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Novel materials, materials design and synthetic strategies: recent advances and new directions†

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There have been major advances in solid state and materials chemistry in the last two decades and the subject is growing rapidly. In this account, a few of the important aspects of materials chemistry of interest to the author are presented. Accordingly, transition metal oxides, which constitute the most fascinating class of inorganic materials, receive greater attention. Metal–insulator transitions in oxides, high temperature superconductivity in cuprates and colossal magnetoresistance in manganates are discussed at some length and the outstanding problems indicated. We then discuss certain other important classes of materials which include molecular materials, biomolecular materials and porous solids. Recent developments in synthetic strategies for inorganic materials are reviewed. Some results on metal nanoparticles and nanotubes are briefly presented. The overview, which is essentially intended to provide a flavour of the subject and show how it works, lists references to many crucial reviews in the recent literature.

I have been working in solid state and materials chemistry for over four decades. When I first got interested in the subject, it was not an integral part of main-stream chemistry. In the first book on solid state chemistry[1a] that I edited in 1970, it was stated in the preface, that 'Solid state chemistry has not become part of the formal training programmes in chemistry. Being one of the frontiers of chemistry, it has a tremendous future and undoubtedly demands the active involvement of many more chemists'. In 1986, in the first edition of the book *New Directions in Solid State Chemistry*,[1b] the preface states, 'At the present time, solid state chemistry is mainly concerned with the development of new methods of synthesis, new ways of identifying and characterizing materials and of describing their structure, and above all, with new strategies of tailor-making materials with desired and controllable properties, be they electronic, magnetic, dielectric, optical, absorptive or catalytic. It is heartening that the subject is increasingly coming to be recognized as an emerging area of chemical science'. In the last few years, solid state chemistry has given room to the broader area of materials chemistry. The subject has come of age and there are many reviews and books dealing with it.[2] I am delighted to have this opportunity to present an overview of the subject in this first materials chemistry discussion meeting. In so doing, I will try to present the highlights of some of the areas and refer to important reviews in the literature, but I cannot help dealing with those aspects which are of personal interest to me in somewhat greater detail. It is indeed impractical to cover every aspect of this vast subject in an article. Furthermore, all research in solid state chemistry is not necessarily related to materials development. Materials chemistry, as distinct from solid state chemistry, deals with structure, response and function, and has an ultimate technological objective. I illustrate this aspect of materials chemistry in Table 1.

Table 1 A description of materials chemistry

Constituent units	State[b]	Function	Advanced technology
atoms molecules[a] ions[a]	crystalline (molecular, ionic, polymeric, metallic *etc.*) non-crystalline (glasses) clusters and nanomaterials liquid crystalline	miniaturization selectivity and recognition transformation transduction transport energy storage	nanolithography microelectronics magnets sensors and transducers photonic devices energy devices porous solids and membranes micromachines

[a]Inorganic or organic. [b]In pure (monophasic) form or in the form of aggregates or composites.

If one were to list the most important discoveries in solid state and materials science in the last decade, it would include high-temperature cuprate superconductors (1986), fullerenes and related materials (1990), mesoporous silica (1992) and colossal magnetoresistance (CMR) in manganates (1993). Three of these deal with metal oxides. I have been involved in research on metal oxides for many years and it has been exciting to witness the increasing importance gained by these materials. I shall deal with certain aspects of the chemistry of transition metal oxides at some length. This discussion is presented as a personal account and would also serve as a case-study. I will indicate the developments in molecular materials, porous solids and biomaterials and highlight out the role of chemical synthesis in inorganic systems. I will end the article with a discussion of some of my recent interests in nanotubes and metal nanoparticles.

Transition metal oxides

Transition metal oxides constitute the most fascinating class of materials, exhibiting a variety of structures and properties.[3] The metal–oxygen bond can vary anywhere between highly ionic to covalent or metallic. The unusual properties of transition metal oxides are clearly due to the unique nature of the outer d-electrons. The phenomenal range of electronic and magnetic properties exhibited by transition metal oxides is noteworthy. Thus, the electrical resistivity in oxide materials spans the extraordinary range of 10^{-10} to 10^{20} ohm cm. We have oxides with metallic properties (*e.g.* RuO_2, ReO_3, $LaNiO_3$) at one end of the range and oxides with highly insulating behaviour (*e.g.* $BaTiO_3$) at the other. There are also

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oxides that traverse both these regimes with changes in temperature, pressure, or composition (*e.g.* V_2O_3, $La_{1-x}Sr_xVO_3$). Interesting electronic properties also arise from charge density waves (*e.g.* $K_{0.3}MoO_3$), charge-ordering (*e.g.* Fe_3O_4) and defect ordering (*e.g.* $Ca_2Mn_2O_5$, $Ca_2Fe_2O_5$). Oxides with diverse magnetic properties anywhere from ferromagnetism (*e.g.* CrO_2, $La_{0.5}Sr_{0.5}MnO_3$) to antiferromagnetism (*e.g.* NiO, $LaCrO_3$) are known. Many oxides possess switchable orientation states as in ferroelectric (*e.g.* $BaTiO_3$, $KNbO_3$) and ferroelastic [*e.g.* $Gd_2(MoO_4)_3$] materials. Then, there are a variety of oxide bronzes showing a gamut of properties.[4] Superconductivity in transition metal oxides has been known for some time, but the highest T_c reached was around 13 K; we now have oxides with T_cs in the region of 160 K. The discovery of high T_c superconductors[5] focused worldwide scientific attention on the chemistry of metal oxides and at the same time revealed the inadequacy of our understanding of these materials.

The unusual properties of transition metal oxides that distinguish them from the metallic elements and alloys, covalent semiconductors and ionic insulators are due to several factors. (a) Oxides of d-block transition elements have narrow electronic bands, because of the small overlap between the metal d and the oxygen p orbitals. The bandwidths are typically of the order of 1–2 eV (rather than 5–15 eV as in most metals). (b) Electron correlation effects play an important role, as expected because of the narrow electronic bands. The local electronic structure can be described in terms of atomic-like states [*e.g.* $Cu^+(d^{10})$, Cu^{2+} (d^9) and Cu^{3+} (d^8) for Cu in CuO] as in the Heitler–London limit. (c) The polarizability of oxygen is also of importance. The divalent oxide ion, O^{2-}, does not exactly describe the state of oxygen and configurations such as O^- have to be included, especially in the solid state. This gives rise to polaronic and bipolaronic effects. Species such as O^-, which are oxygen holes with a p^5 configuration instead of the filled p^6 configuration of O^{2-}, can be mobile and correlated. (d) Many transition metal oxides are not truly three-dimensional, but have low-dimensional features. For example, La_2CuO_4 and La_2NiO_4 with the K_2NiF_4 structure are two-dimensional compared to $LaCuO_3$ and $LaNiO_3$, which are three-dimensional perovskites. Because of the varied features of individual oxides, it has not been possible to establish satisfactory theoretical models for complex transition metal oxides. I started working on transition metal oxides in the late 1950s and my early preoccupation was with the structures, defects and phase transitions of oxides such as TiO_2, Pr_6O_{11} and Bi_2O_3. Soon I became interested in the electronic and magnetic properties of oxides, especially those with the perovskite structure. The perovskite structure dominates all classes of materials, whether they are dielectrics or superconductors.

