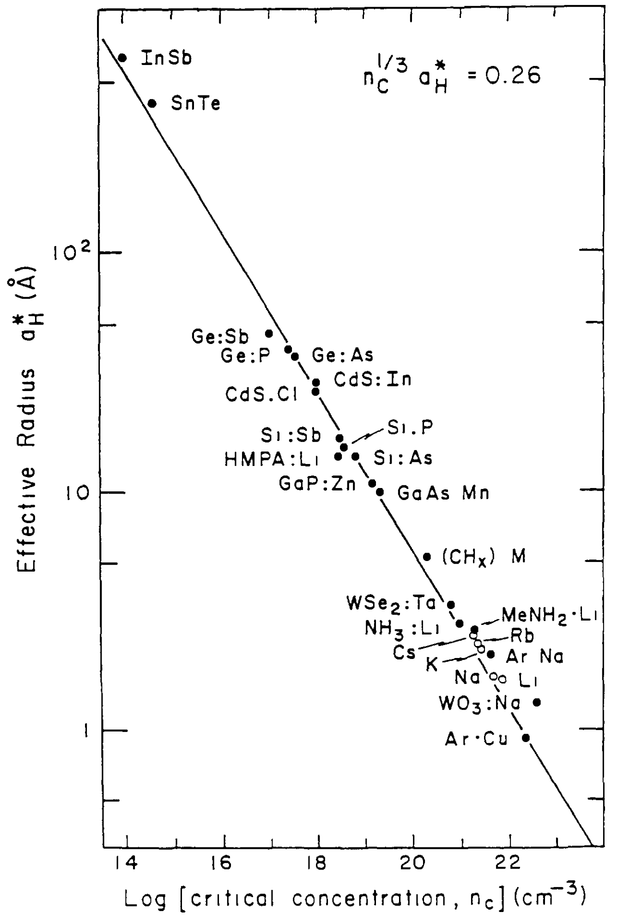

Figure 3 A logarithmic plot of the effective Bohr radius, a_H^* *vs* the critical concentration for metallization, n_c, in a variety of systems (from refs 2, 18, 20)

Recent neutron diffraction studies[23] suggest that the participating ions in K_4^{3+} are for the most part drawn from outside the sodalite cage and held there under the influence of the unpaired electron in four tetrahedrally arranged cations. Figure 5 shows the structure of the sodalite cage in K_5/K–A (K_5 notation denotes an additional five potassium atoms per primitive unit cell) showing a tetrahedron of potassium ions inside a sodalite

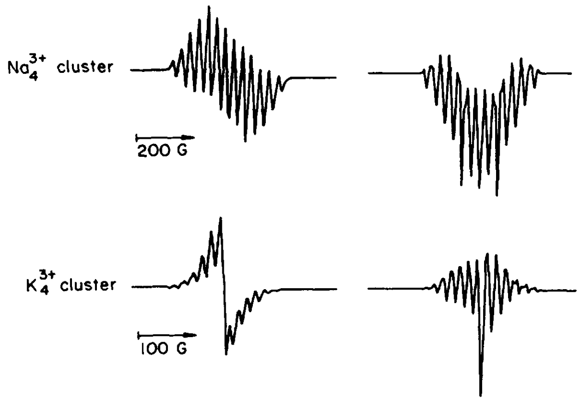

Figure 4 The ESR spectra of Na_4^{3+} and K_4^{3+} showing both first- and second-derivative presentations (from ref 5*a*)

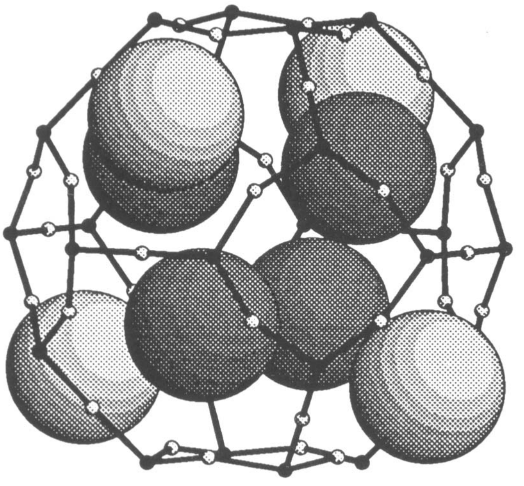

Figure 5 The sodalite cage in K_5/K–A showing a tetrahedron of K^+ ions inside the cage (dark circles) with faces capped by another tetrahedron of K^+ ions outside the cage (pale circles) (from ref 23)

cage (dark circles) with faces capped by a further tetrahedron of potassium ions outside the cage (pale circles).

