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Zeolites as Hosts for Novel Optical and Electronic Materials

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1. Introduction

Small, molecular clusters of metals or semiconductors, having hybrid properties somewhere between those of the molecule and the bulk phase represent a fascinating new class of materials and, as such, have come under intense investigation [1,2]. In some senses, these materials represent the logical extension of the trend toward ever smaller electronic devices. As the size of such devices decreases, one reaches a regime where physics and chemistry meet and novel properties develop. At this size extreme, collective electronic properties become "distorted" by the fact that, at this point, a continuous wave function no longer describes the cooperative interaction of electrons and nuclei in the solid. The system, in fact, tends toward the classical "particle-in-a-box" quantum description.

In preparing materials for the study of phenomena associated with the resulting "quantum dots", a basic problem facing synthetic chemists is the control of surface reactions of such particles so as to arrest their growth at the small cluster stage. Thermodynamics usually dictates that the small cluster nuclei will tend to aggregate and develop into the bulk crystalline structure. Many approaches have been explored for the preparation of the desired small clusters - including the use of micelles [3], colloids [4], polymers [5], glasses [6], and surface-capping agents [7] in an effort to control the aggregation problem. In almost all cases, however, the cluster sizes and crystallinities are poorly defined and one would like to find an approach to this class of materials which produces a mono-dispersion of cluster sizes in a well-defined and characterizable array. The ability to produce such a regular array of single-sized clusters is key to defining the optical and electronic behaviors of these materials, unmuddied by size dispersion effects. These criteria would seem well met by an inclusion-type approach using a host lattice as the template within which the clusters could be constructed and confined.

One example of this type of approach involved CuCl crystallites of ~20-50 Å which were prepared within single crystals of NaCl or KCl by a melt procedure and were shown to exhibit exciton absorption features which were blue-shifted (a quantum confinement effect) from the bulk material [8]. Another approach, and the one which will be explored in this chapter, is the use of a *porous* crystalline host lattice, a zeolite molecular sieve, into which the active material (metal, semiconductor, etc.) is either directly imbibed or else created in situ . The former technique is exemplified by the sublimation of elemental

mercury, selenium, tellurium, etc. into a variety of aluminosilicate zeolites. The second, "ship-in-a-bottle" approach [9] has been used for the generation of numerous clusters and superclusters (cluster arrays) in zeolites [10].

The well-defined and well-ordered cavities provided by a zeolite host are a potentially ideal environment for synthesizing single-sized clusters and cluster arrays. The windows of the zeolite pores provide ready access for transporting reagents to the cavities making a variety of synthesis schemes accessible. The additional potential for producing novel clusters of electronic materials and stabilizing unusual geometries and connectivities by using the surface passivating and templating effects of the host lattice is also most attractive [11].

1.1   WHY SMALL ELECTRONIC PARTICLES ARE INTERESTING

It is useful to understand why there is the current interest in very small particles of metals and semiconductors [1,2,12] and what limitations this interest places on the nature of useful materials. Bulk electronic, optical etc. properties of a material are often the result of the cooperative interaction of all of the molecules or atoms in the ensemble. Studying how these properties are altered as the number of constituent molecules/atoms in the ensemble becomes very small can reveal much about the fundamental source of the bulk property itself.

Theories of the mechanism of superconductivity and magnetism in highly constrained systems as well as interest in the metal-insulator boundary as a function of metallic cluster size has spurred research on small metallic clusters. The possibilities of generating novel magnetic recording systems based on nanoparticulate metals have also sharpened interest in these materials. Of course, there has been a long-standing interest within the catalyst community in small metallic clusters as catalytic sites and embedding these clusters inside zeolite pores introduces molecular sieving selectivity to any catalytic effects.