Transition metal oxides that transform from the metallic state to an insulating or semiconducting state are of great interest. It has always amazed me how a simple oxide like V_2O_3 conducts like copper at ordinary temperatures and becomes like wood on cooling it to 150 K. Interest in these transitions has blossomed over the years and the subject has itself become a frontier area of investigation.[6,7] Typical transitions of this type in oxide materials are: (a) pressure-induced transitions, as in NiO, in which the pressure increases the wavefunction overlap between neighbors to induce a change from localized to itinerant behavior of electrons; (b) transitions as in Fe_3O_4 involving charge-ordering; (c) transitions in $LaCoO_3$ that are initially induced because of the different spin configurations of the transition metal ion; electron transfer between the two spin states initiates a process that eventually renders the oxide metallic around 1200 K; (d) transitions as in EuO arising from the disappearance of spin polarization band-splitting effects when the ferromagnetic Curie temperature is reached; (e) compositionally induced transitions, as in $La_{1-x}Sr_xCoO_3$ and $LaNi_{1-x}Mn_xO_3$, in which changes of band structure in the vicinity of the Fermi level are brought about by a change in composition or are due to disorder-induced localization; (f) transitions in two-dimensional systems, such as La_2NiO_4, in which Ni—O—Ni interactions can only occur in the *ab* plane (unlike in the three-dimensional analogue in $LaNiO_3$) and (g) temperature-induced transitions in a large class of oxides such as Ti_2O_3, VO_2 and V_2O_3. Although I have only mentioned metal–insulator transitions in oxides, it should be noted that these transitions are found in a variety of other systems such as doped semiconductors, metal-ammonia solutions and expanded metals. Global aspects of metal–insulator transitions are truly fascinating.[6,7] In spite of considerable effort, we do not yet understand many aspects of these transitions, specially the 10-million fold jump in resistivity at the transition in V_2O_3.

The perovskite structure is ideal for 180° cation–anion–cation interactions and there are no cation–cation interactions. One can vary the covalency (or the interaction between the metal and oxygen orbitals) in this structure by varying the central cation and/or the transition metal ion and obtain a wide variation in properties. Interestingly, a high proportion of oxide materials of technological importance (*e.g.* ferroelectrics, superconductors, CMR materials) possess the perovskite structure. If we examine the electronic and magnetic properties of the family of perovskites of the type $LnMO_3$ (Ln, rare earth; M, first-row transition metal), we find a great variety. The titanates and nickelates possessing low-spin trivalent transition metal ions are metallic or nearly metallic. On the other hand, $LnCrO_3$, $LnMnO_3$ and $LnFeO_3$ are antiferromagnetic insulators. $LaCoO_3$ and other cobaltates are interesting, in that Co^{3+} can be in the low-spin ($t_{2g}{}^6$) or the high spin ($t_{2g}{}^4e_g{}^2$) state. While at low temperatures, $LaCoO_3$ is a diamagnetic insulator, with increasing temperature, the high-spin population increases eventually resulting in a phase transition due to the ordering of the two spin states. At high temperatures (*ca.* 1000 K), the material becomes metallic, resulting from the electron transfer between different spin/oxidation states of cobalt. Substituting for Ln in $LnCoO_3$ with a divalent ion such as Sr^{2+} or Ba^{2+}, as in $Ln_{1-x}Sr_xCoO_3$, progressively renders it metallic and ferromagnetic due to the fast electron transfer between the Co^{3+} and Co^{4+} states. We have investigated these cobaltates by a variety of methods including ^{57}Co Mössbauer spectroscopy, ferromagnetic resonance, photoemission spectroscopy and EXAFS. Electron transport properties of $LnCoO_3$ doped lightly with Sr^{2+} and other similar oxide systems can be understood in terms of variable range hopping as in disordered systems. The metal–nonmetal transition in $Ln_{1-x}Sr_xCoO_3$ [Fig. 1(*a*)] is a situation similar to impurity doping.[8] Another system showing metal-nonmetal transitions is $LaNi_{1-x}M_xO_3$ (M = Mn, Co, *etc.*), where $LaNiO_3$ ($x = 0.0$) is metallic [see Fig. 1(*b*) for the Mn system]. On increasing x, the material becomes an insulator.[8] Interestingly, in all such systems, the coefficient of resistivity changes sign across a

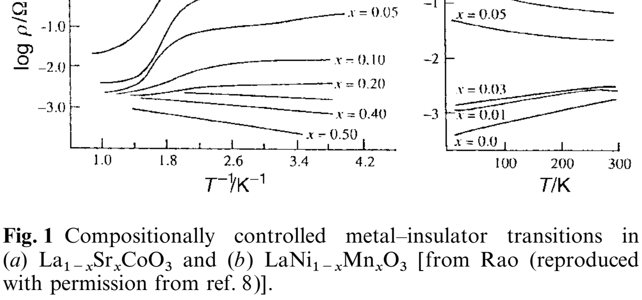

Fig. 1 Compositionally controlled metal–insulator transitions in (*a*) $La_{1-x}Sr_xCoO_3$ and (*b*) $LaNi_{1-x}Mn_xO_3$ [from Rao (reproduced with permission from ref. 8)].

universal value of resistivity, corresponding to Mott's minimum metallic conductivity.