To further highlight the solvent/matrix duality of the host zeolite, the following equations are useful descriptions for the processes under consideration

$$\begin{array}{lllr}
(\mathrm{M^0\text{–}Zeolite}) & \mathrm{M^0 + 4Na^+_{(zeolite)}} & \rightarrow \mathrm{M^+ + Na_4^{3+}} & \\
 & \mathrm{M^0 + 4K^+_{(zeolite)}} & \rightarrow \mathrm{M^+ + K_4^{3+}} & (\mathrm{M = Na,K,Rb,Cs}) \\
(\mathrm{M^0\text{–}NH_3}) & \mathrm{M^0} + x\mathrm{NH_3} & \rightarrow \mathrm{M^+ + (NH_3)_x^-} &
\end{array}$$

A particularly 'clean' example of the ESR spectrum from a localized non-interacting Na_4^{3+} centre (without interference from other resonances) derives from the product obtained from low temperature reaction of Rb vapour with Na–Y;[6]

$$\mathrm{Rb^0 + 4Na^+_{(zeolite)} \rightarrow Rb^+ + Na_4^{3+}} \qquad (3)$$

This reaction is also important since it illustrates that, to first order, the role of the added alkali atoms is simply that of an electron donor. Clearly the fate of the ensuing Rb^+ – presumably integrated into the host structure – may have some effect at the higher doping levels.

We view the zeolite, therefore, as a solid 'solvent' for the dissolution of alkali metals; in much the same way the Na_4^{3+} centre can be viewed as an 'electride' derived, for example, from a solution of alkali metals in various non-aqueous solvents [24]

In the vast majority of cases studied to date,[23] we find that the added 'guest' cation occupies accessible cationic sites in the zeolithic framework. It appears that the incursive alkali atoms, once ionized, are able to benefit from the considerable coordination of the guest cation to the oxygen ions on the zeolite framework. It seems likely that, for example, a 3*s* electron on a sodium atom, entering the zeolite and subject to the intense electrostatic fields generated by the host lattice, finds itself effectively under the influence of a group of ions, rather than just a single one, as in the case of the parent atom. This is, after all, the situation one finds for the four known electron traps in lightly doped sodium zeolite, $Na_n^{(n-1)+}$ (n = 3,4,5,6). This behaviour is dramatically illustrated by our discovery[25] of a family of clusters, Na_5^{4+}, Na_6^{5+}, in zeolite Na–X and Na–Y (Figure 6). Given the degree of vibrational and translational mobility that is well established for zeolite cations, even at room temperature, one may conclude that the excess electron at low densities would be able to pass from one group of ions to another throughout the crystal, before finding a stable site in one of the established clusters.

There is clear evidence that, even at exceptionally long distances between Na_4^{3+} centres, electrons in these traps are able to interact with each other. Here again, one detects strong similarities with the situation for metal–ammonia solutions, where electron–electron interactions become discernible at extremely low metal concentrations.[8,9] It is to these matters that we now turn.

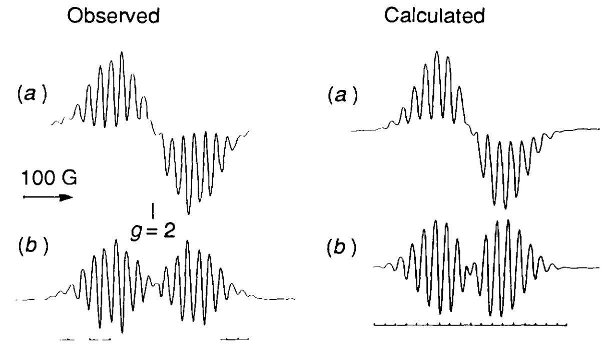

Figure 6 A family of ionic clusters in Na/Na–X the observed ESR spectrum is shown on the lefthand side (a) first derivative and (b) second derivative The simulated ESR spectra for an equal mixture of Na_5^{4+} and Na_6^{5+} are shown on the right hand portion of the diagram (from ref 25)