The concept of an all-optical or opto-electronic computer technology has attracted attention because of its potential for extreme speeds and parallel processing capabilities in areas such as image recognition. Such a technology requires several basic optical materials for the construction of devices which mimic their electronic counterparts. One such fundamental computing element is the optical transistor or bistable device which acts as a light switch or valve/amplifier. Basic requirements placed on materials for such a device are that they have a very rapid switching speed (ideally picosecond) and extreme photostability in order to perform trillions of switching operations/sec for years at a time. One realization of such a material could involve the use of third-order non-linear optical properties, x^3, to effect a transient refractive index change. Illumination of such a material with intense laser light will cause a change of its refractive index leading to a switch from an opaque to transmissive state in an interferometer-type (e.g., Fabry-Perot) bistable device. While semiconductor materials themselves will perform this kind of switching at their band-edge wavelengths, the speed of the effect is slow - usually as a

consequence of a long, free-carrier lifetime. This speed can be increased by providing more sites for efficient removal of these free-carriers - in other words more defect sites. One can view surface sites on a semiconductor particle as such defect sites and one simple way to increase their concentration is to increase the surface to volume ratio, i.e., to go to very small particles. The commercial color filters of Schott and Corning, based on CdS/Se nanoparticulates in a silica matrix, have verified the utility of this kind of material for non-linear-optical devices [6]. Researchers would like to explore a wide range of other semiconductors and matrices for these purposes and the zeolite host provides an almost ideal medium for such studies.

2. Metal Clusters in Zeolites

The incorporation of metallic clusters inside the pores of zeolites has a long history [13], mainly because of interest in the catalytic properties of the resultant materials. Typically, such materials have been prepared by ion-exchange of metal salts followed by hydrogen or CO reduction to produce metal clusters within the zeolite chambers. A classical example of such a process is in the preparation of Pt-loaded zeolites used as hydrogenation, dehydrocyclization, etc. catalysts [14,15]. Other encapsulation techniques involve (i) direct incorporation of the metal from the melt or the vapor and (ii) the absorption of an organometallic precursor which can then be thermally or optically decomposed to the metal inside the zeolite pores. Examples of each technique are described below.

A significant amount of the early work in this area concentrated on optimizing synthetic procedures in order to maintain a high dispersion and small cluster size for the metals during the incorporation protocol since this usually correlated directly with catalytic activity. In particular, the ability to maintain the metal clusters within the zeolite pore system and avoid their migration to the intercrystalline spaces and crystallite surfaces has been a major focus [16]. Later work began, however, to concentrate on the characterization of these small clusters and to explore their electronic properties as the loading density became sufficient to allow the clusters to interact electronically and eventually to form a contiguous metallic phase within the pore system. These electronic effects will be the main focus of this review.

2.1 ALKALI METALS

When vapors of the alkali metals Na, K, Rb, and Cs are exposed to dehydrated zeolites in their Na^+ or K^+ forms, the atoms of the alkali metals are spontaneously ionized inside the pores. The metal atoms essentially dissolve in the zeolite host solvent (*cf.* similar dissolution in liq. NH_3). The atoms of the incoming alkali metal form clusters with the resident cations of the zeolite to produce paramagnetic guest clusters within the zeolite host chambers. At low levels of Na incorporation, the resulting pink/red solids contain

species such as Na_4^{3+}, Na_5^{4+} (which has been characterized crystallographically as a Na centered tetrahedron [17]) and Na_6^{5+} as identified by EPR [18]. As the loading of the alkali metal is increased, the pink zeolite eventually becomes blue/black - for example, up to four extra sorbed Na atoms per supercage of zeolite Na-Y can be achieved. At this loading level, the individual clusters begin to interact electronically and electron-hopping sets in. The resulting materials apparently allow electrons to hop between Na_4^{3+} clusters within the sodalite cages of zeolite Y provided the distance between such clusters is less than ~20 Å. Magnetic and transport properties of these physically constricted, highly electron deficient, dilute metallic states are of intense interest in studying the onset of an insulator-metal transition. The structural and electronic properties of these metallic superlattices has recently been reviewed [19]. Potassium clusters in zeolite LTA exhibit ferromagnetic properties in a limited range of K-loading with Curie temperatures <7 K. The magnetic properties show spin-glass behavior and are interpreted with a model of itinerant electron ferromagnetism [20]. For further details see Chapter 11 in this volume.