Studies of the properties of quasi two-dimensional oxides with the K_2NiF_4 structure were initiated in this laboratory as early as 1970. It was found that Cu in Ln_2CuO_4 had no magnetic moment and that La_2CuO_4 was antiferromagnetic. Magnetic and electrical properties of La_2NiO_4 and its oxygen-excess nonstoichiometry were investigated. Solid solutions of La_2CuO_4 (T) and Nd_2CuO_4 (T′) showed an interesting phase diagram. When we wrote an overview article[9] on the structure and properties of two-dimensional oxides with the K_2NiF_4 structure in 1984, little did we realize then that La_2CuO_4 was going to become famous because of its high-temperature superconductivity. The effect of dimensionality on the electronic and magnetic properties of layered nickel oxides (*e.g.* $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$, La_2NiO_4 with decreasing dimensionality from 3 to 2) was examined some time ago. Materials of this type have the general formula $(LaO)(LaMO_3)_n$ where the (LaO) is the rock salt layer and the $LaMO_3$ is the perovskite layer.[10] When $M = Ni$, the $n = \infty$ member ($LaNiO_3$) is metallic, but the metallicity decreases as n decreases. The $n = 1$ material has the K_2NiF_4 (two-dimensional) structure. One of the more fascinating families of such materials prepared by us was of the type $(SrO)(La_{1-x}Sr_xMnO_3)_n$. These materials have now become familiar because of the colossal magnetoresistance recently discovered in them.[11] In $La_{2-x}Sr_xNiO_4$, the electronic and magnetic properties depend crucially on x and on the oxygen stoichiometry.

Of the many other oxide systems we have investigated, I would like to briefly discuss oxides forming intergrowth structures. Several metal oxide systems exhibit chemically well defined recurrent intergrowth structures with large periodicities, rather than random solid solutions with variable composition. The ordered intergrowth structures themselves frequently show the presence of wrong sequences. High resolution electron microscopy (HREM) enables direct examination of the extent to which a particular ordered arrangement repeats itself, and the presence of different sequences of intergrowths, often of unit cell dimensions. Selected area electron diffraction, which forms an essential part of HREM, provides useful information (not generally provided by X-ray diffraction) regarding the presence of supercells due to the formation of intergrowth structures. Several systems forming ordered intergrowth structures have been discovered and they generally exhibit homology.[12]

Aurivillius described a family of oxides of the general formula $Bi_2A_{n-1}B_nO_{3n+3}$ where the perovskite slabs, $(A_{n-1}B_nO_{3n+1})^{2-}$, n octahedra thick, are interleaved by $(Bi_2O_2)^{2+}$ layers. Typical members of this family are Bi_2WO_6 ($n = 1$), $Bi_3Ti_{1.5}W_{0.5}O_9$ ($n = 2$), $Bi_4Ti_3CrO_{12}$ ($n = 3$) and $Bi_5Ti_3CrO_{15}$ ($n = 4$). These oxides form intergrowth structure of the general formula $Bi_4A_{m+n-2}B_{m+n}O_{3(m+n)+6}$ involving alternate stacking of two Aurivillius oxides with different n values (Fig. 2). The method of preparation simply involves heating a mixture of the component metal oxides around 1000 K. Ordered intergrowth structures with (m, n) values of (1,2), (2,3) and (3,4) have been fully characterized by X-ray diffraction and HREM. What is amazing is that such intergrowth structures with long-range order are indeed formed while either member (m and n) can exist as a stable entity. These materials seem to be truly representative of recurrent intergrowth. The periodicity found in recurrent intergrowth solids formed by the Aurivillius family of oxides is indeed impressive.[12] WO_3 forms tetragonal, hexagonal or perovskite-type bronzes by interaction with alkali and other metals. The family of intergrowth tungsten bronzes (ITB) involving the intergrowth of nWO_3 slabs and one to three strips of the hexagonal tungsten bronze (HTB), first described by Kihlborg, is of relevance to the discussion here. In the intergrowth tungsten bronzes of the general formula M_xWO_3, x is generally 0.1 or less and depends on whether the HTB strip is one or two tunnels wide. In the ITB phases of bismuth characterized by us some time ago, the HTB strips were always one tunnel wide. Displacement of adjacent tunnel rows due to the tilting of WO_3 octahedra often results in doubling of the long-period axis of the ITB. Evidence for the ordering of the intercalating bismuth atoms in the tunnels is found in terms of satellites around the superlattice spots in the electron diffraction patterns. The occurrence of recurrent intergrowth structures continues to fascinate chemists and crystallographers alike.

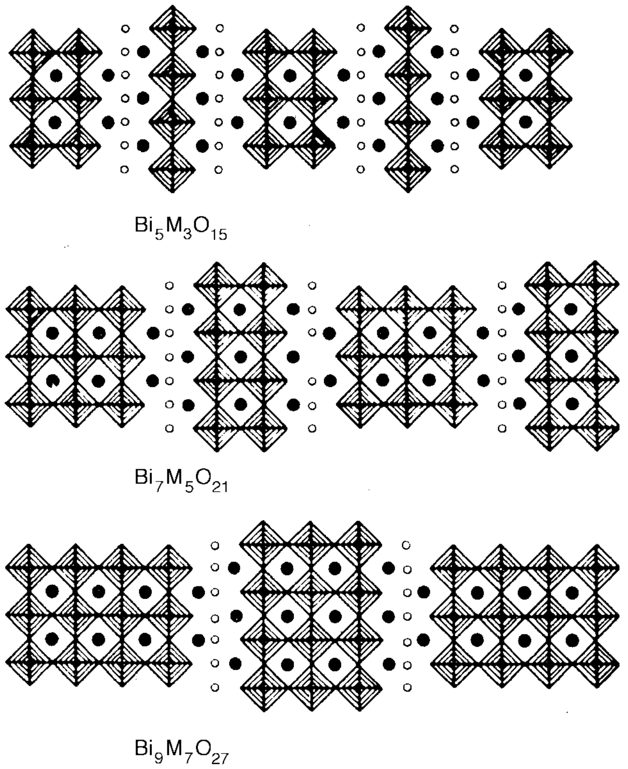

Fig. 2 Different types of intergrowth structures formed by the Aurivillius family of bismuth oxides.