3.2 Intermediate and High Concentrations: Interacting Electrons, Spin Delocalization, and the Onset of an Insulator–Metal Transition

The onset of substantive electron–electron interactions in alkali doped zeolites is highlighted by several experimental observations on samples of progressively increasing alkali metal content. The exposure of, for example, dehydrated Na–Y to sodium vapour causes the white solid first to turn pink, then bright red, deep red, and eventually blue/black. In Figure 7 we reproduce the salient features[6] of the ESR spectra from such products formed upon the controlled reaction of Na–Y with 3, 8, 13, and 32 (extra) sorbed sodium atoms per unit cell (p.u.c.).

The pink to red solids, obtained by the treatment of zeolite–Y with relatively low concentrations of metal (< 1 additional sodium atom p.u.c.) exhibit the fingerprint ESR spectrum of Na_4^{3+}, and at higher metal concentrations, typically 3 atoms

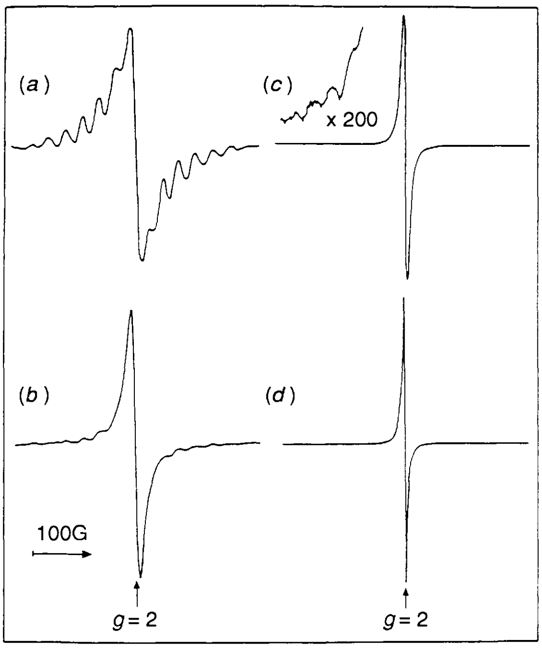

Figure 7 The evolution of the ESR spectrum of Na/Na–Y containing (a) 3, (b) 8, (c) 13, and (d) 32 extra sodium atoms per unit cell

p u c and above, a singlet resonance appears whose relative intensity grows with increasing sodium content, eventually to eclipse the spectrum of 13 hyperfine lines From detailed studies[26] of the microwave power saturation characteristics of these signals, it is clear that the singlet resonance makes an important contribution to the spectrum, even at metal concentrations as low as 3 atoms p u c This change in ESR behaviour, represented by the emergence of the singlet resonance, is caused by the interaction of Na$_4^{3+}$ centres such that unpaired electron spin hops between centres effectively 'scrambling' the individual sodium hyperfine components This exchange narrowing becomes more and more effective as the electron spin extends over larger and larger numbers of trapping sites It is important to stress that although the faujasite unit cell contains 8 potential sites (sodalite cages, Figure 1) for Na$_4^{3+}$, the ESR singlet is already important at concentrations as low as 3 atoms p u c and dominant at 8 atoms p u c when all the sodalite cages should be filled with Na$_4^{3+}$ centres Thus, the ESR singlet emerges at just the stage when the probability of two Na$_4^{3+}$ centres occupying adjacent sodalite cages becomes significant

At first sight the emergence of a single ESR line from the hyperfine multiplet might be invoked as evidence of the transition to genuine itinerant electrons in a truly metallic system [5,27,28] There is no question that ESR (and indeed NMR) measurements are potent indicators of the transition from spatially localized to completely itinerant electron states [13,29] However, it is important to point out that ESR is sensitive also to spin delocalization involving the extension of the excess electron wavefunction over several centres [17,30,31] For such interactions to be detected, the exchange energy between contributing paramagnetic centres need only be of the order-of-magnitude of the magnetic hyperfine interaction (energy) This contrasts with the situation, for example, in d c conductivity measurements whereby complete electron delocalization requires the creation of an electron–hole pair at the Mott transition [17,31] There are clearly large energy differences between the two processes