2.2   OTHER MAIN GROUP METALS

A limited number of studies of the incorporation of a continuous metallic phase within a zeolite pore system have been reported. Such studies typically involve the incorporation of the main group metal from the molten or vapor phase via the application of high pressure in order to overcome the surface tension effects. Liquid Ga at 10-20 kbar was forced into zeolite Na-X and the resultant conductivity of the entrained metal studied as a function of temperature and applied pressure [21]. Two types of metal-insulator transitions were detected corresponding to breaking connectivity between clusters inside the pore system. These same workers also studied In metal forced into zeolite Na-A at 20 kbar and 535 K. The inferred In_8 cluster which is produced appears to have optical and electronic properties intermediate between In atoms and bulk metallic In [22]. In both cases, release of the pressure causes immediate migration of the metal to the exterior of the pore system.

2.3   TRANSITION METALS

Classical work on the sorption of mercury vapor into zeolites [23] demonstrated that the sorption phenomenon could be effectively driven by a redox mechanism whereby the intrinsic cations of the zeolite are reduced by the incoming Hg vapor. This leads to anchoring of the growing Hg clusters at these original cation sites. In Hg-X and Ag-X zeolites, mercury uptake was "copious" and up to 25 metal atoms were absorbed per supercage. As this absorption proceeds, the zeolite changes in color from white through yellow, green, grey, and black suggestive of quantum size effects and cluster-cluster electronic interactions. In extreme cases, (especially Ag-X), the mercury filling of the pore system can be complete, producing a true nanofilamentary metallic system. Such

systems have been investigated as composite superconductors with increased T_cs [24].

Silver ion-exchanged zeolite Y may be reduced by several methods [25] to produce metallic Ag clusters inside the pores. Yellow and red materials result and have been interpreted in terms of Ag_2 and Ag_3 charged clusters which can begin to interact as the loading density increases [26]. These materials can be highly luminescent and such luminescence is extremely sensitive to quenching by water.

Cadmium cluster species are produced in zeolite A by exposure of Cd ion-exchanged A, Cd_6-A, to Cd vapor at 550° C. The resultant red crystal has stoichiometry Cd_{11}-A and crystallographic analysis reveals a Cd_2 dimeric molecule with Cd-Cd distance of 2.97 Å in the midst of a low symmetry cluster of Cd_5^{4+} inside the A α-cage [27]. This identification of novel Cd clusters and reduced Cd^+ species demonstrates one of the powerful abilities of the zeolite framework to stabilize very unusual molecular species under otherwise normal conditions of temperature and pressure.

As was mentioned above, many metals in zeolite systems have been explored as catalysts and some of the best characterized are of the noble metals Pd and Pt. The metal-cluster size in the pore system is often controlled by careful manipulation of drying, calcination, and reduction conditions following ion-exchange with complex metal ions such as $Pd(NH_3)_4^{2+}$ [28]. A detailed study (using EXAFS) of Pd in zeolite X by Bein et al. [29] has revealed the Pd clusters as comprising 2-4 correlated atoms of Pd which have only weak Pd-oxygen coordination to the zeolite framework at 2.76 Å. The Pd clusters are proposed to lie within the sodalite units of the cage system as Pd_2 and Pd_4 units.

3. Semiconductors in Zeolites

The zeolite confinement approach has been developed to include many semiconductor guests in zeolite hosts. Again, the synthetic approaches mimic those adopted for inclusion of metallic species - e.g., direct absorption from the vapor phase or ion-exchange and subsequent reaction chemistry. The generation of compound semi-conductors inside the zeolite pore structure is another example of the "ship-in-a-bottle" synthesis technique where the individual components of the compound are introduced by any of a variety of methods and reacted together inside the pores to generate the semiconductor directly in situ as trapped, physically constrained particles. Our own work on Se in a variety of zeolites and CdS in zeolite Y represents some of the early steps towards exploring this new class of materials and is given as detailed examples below.

3.1 ELEMENTAL SEMICONDUCTORS

Some of the synthetically most accessible and thus most heavily studied examples of semiconductors in zeolites are the chalcogenides Se and Te. Simple sublimation of the pure chalcogenide into a dehydrated zeolite can lead to composites displaying band gap and optical absorption features which indicate size quantization. Our, and other, work on

the Se materials is discussed in detail below. The Te-loaded zeolites have attracted additional interest because of their catalytic activity in hydrocarbon conversions including dehydrocyclization [30]. In the bulk phase, Te forms exclusively helical chain structures and no 8-membered rings - the analogs of those found, for example, for sulfur in zeolite A [31] - have been reported. In zeolites A and X, however, Te_8 rings have been suggested based on Raman spectroscopy (168 cm^{-1} band) of Te vapor absorbed into the zeolite crystals [32]. A similar Raman [33] and optical [34] study of Te in mordenite concluded that Te lay in the linear channels as relatively isolated and disordered chains similar to those proposed in the amorphous form of bulk Te. Finally, some unusual effects of dispersion of Te on its magnetic properties have been investigated by a careful study of Te dispersed (by vapor absorption) into zeolites X and A [35].