Superconducting cuprates

Late in 1986 the solid state community received the big news of the discovery of a high temperature oxide superconductor.[5] The material that was found to be superconducting with a T_c of *ca.* 30 K was based on the cuprate La_2CuO_4 (Fig. 3). In February 1987, we decided to look for an yttrium cuprate in the Y–Ba–Cu–O system as a candidate for high T_c superconductivity. Wu *et al.*[13] announced an yttrium cuprate with superconductivity above liquid nitrogen temperature around March 1987. Our strategy to prepare such a material was different. Wu *et al.* obtained a mixture of black and green compounds in their effort to make an yttrium cuprate doped with Ba. The black compound was superconducting ($T_c \approx 90$ K), but they did not know its composition or structure. Since we knew that Y_2CuO_4 could not be made, we started examining the $Y_{3-x}Ba_{3+x}Cu_6O_{14}$ system. We obtained 90 K superconductivity in the $x = 1$ composition corresponding to $YBa_2Cu_3O_7$. When we independently discovered 90 K superconductivity in March 1987, we knew the composition and the approximate structure.[14]

We worked on a variety of cuprates but unfortunately the area was so competitive and overcrowded that it became difficult to get due credit for much of the work. In spite of these limitations, we made several contributions to this area. These include, besides the independent synthesis and charac-

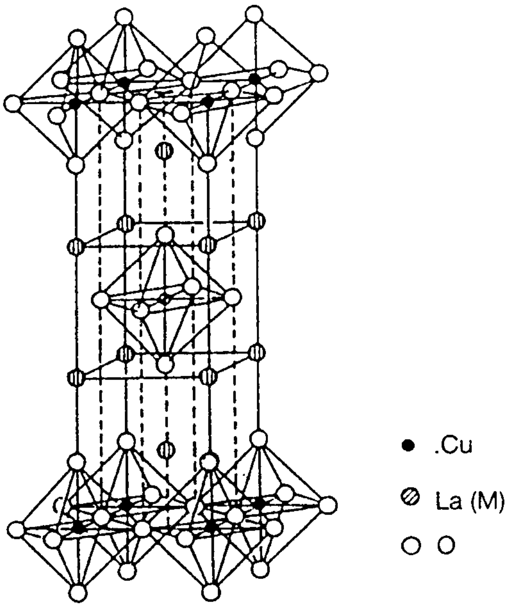

Fig. 3 Structure of La_2CuO_4 and $La_{2-x}A_xCuO_4$ (A = Sr or Ba). The CuO_6 octahedra are Jahn–Teller distorted.

terization of $YBa_2Cu_3O_7$, the first observation of non-resonant microwave absorption in high T_c cuprates, metastability of $YBa_2Cu_3O_{7-\delta}$ (in the 60 K regime, $\delta = 0.3$–0.4) and its transformation to a novel type of $YBa_2Cu_4O_8$, the importance of Cu–O charge transfer energy in relation to the superconductivity of cuprates and the nature of charge carriers, optimization of hole concentration in cuprates and the relation between T_c and hole concentration. On the synthetic front, we made some contributions which we can consider to be Bangalore brand. For example, we could make a series of superconductors in the Tl–Ca–Sr–Cu–O system by substitution of Tl by Pb or Ca by a rare earth metal; a new family of superconductors of the type $TlSr_{n+1}Cu_nO_{2n+3}$ ($n = 1$ and $n = 2$) wherein Sr is partly substituted by a rare earth or Tl by Pb was discovered. Another noteworthy contribution was the synthesis of bismuth cuprate superconductors without superlattice modulation. This was significant since all the Bi cuprates showed such modulation. The modulation could be removed by suitable cation substitution (Pb/Bi) and the adjustment of oxygen stoichiometry. An interesting aspect was the synthesis and characterization of oxyanion derivatives of cuprate superconductors containing anions such as CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and BO_3^{3-}, as integral parts of the oxide framework. Besides the mercury cuprates with the highest T_c to date, many interesting cuprates have been synthesized in the last 4–5 years.[15,16] These include copper oxycarbonates, copper oxyhalides, $Sr_2CuO_2F_{2+\delta}$ and ladder cuprates. Here, I must place on record the enormous contributions of Raveau and coworkers[17] to the synthesis and characterization of cuprate superonductors.

The several families of cuprate superconductors with holes as carriers all have the general features shown in Fig. 4. These features are common to the mercury cuprate showing the highest T_c as well. Electron superconductors of the type $Nd_{2-x}M_xCuO_4$ (M = Ce, Th) with the T′ structure possess square-planar CuO_4 units instead of the elongated octahedra in the T structure. The hole superconductors generally have the square pyramidal units. Many of the cuprate families have an antiferromagnetic insulator member at one end of the composition. What is more interesting is that all the cuprates are at a metal–insulator boundary. Some of them undergo a metal–nonmetal transition as a function of composition (*e.g.* $Bi_2Ca_{1-x}Y_xSr_2Cu_2O_8$ and $TlY_{1-x}Ca_xSr_2Cu_2O_7$ with change in x). The essential feature of the cuprates is the presence of CuO_2 sheets with or without apical oxygens. The mobile charge carriers in the cuprates are in the CuO_2 sheets. All the cuprates have charge reservoirs as exemplified by the Cu–O chains in the 123 and 124 cuprates and the TlO, BiO and HgO layers in the other cuprates. That the CuO_2 sheets are the seat of high-temperature superconductivity is demonstrated by the fact that intercalation of iodine between BiO layers in the bismuth cuprates does not affect the superconducting transition temperature while introduction of fluorite layers between the CuO_2 sheets adversely affects superconductivity. In the different series of cuprates with varying number of CuO_2 sheets studied hitherto, the T_c reaches a maximum when $n = 3$ except in single thallium layer cuprates where the maximum is at $n = 4$. The infinite layered cuprates, where the CuO_2 sheets are separated by alkaline earth and other cations, show T_c values in the 40–110 K range. Superconductivity in these materials appears to be due to the presence of Sr–O defect layers corresponding to the insertion of $Sr_3O_{2\pm x}$ blocks. We shall briefly present the common features of cuprate superconductors[18] and examine some of the outstanding problems.

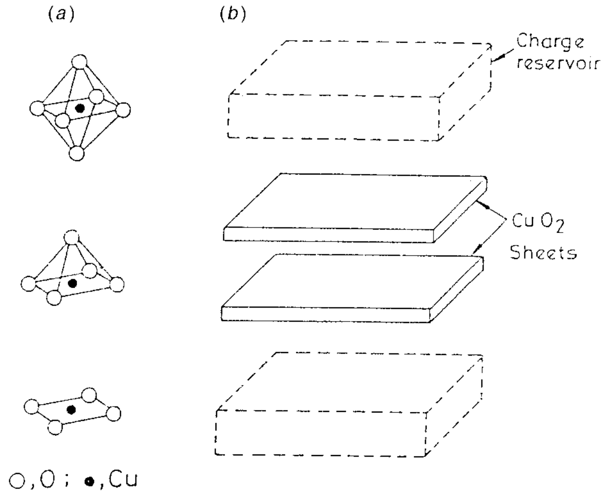

Fig. 4 (*a*) Cu–O polyhedra found in superconducting cuprates. (*b*) Schematic representation of the cuprates.