Such spin – not necessarily charge – delocalization over a finite number of centres is again reminiscent of the situation found, for example, in doped semiconductors[17] and metal solutions [31] In the former case, this embryonic spin delocalization was regarded by Slichter[30] as " simply the first step in the process of turning into a metal" This may be a good summary of the situation shown in Figure 7

Paradoxically, there is ample evidence that the isolated electron traps such as Na$_4^{3+}$, may have quite considerable spatial extent leading to recognizable electron–electron interactions, even at quite low loading levels In sodalite, for example, pulsed ENDOR and spin-echo measurements have demonstrated[32] isotropic hyperfine interactions with sodium nuclei located in neighbouring sodalite cages (Figure 1) Evidence that electrons in Na$_4^{3+}$ do indeed interact over relatively large distances is also forthcoming from measurements of the relative electron spin susceptibility (χ_S) for the dilute sample Rb/Na–Y A plot of $1/\chi_S$ *vs* T has, when extrapolated, an intercept of ~ 25K on the negative temperature axis, consistent with weak antiferromagnetic coupling between the isolated Na$_4^{3+}$ centres (Figure 8) This observation is given yet more weight by the fact that the Na$_4^{3+}$ centres at this level of loading can occupy no more than $\frac{1}{8}$ of the sodalite cages and are, therefore, on average, at least 24 Å apart

Given the anticipated a_H^* for the Na$_4^{3+}$ centre in zeolites (see below) this means that the onset of significant (*i e* measurable in magnetic measurements) electron–electron interactions sets in when the average distance between participating centres is $\approx 10 \times a_H^*$ This is again reminiscent of the conditions for the onset of electron spin-pairing in metal–ammonia solutions at extremely low metal concentrations [9] Interestingly, electron transfer in biological systems also generally involves hop distances of between 10 to 20 Å for the electron to go from membrane surface to an opposite surface [33]

Logically, a much stronger interaction can be expected between centres in *adjacent* sodalite cages whose midpoints are a mere 12 Å apart (Figure 1) Evidence for such strong interactions, leading now to the formation of diamagnetic singlet ($S = 0$) states results from recent measurements on the magnetic and spin susceptibilities of these samples [34] Briefly, the picture that emerges is that a large fraction of excess electron spins (*ca* 90%) are 'frozen out' in electron spin singlet states with only a very small (but immediately recognizable, Figure 4) fraction of paramagnetic, and interacting (Figure 9) Na$_4^{3+}$ centres

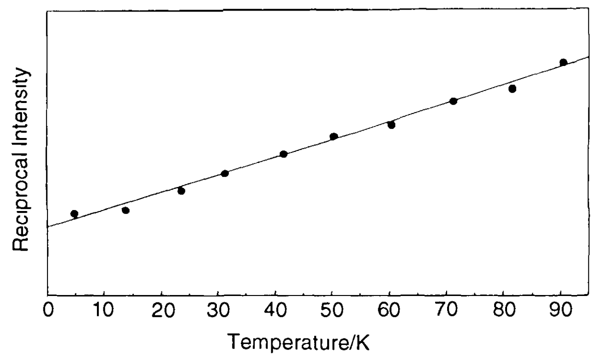

Figure 8 The reciprocal ESR intensity (directly related to the electron spin susceptibility) of Na$_4^{3+}$ as a function of temperature The sample was Rb/Na–Y (from ref 6)

The turn-over, or cusp in the magnetic susceptibility data at low temperatures[34] (*ca* 10 K, Figure 9) is reminiscent of spin-glass behaviour This observation hints at the disordered nature of these electronic states For although the host matrix is unquestionably crystalline, the doping with alkali metals to generate Na$_4^{3+}$ is random in the sense of the occupation of sodalite cages It is interesting to note similar behaviour in the paramagnetic spin susceptibility of Si P at temperatures around 0 02 K,[35] this scaling in temperature between the two systems may originate from the large differences in binding energies for the excess electron states in Si P and alkali metals in zeolites (Figure 9)