3.1.1   Se in Zeolite Hosts

Se in zeolite hosts has been extensively studied and numerous reports of the sundry properties which result have appeared. This is probably a direct result of the ease of synthesis of such materials via direct sublimation of Se into the pores of the dehydrated zeolite. Very substantial loadings of Se - for example 34 wt % Se in Y (~10 Se/13 Å supercage) [36] and 23 wt % Se in mordenite (~25 Se/15 Å channel length) [37] - have been reported and the pore systems can be essentially completely filled by a network of Se species. The exact nature of these size-restricted species has been the subject of many of the investigations. Raman spectra [33] of zeolite A and mordenite loaded with Se concluded that isolated rings and chains (respectively) were present, similar to those present in amorphous bulk Se. This use of the zeolite-entrained Se materials as structural models for amorphous Se has been extensively exploited in the work of Bogomolov et al. [38-41] who have studied both vibrational and electronic spectra in detail.

Our own work [36] has sought to further define in detail the structural and electronic consequences of the entrainment of Se in zeolites A, X, Y, mordenite, and AlPO$_4$-5. Using a combined MAS-NMR, electronic spectroscopy, and EXAFS approach, we have concluded that in all zeolites the Se-Se bond length is shortened relative to helical chains of t-Se (2.34 vs 2.37 Å). As might be expected, when only chains of Se are present (in the linear channel zeolites mordenite and AlPO$_4$-5), there is no interchain correlation indicating that the chains are isolated as "quantum wires" of the semiconductor and the band edge is shifted to significantly higher energy as a result of the chain isolation (1.98 → ~2.3 eV). The zeolites X and Y, with their 3-D interconnected channel system of large cages (13 Å), show the presence of both helical chains and ring structures with a wide variety of conformations. Zeolite A, having much smaller windows between the cages shows the presence of only the Se$_8$ entity (analogous to S$_8$ reported earlier [31]) with no extended chains. Again, the rings are essentially isolated from each other in separate cages and this isolation as "quantum dots" manifests itself as a blue-shift of the band edge from bulk α-Se (consisting of packed Se$_8$ rings) where inter-ring contacts modify the electronic behavior (2.53 → 2.85 eV).

3.2 COMPOUND SEMICONDUCTORS

AgI in zeolite mordenite has been shown to have unusual optical behavior in terms of its photosensitivity [42]. In a follow-up on this work, Ozin et al. [43] have generated silver halides in the sodalite zeolite family where reversible photo-, radiation-, thermal-, and pressure-sensitivity are observed and proposed for utility in a range of device applications, e.g., reversible image capture/data storage devices, [44] etc. Isolated Ag^+ ions in the sodalite cages can be reduced and then interact with one another forming an "expanded-metal" where the metal-metal distances are much greater than in metallic Ag and are modulated topologically by the interpenetrating sodalite framework.

WO_3 and MoO_3 are so called "intelligent" materials [45] because of their utility as components of electrochromic devices, rechargeable solid-state batteries, pH-microelectrochemical transistors, sensors, and solar cells. Absorption of the metal hexacarbonyl complex from the vapor state into zeolite Y followed by photooxidation yields encapsulated MO_3 clusters in the zeolite supercage system. Such loading can proceed to very high levels following a sequential absorption protocol such that up to 4 MO_3 units can be absorbed per supercage. Ordered supralattices of these clusters appear to form and they may reversibly lose and regain oxygen depending on annealing conditions, e.g., transforming from white $[WO_3]_n$ materials to blue $[WO_{3-x}]_n$ upon heating to >200° C in vacuum. The precise control over loading density translates into control over the optical and electronic properties which show loading dependent shifts similar to the behavior reported below for our own CdS system.