The chemistry of the majority of the cuprate superconductors is governed by oxygen holes. (Rouxel[19] has carried out fine work with sulfur holes in metal sulfides). The excess positive charge in cuprates can be represented in terms of the formal valence of copper, which in the absence of holes will be +2 in the CuO_2 sheets. In hole superconducting cuprates, it is generally around +2.2. In electron superconductors, it would be less than +2 as expected. The actual concentration of holes, n_h, in the CuO_2 sheets in $La_{2-x}A_xCuO_4$, $YBa_2Cu_3O_7$ and Bi cuprates is readily determined by redox titrations. In the 123 cuprates, the concentration of mobile holes in the CuO_2 sheets can be delineated from that in the Cu–O chains. Determination of n_h in thallium cuprates poses some problems, but in single Tl–O layer cuprates, chemical methods have been developed to obtain reasonable estimates. Generally, T_c in a given family of cuprates reaches a maximum value at an optimal value of n_h as shown in Fig. 5; the maximum is around $n_h \approx 0.2$ in most cuprates. Notice that the points in the underdoped region in Fig. 5 fall close to a straight line, but deviations occur in the overdoped region. Single layer thallium cuprates also show this behaviour. In $Tl_{1-y}Pb_yY_{1-x}Ca_xSr_2Cu_2O_7$ where the substitution of Tl^{3+} by Pb^{4+} has an effect opposite to that due to the substitution of Y^{3+} by Ca^{2+}, the T_c becomes a maximum at an optimal value of $(x-y)$, which is a measure of the hole concentration. By suitably manipulating x and y, the T_c of this system can be increased from 85–90 K to 110 K.

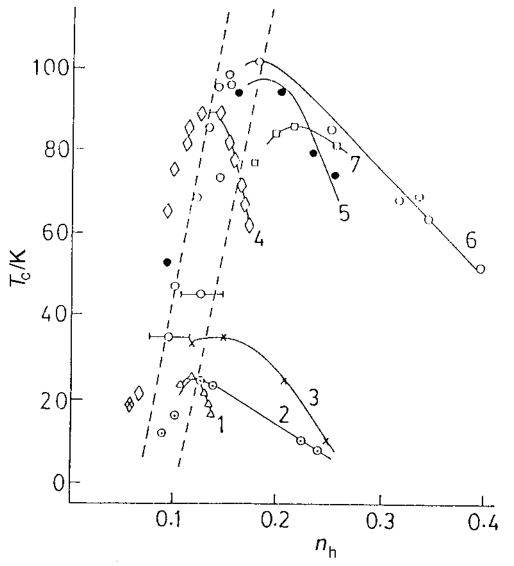

Fig. 5 Variation of T_c with the hole concentration, n_h: 1,2,6 and 7, Bi cuprates; 5, 123 cuprates; 3, $La_{2-x}Sr_xCuO_4$; 4, Tl cuprates (from Rao and Ganguli[18a]).

It is possible to obtain useful correlations between T_c and the Cu–O distances, both in-plane and apical. The Cu and oxygen Madelung energies also provide good correlations.[18a] The T_cs vary sensibly with the Cu–O charge-transfer energy as determined by core-level intensities. In spite of such relations with structural parameters, we are far from understanding the high T_c cuprates, particularly in the normal state.[18] The doped and undoped cuprates are both strongly correlated and we do not fully understand the strong correlation in these materials. Many puzzles remain. (i) For example, we do not fully understand the global composition–temperature phase diagram and the apparent lack of symmetry between hole and electron superconductors. (ii) The cuprates are unusual metals in-plane and insulators perpendicular to it; on cooling, they become three-dimensional superconductors. The anomalous temperature variation of resistivity in cuprates is noteworthy (Fig. 6), particularly the extraordinary linear variation of the *ab* plane metallic resistivity. (iii) The ac optical conductivity data do not conform the behavior expected of metals. (iv) The absence of splitting in the energy of states coupled by bilayer tunneling (as found from ARPES) is surprising. All the above observations cannot be reconciled with the picture of an anisotropic metal. (v) The linear resistivity (*ab* plane) with respect to temperature, with zero-intercept and nearly constant slope (independent of T_c) cannot be explained easily. The anisotropy is large and temperature dependent. The Hall resistivity varies inversely with temperature. (vi) Photoemission spectra suggest that the quasiparticles are not well defined in the normal state. (vii) Above all, there appears to be a characteristic low energy scale in cuprates. These pseudogap effects are indeed unique to cuprates. (viii) The superconducting state also has some unusual features, such as anisotropic order parameter, and well defined quasiparticles. Even a doped ladder cuprate has been rendered superconducting. Clearly, the status of our theoretical understanding of cuprate superconductors is far from satisfactory. It appears that cuprates constitute an experimentally overdetermined system. In the meantime, if one discovers a room-temperature superconductor, it will be an experimentalist's joy, but a theoretician's nightmare. It is noteworthy that the high T_c cuprates are finding applications in electronic devices, although their use in fabricating generators and magnets may take time.

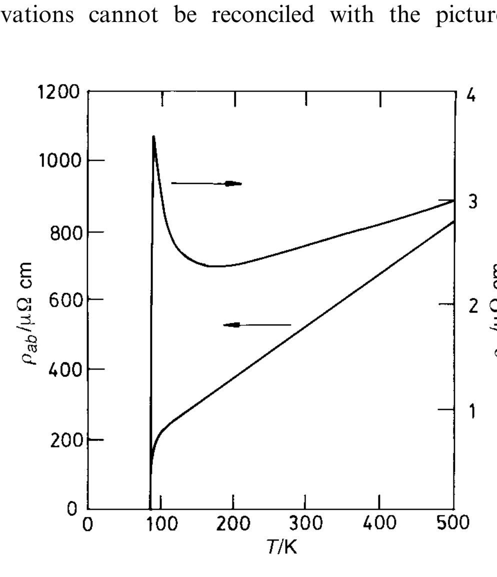

Fig. 6 Temperature variation of resistivity of $Bi_2Sr_2CaCu_2O_8$ single crystal along the *ab* plane and *c*-axis [data from Ong *et al.* as quoted by Ramakrishnan[18c] reproduced with permission from ref. 18(*c*)].