Recent ^{23}Na NMR studies[36] of sodium-doped Na–X at these low temperatures also reveal direct evidence of inter-site interactions Nuclear relaxation measurements reveal a rapid relaxation component of likely electronic origin At sub-helium temperatures, there is an abrupt disappearance of the NMR signal, suggestive of a magnetic phase transition The onset of this phase transition is highlighted by the temperature dependence of the nuclear relaxation rate (Figure 10) The existence of these magnetic phase transitions once again emphasizes the importance of interactions between paramagnetic clusters in neighbouring cavities in the zeolite The clusters form an electronic network coupled by inter-cluster exchange interactions in the energy range 0 0001—0 001 eV (See also ref 37)

All the indications are that at these accessible levels of loading, the systems are indeed close to an Insulator–Metal Transition The majority of the effects discussed above may be viewed in terms of (embryonic or spin) delocalization As yet there are no firm measurements on electrical transport properties which would constitute strong experimental evidence for a transition to a true 'metallic' state in the zeolite channels

As we have outlined, in the case of both silicon doped with phosphorus,[17,30] and metal–ammonia solutions,[31] an important distinction has been drawn between 'spin delocalization' and 'charge transport delocalization' which defines the compound as a genuine 'metal', able to conduct a current In both cases, the former has been shown to occur before the latter

Applying the Edwards–Sienko[18] criterion to the case of Na$_4^{3+}$ centres in zeolites, and using the estimates[27] of Xu *et al* for a_H^*, we can predict that a transition to metallic behaviour should occur at concentrations between 10^{21} and 10^{22} centres 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$_4^{3+}$ centre is