PbI_2 in X, Y, A, and L zeolites shows evidence of a strong size effect on the exciton absorption [46]. TiO^+ ion-exchanged in zeolites Y, L, and mordenite has been characterized by XPS and photochemistry and shows characteristic behavior of entrapped TiO_2 in the zeolite cages [47]. The entrapped clusters have a significant blue shift of the absorption band edge relative to anatase or rutile TiO_2. The material will photocatalyze the reduction of methylviologen (MV^{2+}) using 300 nm UV light and the reduced $MV^{+\cdot}$ radical cation was shown to have a remarkably long lifetime (hours) compared to equivalent non-zeolite systems. The indication is that the zeolite may be effectively moderating the back electron transfer between the TiO_2 hole and the radical cation.

PbS clusters in zeolite Y or mordenite have been briefly reported [10,48] being prepared from Pb-exchanged zeolite Y after exposure to H_2S. However, they have so far shown only featureless optical absorption spectra making it difficult to assess the true extent of quantum confinement effects. EXAFS analysis [49] suggests that isolated PbS_2^{2-} species exist and are strongly coordinated to the zeolite framework. The bright yellow PbS/Y material is very moisture sensitive, darkening in color upon exposure to atmospheric moisture, and eventually becoming brown/black. This behavior is interpreted as a migration of the physically entrapped PbS clusters out of the zeolite cages to the exterior zeolite surface where aggregation takes place forming bulk PbS. The same behavior is reported for CdS in zeolites and the observation seems to be general - zeolite encapsulated clusters may migrate under the influence of a coordinating solvent and form bulk phases on the zeolite exterior surface.

We have prepared one example of a III-V semiconductor, GaP, in zeolite Y [50]. Using a synthetic approach akin to that used for MOCVD deposition of GaP (i.e., absorption of $Ga(CH_3)_3$ vapor followed by calcination at ~400° C in an atmosphere of PH_3), a cluster of ~26-28 atoms (as revealed by electronic spectra, MAS-NMR, and EXAFS) was detected in the zeolite supercage. The absorption behavior of these clusters shows an interesting example of a red-shift of the band-edge relative to the bulk and may be a manifestation of a shift from an indirect band gap (as is seen in the bulk) to a direct band gap for the small clusters.

One of the most popular areas of investigation of compound semiconductors has been the II-IV materials, such as Zn/Cd:O/S/Se, etc. These materials have been exhaustively studied in the bulk phases and so an extensive literature exists for comparison with the behavior manifested by extremely small clusters entrapped in a zeolite host. In addition, the relative ease of synthesis - simply reaction of the metal cations with a source of chalcogenide anions - makes for simple sample preparation (see below). A pronounced blue shift of the optical absorption band edge of ZnO embedded inside zeolite A has been reported (from 370 nm (bulk) to ~280 nm) although characterization of the ZnO particles is poor [51]. CdS and CdSe in zeolites have been of particular focus and our own work, along with others, is reviewed below.

3.2.1   CdS in Zeolite Y

CdS in zeolites has been a very popular system for study because of the reasons given above and numerous reports on preparation and characterization of such systems have appeared [52-54]. Our own work on this system was some of the earliest [10,55,56] and provides a useful example of the whole approach towards synthesis and characterization of encapsulated electronic species and so is now described in some detail.

Cadmium ion-exchange of zeolite Y is carried out by slurrying 10 g of zeolite LZ-Y52 (Na-Y from Linde) in 1 L of distilled water and the pH is adjusted to 5 with nitric acid. A calculated amount of cadmium nitrate designed to give a specific exchange level is added to the slurry and the mixture is stirred at room temperature overnight. Collection of the exchanged zeolite by filtration and washing with distilled water is followed by drying and calcination. The powder is heated to 400° C at 3°/min in flowing dry oxygen (100 mL/min) then cooled in vacuo to 100° C. The zeolite is then exposed to flowing H_2S (40 mL/min) at 100° C for 30 min.