Colossal magnetoresistance, charge ordering and related properties of rare earth manganates

Giant magnetoresistance was known to occur in bilayer and granular metallic materials. Perovskite manganates of the general formula $Ln_{1-x}A_xMnO_3$ (Ln = rare earth, A = alkaline earth) have created wide interest because they exhibit colossal magnetoresistance (CMR). These oxides become ferromagnetic at an optimal value of x (or Mn^{4+} content) and undergo an insulator–metal (I–M) transition around the ferromagnetic T_c. These properties are attributed to double exchange associated with electron hopping from Mn^{3+} to Mn^{4+}. The double-exchange which favours itinerant electron behavior is opposed by the Jahn–Teller distortion due to the presence of Mn^{3+}. The manganates show charge ordering especially when the average size of the A-site cations is small. Charge ordering also competes with double exchange and favours insulating behavior. Thus, the manganates exhibit a variety of properties associated with spin, charge as well as orbital ordering. In what follows, we discuss some important aspects of colossal magnetoresistance, charge ordering and related properties of the manganates.[8,11,20]

$LaMnO_3$ is an insulator with an orthorhombically distorted perovskite structure ($b > a > c\sqrt{2}$) due to Jahn–Teller distortion. Typically, as prepared samples of $LaMnO_3$ contain some Mn^{4+}. $LaMnO_3$ with a small proportion of Mn^{4+} (<5%) becomes antiferromagnetically ordered at low temperatures ($T_N \approx 150$ K). When the La^{3+} in $LaMnO_3$ is progressively substituted by a divalent cation as in $La_{1-x}A_xMnO_3$ (A = Ca, Sr or Ba), it becomes ferromagnetic with a well defined Curie temperature, T_c, and metallic below T_c. The saturation moment is typically *ca.* 3.8 μ_B which is close to the theoretical estimate based on localized spin-only moments, suggesting that the carriers are spin-polarized. Below T_c, the manganates exhibit metal-like conductivity. Fig. 7 illustrates how the ferromagnetism and the I–M transition occur around T_c in a typical $La_{1-x}Ca_xMnO_3$ composition. The simultaneous observation of itinerant electron behavior and ferromagnetism in the manganates is explained by Zener's double-exchange mechanism. The basic process in this mechanism is the hopping of a d hole from Mn^{4+} (d^3, t_{2g}^3, $S = 3/2$) to Mn^{3+} (d^4, $t_{2g}^3e_g^1$, $S = 2$) *via* the oxygen, so that the Mn^{4+} and Mn^{3+} ions change places. The t_{2g}^3 electrons of the Mn^{3+} ion are localized on the Mn site giving rise to a local spin of 3/2, but the e_g state, which is hybridized with the oxygen 2p state, can be localized or itinerant. There is a strong Hund's rule interaction between the e_g and the t_{2g}^3 electrons. Goodenough pointed out that the ferromagnetism is governed not only by double exchange,

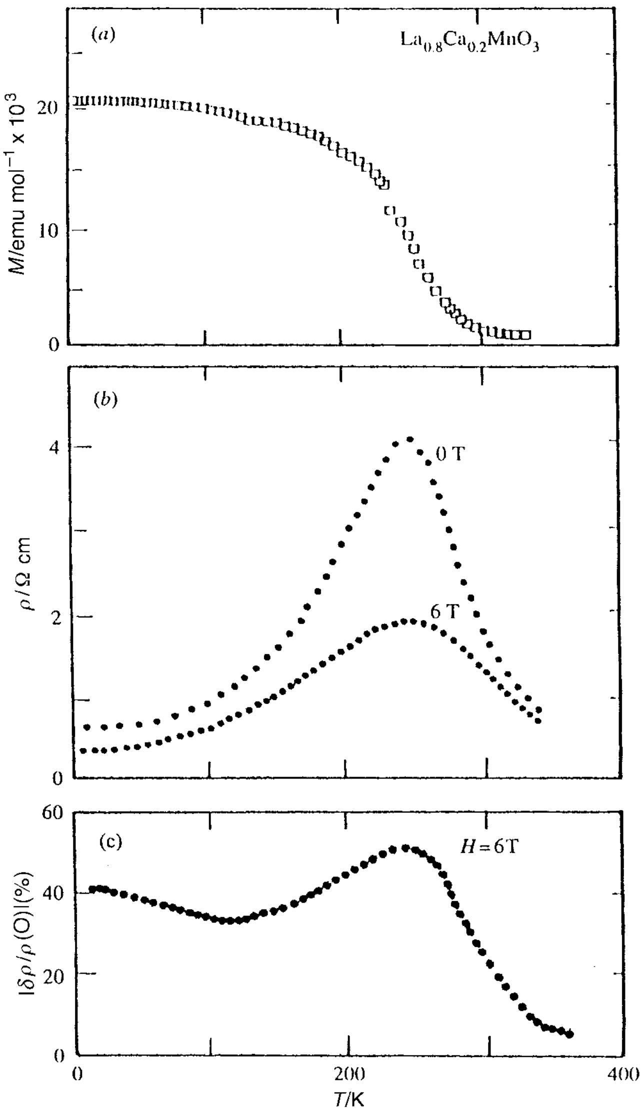

Fig. 7 Temperature variation of (*a*) the magnetization, (*b*) the resistivity (at 0 and 6 T) and (*c*) the magnetoresistance in $La_{0.8}Ca_{0.2}MnO_3$ [from Rao (reproduced with permission from ref. 8)].

but also by the nature of the superexchange interactions. It should be noted that the Mn^{3+}–O–Mn^{4+} superexchange interaction is ferromagnetic while both the Mn^{3+}–O–Mn^{3+} and Mn^{4+}–O–Mn^{4+} interactions are antiferromagnetic.

The orthorhombic distortion of $LaMnO_3$ decreases as La is progressively substituted by a divalent ion and until it becomes rhombohedral or pseudocubic. The Mn–O–Mn angle approaches 180° as the distortion decreases. When the size of the A-site cations is small, orthorhombic distortion is favoured. The key factor responsible for the distortion in $LaMnO_3$ is the Jahn–Teller distortion due to Mn^{3+} ions. Accordingly, $LaMnO_3$ has three Mn–O distances (1.91, 1.96 and 2.19 Å). Across the I–M transition, the Jahn–Teller distortion decreases in $Ln_{1-x}A_xMnO_3$, the distortion being greater in the insulating regime. The structural parameters, specifically the oxygen thermal parameters, show a significant change across the M–I transition. Clearly, Mn^{4+} ions decrease the Jahn–Teller distortion, increase the itinerancy of electrons through double exchange and increase the tolerance factor of the perovskite structure. Temperature–composition phase diagrams for $La_{1-x}A_xMnO_3$ have been worked out with increasing x or Mn^{4+} content. A composition of $x \approx 0.3$ is ideal to observe a good I–M transition and negative CMR. The magnitude of CMR is maximum at the I–M transition (Fig. 7) and scales with the field-induced magnetization. CMR is found in cation-deficient $LaMnO_3$ containing Mn^{4+} as well, and the features of the magnetic and metal–insulator transitions are similar to those in Fig. 7.