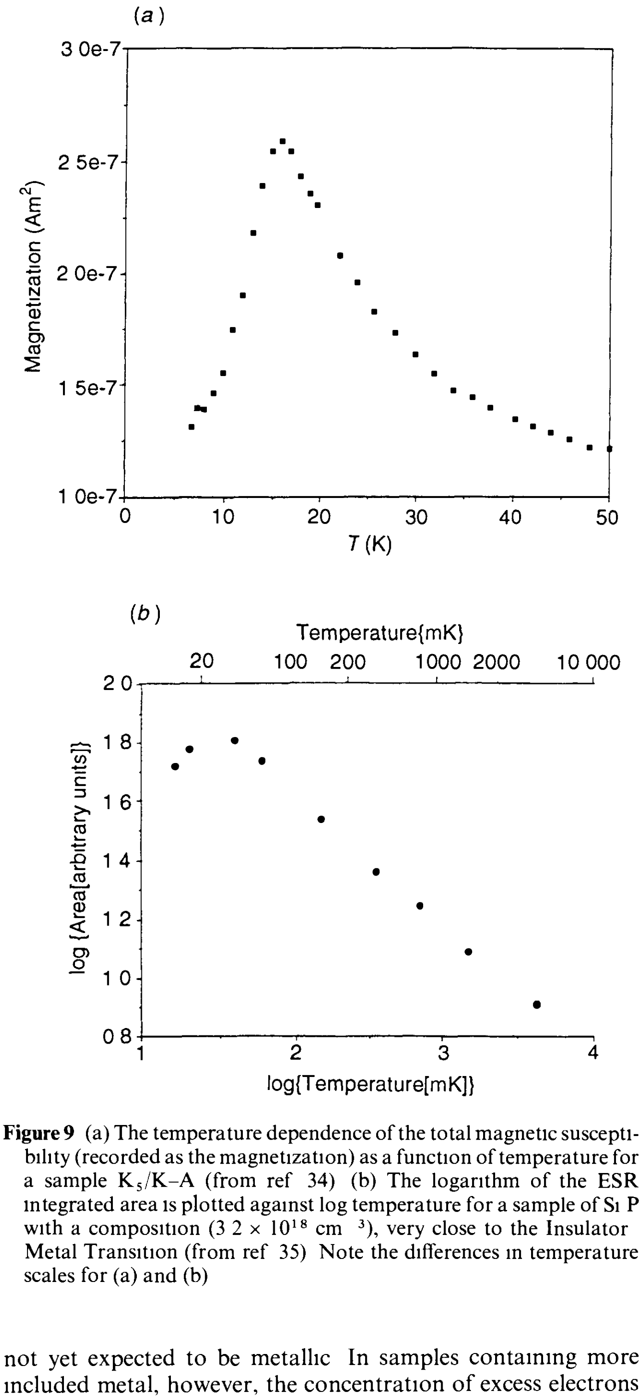

Figure 9 (a) The temperature dependence of the total magnetic susceptibility (recorded as the magnetization) as a function of temperature for a sample K_5/K-A (from ref 34) (b) The logarithm of the ESR integrated area is plotted against log temperature for a sample of Si P with a composition (3 2 × 10^{18} cm ^{3}), very close to the Insulator Metal Transition (from ref 35) Note the differences in temperature scales for (a) and (b)

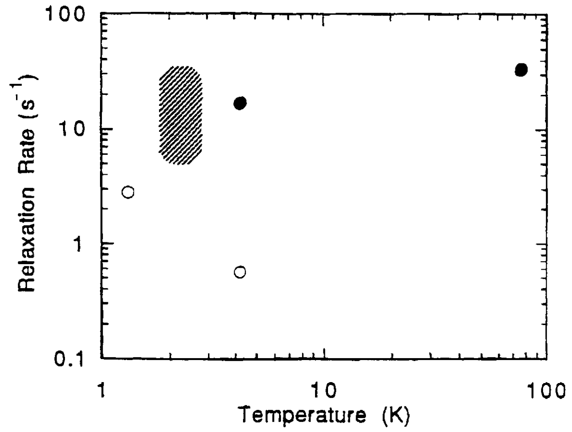

Figure 10 A log log plot of the ^{23}Na nuclear spin–lattice relaxation rates *versus* temperature for Na/Na Y (solid points) and Na/Na-X (open points) The shaded region indicates the approximate temperature range at which the resonance vanishes in Na/Na Y (from ref 36)

not yet expected to be metallic In samples containing more included metal, however, the concentration of excess electrons introduced to the zeolite may well reach – or even exceed – the critical values just mentioned

In summary, no experimental evidence, to date, has yet been collected which suggests that any compound of sodium metal in zeolites is indeed 'metallic' Our own magnetic data, coupled with the optical work of Srdanov[38 39] *et al* suggests that we are indeed very close to an incipient Insulator–Metal Transition

However, such statements are not as conclusive as they may sound If genuine charge transport were to occur in such materials, with their interpenetrating aluminosilicate lattice and less than one electron for every two cations, it would constitute a rather unusual metal indeed For example, 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 filamentary and highly electron deficient, diluted metallic state Clearly further magnetic and transport studies are urgently needed, these will have to be allied with viable synthetic options aimed at maximizing the amount of doped alkali metal in the zeolite

Crystal structure data, to which we now turn, lend strong support to the picture of a gradual buildup towards metallization, which has been developed from magnetic measurements At low concentrations of added metal, powder neutron diffraction studies have established the presence of included potassium in K_1/K–L in cationic sites indistinguishable from those occupied in dehydrated K–L, direct proof of the incorporation and ionization of alkali metals within the zeolite pores[40]

At high concentrations Sun *et al*[41] have determined the structure of caesium-loaded zeolite X by single crystal *X*-ray diffraction Although the zeolite cavities were in this case said to be filled with caesium atoms, virtually all were found in sites coordinated to the anionic zeolite framework, suggesting that they were predominantly cationic in character The distribution of the cations was such that each supercage contained an icosahedron of caesium ions ostensibly linked to form a 'cationic continuum', with caesium–caesium distances in the range 3 89—7 27 Å The electronic properties of this compound remain unknown