Finally, the still white zeolite is evacuated at 100° C for 30 mins, then sealed, and transferred to an inert atmosphere dry box for handling and storage. The zeolite turns pale yellow/cream during the final evacuation step. All zeolites prepared in this manner are moisture-sensitive becoming deep yellow (zeolite Y or X) or pale yellow (zeolite A) on prolonged exposure to atmospheric humidity. Chemical analysis confirms Cd and S are present in from 0 to 25 wt % depending on exchange conditions. XPS shows that there is no detectable Cd on the exterior surface of the zeolite crystallites. IR spectra show no SH groups but there are the expected OH groups attached to the zeolite

framework. The exact nature of the CdS cluster units is revealed by a combined application of optical spectroscopies and X-ray techniques.

3.2.2   The Structure of the CdS Clusters in Zeolite Y and its Optical Consequences

Detailed analysis of the powder X-ray diffraction data on a series of CdS-loaded zeolite Y samples reveals the fundamental CdS cluster present consists of interlocking tetrahedra of Cd and S atoms (although some of the S atoms are occasionally replaced by O atoms) forming a distorted cube (Cd-S = 2.47 Å) (Figure 1). This structure, which is heavily dictated by the zeolite symmetry, is confirmed by EXAFS data at the Cd edge (which reveal the local symmetry and coordination environment of the Cd) and theoretical calculations [54] .
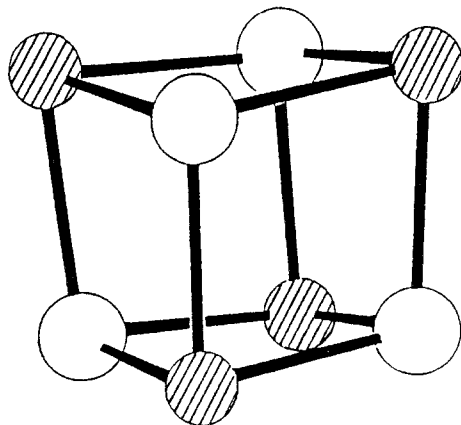

Figure 1.   Structure of the $(CdS,O)_4$ unit found within the sodalite unit of zeolite Y (hatched circles = Cd; open circles = S).

   To our initial surprise, these Cd_4S_4 cubes were not located in the supercages of the Y structure but were, instead, sited within the smaller sodalite cages. In retrospect, this location is entirely reasonable since these cages are the preferred sites for the original Cd ions upon exchange [57] and all that need occur upon exposure to H_2S is that the cube zips together. The Cd ions of the ideal cluster are in octahedral coordination to three sulfur atoms of the cube and three oxygen atoms of the zeolite framework six-ring window (Figure 2). The sodalite cage seems to have been made for this CdS cluster!
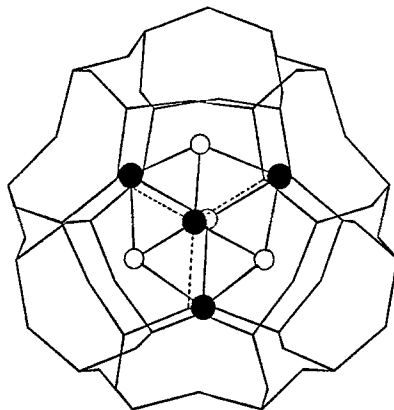
Figure 2.   Representation of the $(CdS,O)_4$ cube inside a sodalite unit with dotted lines representing
the bonds between the framework six-ring oxygen atoms (shown here as points connected
to Si or Al atoms by sticks) and Cd atoms of the cluster (solid circles = Cd; open
circles = S).