CMR is found over a wide range of compositions of $La_{1-x}Ca_xMnO_3$ ($x<0.5$). However, this material shows significant lattice effects in particular for low x. EXAFS studies reveal significant changes in the local structure in the $x=0.3$ composition in the 80–300 K range which are attributed to the formation of small polarons due to the Jahn–Teller distortion when $T>T_c$. Lattice polaron formation and local structural distortion have important implications on the electron transport (high resistivity) in these materials. $La_{1-x}Sr_xMnO_3$ is somewhat different from $La_{1-x}Ca_xMnO_3$, the A-site ion size being larger. The ferromagnetic metallic regime in $La_{1-x}Sr_xMnO_3$ extends over larger values of x and the Curie temperatures are higher. Magnetization in the manganates decreases as T^2 and the resistivity increases as T^2. In $La_{1-x}Sr_xMnO_3$ ($x=0.17$), the local spin moments and charge carriers couple strongly to changes in the structure and the structure can be switched by the application of a magnetic field depending on the temperature. The magnetic field which causes this crossover from the orthorhombic to the rhombohedral structure is rather low (*ca.* 2 T), showing thereby that a very small energy difference exists between these two structures.

Hydrostatic pressure stabilizes the ferromagnetic metallic state in $La_{1-x}A_xMnO_3$ (*i.e.* increases T_c). A similar effect can be brought about by increasing the radius of the A-site cation. There is a direct relationship between T_c and the average radius of the A-site cation, $<r_A>$, the T_c increasing with $<r_A>$. A small $<r_A>$ gives rise to a distortion of the MnO_6 octahedra by bending the Mn–O–Mn bond and in turn causing the narrowing of the e_g bandwidth to a greater extent. Accordingly, yttrium substitution in $La_{1-x}A_xMnO_3$ decreases T_c, and enhances the magnitudes of resistivity as well as magnetoresistance. By plotting the T_c against $<r_A>$, one obtains a phase diagram separating the ferromagnetic metal and the paramagnetic insulator regimes. In Fig. 8, we show a phase diagram obtained in this manner. In the lower left-hand corner, we see the ferromagnetic insulator regime. CMR generally decreases with increase in $<r_A>$, just as the peak resistivity at the I–M transition.

The effect of particle size on the electron transport and magnetic properties of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ has been investigated. Although T_c decreases with decreasing particle size, the magnetoresistance (MR) is insensitive to particle size. The I–M transition becomes broader when the particle size is small, but the %MR is nearly constant over a

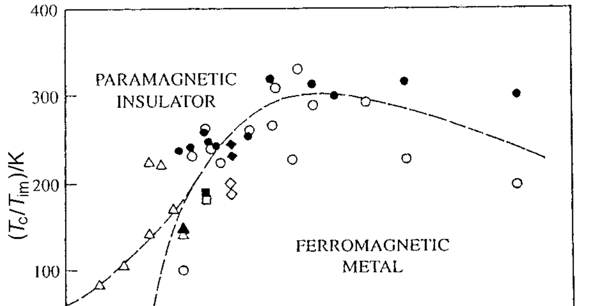

Fig. 8 Variation of the ferromagnetic T_c or the metal–insulator transition temperature, T_{im}, in $Ln_{1-x}A_xMnO_3$ with weighted average radius of the A site cations, $<r_A>$ [from Rao (reproduced with permission from ref. 8)].

wide temperature range. The low-temperature MR is significantly dependent on the grain size. For larger grain sizes, the MR at the lowest temperature decreases eventually becoming zero as in good single crystals. Samples of manganates with different particle sizes prepared with different heat treatments often show large differences between the ferromagnetic T_c and the temperature of the I–M transition. Grain boundaries appear to contribute substantially to magnetoresistance in polycrystalline materials, in particular at $T \ll T_c$.

The effects of dimensionality on CMR and related properties have been studied by examining the $(SrO)(La_{1-x}Sr_xMnO_3)_n$ family. The $n=1$ member which is two dimensional with the K_2NiF_4 structure, is an insulator, while the $n=\infty$ member is the three-dimensional perovskite showing CMR and other properties. The $n=2$ member exhibits the sharpest I–M transition and high MR. In $La_{1.4}Sr_{1.6}Mn_2O_7$, the current perpendicular to the MnO_2 planes is large, particularly close to T_c, and the barrier to transport provided by the intervening insulating layers is removed by the magnetic field as shown by Tokura *et al.* Interlayer transport seems to involve tunneling. We see some comparable features between the layered cuprate superconductors and the layered manganates. The big difference is that electrons are spin polarized in the latter.

Studies of the electrical, magnetic and other properties of $Ln_{1-x}A_xMnO_3$ systems have revealed certain unusual features with respect to the charge carriers in these oxides. The manganates exhibit high resistivities even in the metallic state, particularly at low temperatures. The values of resistivities are considerably higher than Mott's value of maximum metallic resistivity in many of these materials, the resistivity reaching constant values as high as 10^3–10^4 ohm cm at low temperatures. A clear picture of the nature of carriers responsible for the high resistivity is yet to emerge. The cause of the observed temperature dependence of resistivity at low temperatures is also not entirely clear. Another unusual feature of the manganates is related to the occurrence of large MR in a small field at relatively high temperatures. The scale of Zeeman energy associated with a field of 1 T in these spin systems is ≈ 5 K. This is much too small compared to the scale of thermal energy (200–300 K) where one sees such a large MR.

That double exchange is necessary for CMR in the manganates is shown by a study of the $LnMn_{1-x}Cr_xO_3$ system where Cr^{3+} replaces Mn^{4+}. In fact, double exchange probably suffices to explain most properties of $La_{1-x}Sr_xMnO_3$. The basic question that remains is why these manganates are insulating when $T > T_c$. The anomalous resistance has been explained by considering electron–phonon interactions arising from the Jahn–Teller splitting of the Mn d-levels. Jahn–Teller distortion localizes conduction electrons as polarons, especially in narrow band materials like $La_{1-x}Ca_xMnO_3$. As the temperature decreases, the transfer integral t_{ij} increases and the ratio of the Jahn–Teller energy to t_{ij} decreases. The coupling varies with temperature and composition, and increases across the metal–insulator transition. The large effects of local lattice distortion and crystal structure symmetry on electron transport and magnetism show that one cannot explain the unusual behavior without taking the lattice into account, especially in systems such as $La_{1-x}Ca_xMnO_3$. The observed T_c (*ca.* 250–400 K) in most manganates is considerably lower than that estimated from the measured spin-wave stiffness constant implying that the ferromagnetic exchange arising from the double exchange mechanism is not the only factor that affects T_c. The electrical resistivity of the rare earth manganates across the I–M transition is indeed difficult to understand especially at low temperatures based on double exchange or electron–phonon interaction alone. We also do not understand why CMR actually occurs in these oxides.[20] There is however every expectation that CMR will be exploited in the recording and sensor industries. We need to explore pure as well as composite materials showing CMR at ambient temperatures at low magnetic fields. The exploration should not be limited to rare earth manganates since many other inorganic materials, including $Fe_{1-x}Cu_xCr_2S_4$ and EuO_x, exhibit large MR effects.