The same group has reported[42] similar features in potassium-loaded zeolites but the interpretation of these results is hampered somewhat by a lack of control over the composition of the final products Using high-quality powder neutron diffraction data, we have determined[23] the structure of potassium zeolite A saturated with potassium metal (K_5/K–A) Although each sodalite cage in zeolite A contains eight equivalent cationic sites, only four potassium ions can be accommodated, and it is this intrinsic topological constraint which leads to cation ordering and the subsequent self-assembly of a potassium superlattice (Figure 11) Alternate α-cages are thus found to contain either 8 or 12 cations, those containing 8 retain, more or less, the structure of the parent zeolite, whilst those containing 12 are much more densely packed Although potassium–potassium nearest neighbour distances, ranging from 4 24—4 88 Å, cluster closely around the potassium metal value of 4 54 Å, bond valence sums calculated for the various potassium sites suggest that cations located in the more densely packed fraction of α-cages may be significantly electron-rich compared with those in the remainder, which appear to carry a full ionic charge[23] The possibility that the observed segregation may be electronically as well as structurally driven is of particular importance in the current context, as structural instability and phase separation are frequent harbingers of an incipient Insulator–Metal Transition[2 10 11 15]

4 Concluding Remarks

Barrer first expounded the view[12 43] of dehydrated zeolites as " crystals porous on the scale of molecules" Here we have

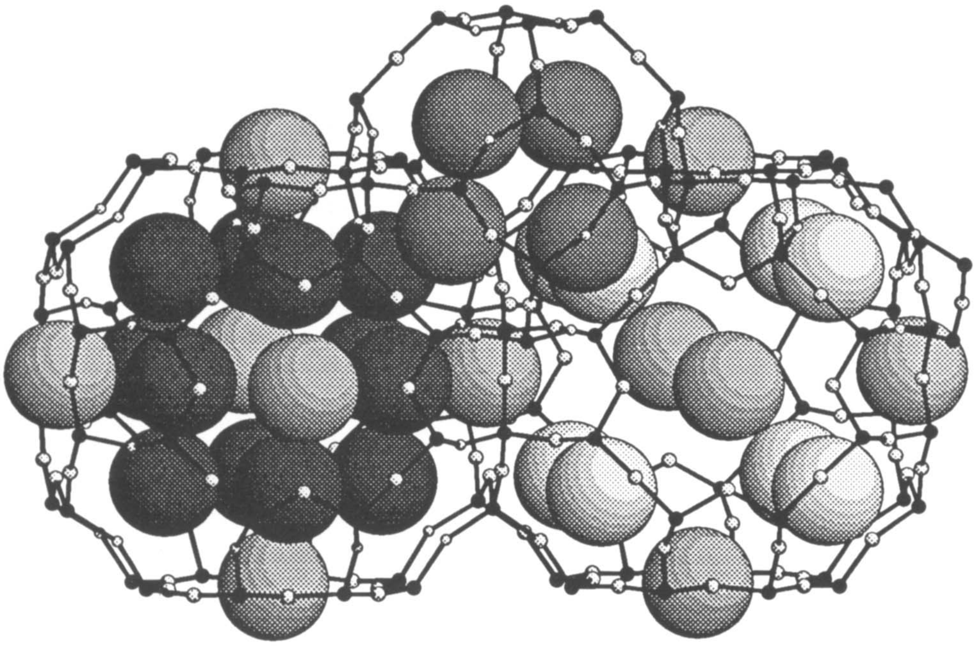

Figure 11 The origin of the potassium superlattice in K_5/K–A A fragment of the crystal structure showing neighbouring α cages and a sodalite cage (see also Figure 1) The much less open structure of the lefthand cage is readily apparent (ref 23)

illustrated the efficacy of zeolites as porous hosts for *atoms* of the alkali metals

The incoming alkali atoms give up their *ns* valence electron to the solid in return for a framework coordination site for the resulting cation. The reaction with alkali metal vapour can thus be considered to simultaneously increase the number of cations in the zeolite framework and introduce excess electrons, both processes are fundamentally important in the evolution of electron delocalization Our review of the current structural magnetic and magnetic resonance data leads us to propose that these systems are close to an Insulator–Metal Transition

It may be possible – *via* judicious choice of zeolite and synthetic routes – that one can engineer a genuine metallization transition within this continuous porous host structure We therefore place alkali metal-doped zeolites in the realms of other chemical systems[11] close to and spanning, the Insulator–Metal Transition What is clear is that the electronic properties of these systems – and indeed the metallization conditions – will depend not only upon details such as electron density and screening (*a la* Mott, *etc*) but also upon the geometrical constraints imposed by the host zeolite. One can anticipate very interesting electronic properties for such systems

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