The evolution of the optical spectra as a function of CdS loading density is particularly
revealing. At loading densities of < 5 wt %, the sample has an optical absorption
spectrum with a shoulder at 280 nm. This represents a shift of the band edge by ~230 nm
and correlates well with the extremely small clusters of Cd_4S_4 found in the X-ray
analysis. However, as the loading rises above 5 wt %, a new absorption feature at 350
nm begins to appear and grows as the loading increases up to the maximum yet attained
of ~25 wt %. While still quantum-confined CdS, the structural nature of the material
responsible for this new absorption feature was unknown. The band edge observed is
similar to that of colloidal CdS particles with 25-30 Å diameters [58], yet there are no
void spaces of this kind of dimension within zeolite Y. The real clue as to the nature of
this species comes from the threshold-loading density of 4±1 wt % - this corresponds to
the concentration at which, statistically, CdS cubes must now populate adjacent sodalite
units. Simple calculations based on the bulk density of CdS and the sodalite pore volume
of Y reveal that the 4 wt % loading density corresponds to filling of ~14 % of the
available sodalite volume. Percolation theory [59] predicts the percolation threshold in
such systems to be at ~15 volume %, i.e., above 5 wt % of CdS, the individual clusters
must begin to interact with one another in adjacent sodalite cages in a percolative fashion.
In the limit, when all sodalite units are occupied (~28 wt % CdS), the structure would be
such as that represented in Figure 3 and a hyperlattice of CdS clusters dictated by the
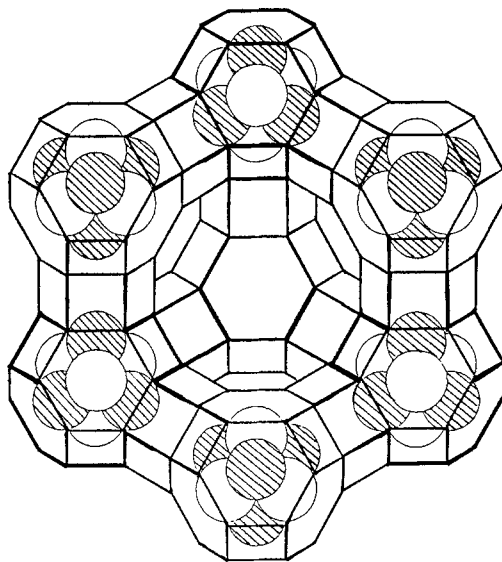zeolite Y topology results.

Figure 3. The ultimate, hyperlattice arrangement of CdS cubes in adjacent sodalite units of zeolite Y (hatched = Cd; open = S). The zeolite framework is represented as simple sticks connecting Si or Al atoms and the intervening O atoms are omitted for clarity.

This unique arrangement of individual clusters into an interconnected network gives rise to the luminescence and excitation spectra shown in Figure 4. As anticipated, the luminescence is not band-gap recombination in nature, but rather is dominated by Cd-related defects.

Since the novel optical behavior at higher loading densities of CdS is a consequence of the interaction between individual clusters as modulated by the zeolite structure, it is interesting to examine a zeolite with a different connectivity between the same kinds of Cd/S sodalite clusters. The spectral behavior should be very similar to zeolite Y at low loading densities but differ significantly as the interconnected CdS hyperlattice develops. Zeolite A is just such a zeolite system. In this case, the sodalite cages are connected via double 4-rings in a cubic arrangement and the distance between Cd_4S_4 cubes is projected at ~9 Å, i.e., the cluster-cluster interaction must be much weaker in A than in Y. The optical behavior follows these predictions precisely. While at low loading the absorption spectra of A and Y look very similar (isolated clusters), as the loading increases, there is no shift in the absorption edge of the A zeolite material indicating a much weaker interaction between clusters than in Y and so no significant development of an electronically cogent hyperlattice.
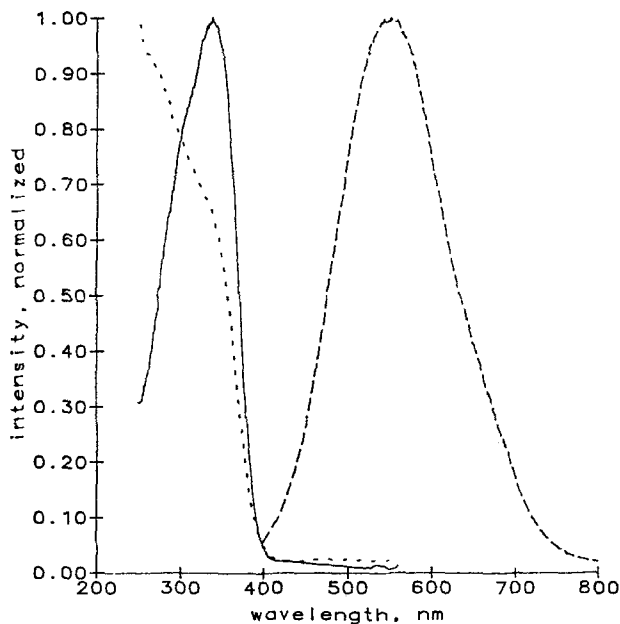
Figure 4.   The absorption (dotted), excitation (solid), and emission (dashed) spectra of 6.5 wt %
CdS in Y.

4. Conducting Polymers in Zeolites

One of the more intriguing developments in composite materials is the recent preparation
of conductive polymeric materials within the channels of a zeolite host. Conjugated
polymers of polypyrrole, polyaniline, and polythiophene have been introduced into
zeolite channels using a strategy of monomer incorporation followed by polymerization
in situ using oxidizing initiators [60-63]. Polyacetylene has also been generated using the
acid sites of the zeolite host to initiate oligomerization of methylacetylene [64].
Conductive polythiophene was produced by oxidative doping of the polymer within the
pores of pentasil zeolites [65]. All of these systems are examples of the concept of
molecular wires - molecularly thin, conductive strands, electrically insulated from each
other and aligned so as to allow a potentially high density of connections between tiny
electronic devices. Bein's work on polyacrylonitrile (PAN) is a good example of the
synthetic approach to these materials [66]. Acrylonitrile is absorbed from the vapor
phase into zeolite Y to the level of ~7 molecules per supercage and then polymerized in
situ using radical initiators (e.g., peroxodisulfate). The resultant polymer chains have
been thoroughly characterized after removal from the zeolite pore system (via dissolution

of the framework of the zeolite in HF) and proven to be true PAN with a molecular weight (by GPC) of ~19,000 (~360 monomer units) and approximate length of ~0.2 μ. After pyrolysis (400-650° C) of the PAN in the zeolite host, the material turns grey black and it is suggested to contain graphite-like conductive chains with a conductivity of ~10^{-5} S.cm^{-1}.

By careful control of the synthesis and orientation of these kinds of conductive molecular wires, an intriguing (albeit distant) possibility exists for generation of electronic devices on the molecular scale. Semiconductor nanoparticulates in zeolite chambers (see section 3) may be connected using these molecular wires to set up an interconnected electronic network where information processing may be done at an unprecedented density. The zeolite framework acts essentially as the electrical insulation for the molecular wires, preventing short circuits and maintaining the spatial isolation of the active components. Input and read-out to such devices presents major difficulties, but may be able to take advantage of the spatial resolution of the Scanning Tunneling Microscope to control, program, and access the electronic network. An alternative approach to the same problem has been explored by Mallouk et al. who have created simple molecular diodes at the zeolite/solution interface and have used molecular species such as $Ru(bipy)_3^{2+}$ as a messenger molecule to both create and access the device [67].

5. Summary and Prospects

Zeolites provide novel hosts for the generation of both isolated and electronically connected metal and semiconductor hyperlattices within their pore volume. Furthermore, the dimensional confinement of conducting polymer filaments, "quantum wires", following their encapsulation as guests within zeolite frameworks produces fascinating novel composite materials. The control of the connectivity between these quantum dots and wires is unparalleled in any other host medium and so has allowed a detailed study of the optical consequences of such connectivity. One must always bear in mind, however, that these guest-host systems are intrinsically composites, by which I mean, that one should not think of the guest clusters as being an isolated electronic system, but rather a system which is intimately linked and even chemically bonded to the host zeolite framework. Of necessity, the small clusters discussed above have very high surface to volume ratios and so most of the cluster atoms are on the surface where their coordination needs are unfulfilled by the cluster lattice. The zeolite lattice then serves to passivate this unsatiated coordination demand with electronic consequences which are likely to be profound. This is strikingly evident in the case of the CdS/Y material described in section 3.2 above. These materials are best thought of as novel compositions of matter which may have unique electronic properties in their own right.

From a practical standpoint, such materials also have some severe drawbacks - most notably the lack of single crystals of sufficient size to produce viable, advanced optical devices such as optical transistors, spatial light modulators etc. Practical device applications of these kinds of novel electronic materials must await advances in the

preparation of larger single crystals of the zeolite hosts coupled with an increased variety of pore and cavity sizes for the internal porosity of such systems. Once achieved, these materials offer the promise of an entire new field of quantum electronics where the skills of the device physicist and inclusion chemist merge [68].

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Abstract. A review of the use of zeolites as hosts for electronically active guest materials is presented. Metal, semiconductor and conductive polymer nanoparticles as electronic and optical material composites are reported with special emphasis on their synthesis.