Marginal metallicity in oxide materials

We had earlier looked briefly at the metal–insulator transitions in oxides of the type $La_{1-x}Sr_xCoO_3$ or $LaNi_{1-x}Mn_xO_3$ where the temperature coefficient of resistance changes sign across a universal value of conductivity, *viz.* Mott's minimum metallic conductivity. These oxides not only obey the minimum metallic conductivity criterion arising from consideration of disorder, but also the $n_c^{1/3}a \approx 0.25$ criterion (n_c = critical carrier concentration at the transition) arising from electron interactions. The same situation holds for the cuprate superconductors which follow both these criteria. The rare earth manganates, $Ln_{1-x}A_xMnO_3$, exhibiting colossal magnetoresistance, on the other hand, are quite different in that many of them exhibit high residual resistivities far above Mott's value. The nature of carriers in the manganates would be much more difficult to describe than those in cuprate superconductors, which are themselves far from being understood. What is to be noted is that three of the most fascinating phenomena in materials, namely insulator–metal transitions, high temperature superconductivity and CMR are exhibited by oxide materials which are marginally metallic. Marginal metallicity appears to be a universal feature,[21] which requires further probing. It is interesting to speculate whether a universal minimum electron diffusivity due to localized states is present in these materials, besides the extended states.

Charge ordering in the manganates

Charge ordering is not new to transition metal oxides. Fe_3O_4 undergoes the Verwey transition with a resistivity anomaly due to charge ordering at 120 K and ferrimagnetic ordering at 860 K. Charge ordering of the Mn^{3+} and Mn^{4+} ions occurs in the perovskite manganates. $Ln_{1-x}A_xMnO_3$ is more interesting and is associated with dramatic changes in properties.[8,11,20] Charge ordering in the manganates is strongly dependent on the average radius of the A-site cations, $<r_A>$. The ferromagnetic T_c increases with increase in $<r_A>$ while charge ordering is favoured by small $<r_A>$. Charge ordering and double exchange are thus competing interactions. We shall examine charge ordering in $Ln_{0.5}A_{0.5}MnO_3$ with equal proportions of Mn^{3+} and Mn^{4+}.

When $<r_A>$ is sufficiently large, as in $La_{0.5}Sr_{0.5}MnO_3$ ($<r_A> = 1.26$ Å), the manganates become ferromagnetic and undergo an insulator–metal transition around T_c as described earlier. $Nd_{0.5}Sr_{0.5}MnO_3$ with a slightly smaller $<r_A>$ (1.236 Å), is ferromagnetic and metallic at 250 K (T_c), but transforms to a charge-ordered (CO), antiferromagnetic state at 150 K as shown by Tokura.[20] The charge-ordering transition temperature, T_{CO}, is the same as T_N. There is a significant specific heat anomaly at T_{CO} (T_N) and the resistivity increases markedly due to the metal–insulator (FM–CO) transition. This situation is to be contrasted with that of $Nd_{0.5}Ca_{0.5}MnO_3$ ($<r_A> = 1.17$ Å) which exhibits a T_{CO} of 250 K in the paramagnetic state exhibiting a small heat capacity anomaly. $Nd_{0.5}Ca_{0.5}MnO_3$ is an insulator at all temperatures. $Y_{0.5}Ca_{0.5}MnO_3$ with a $<r_A>$ of 1.13 Å also gets charge ordered in the paramagnetic state (T_{CO}, 240 K) and becomes antiferromagnetic at 140 K (T_N). In Fig. 9 we show a simple diagram where we delineate the different types of behavior of the manganates depending on the $<r_A>$. The charge ordered state of $Nd_{0.5}Sr_{0.5}MnO_3$ is melted by the application of a magnetic field, rendering the material metallic. On the other hand, a magnetic field of 6 T has no effect on the charge-ordered insulating state of $Y_{0.5}Ca_{0.5}MnO_3$. The charge ordered states in $Nd_{0.5}Sr_{0.5}MnO_3$ and $Nd_{0.5}(Y_{0.5})Ca_{0.5}MnO_3$ are

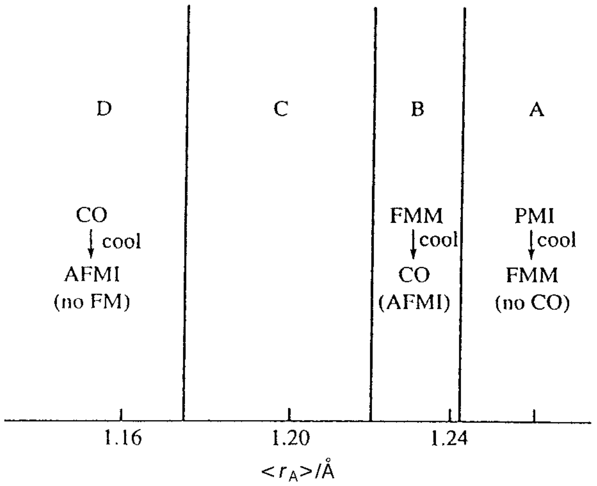

Fig. 9 Schematic diagram showing the different types of behavior in $La_{0.5}A_{0.5}MnO_3$. Region A corresponds to manganates showing CMR while region B corresponds to manganates of the type $Nd_{0.5}Sr_{0.5}MnO_3$ transforming from the ferromagnetic metallic (FMM) state to a charge-ordered (CO) state on cooling. Region D corresponds to manganates where the CO state is generally found in the paramagnetic insulating (PMI) state (*e.g.* $Nd_{0.5}Ca_{0.5}MnO_3$ and $Y_{0.5}Ca_{0.5}MnO_3$). Region C is expected to show complex behavior. AFMI stands for the antiferromagnetic insulating state [from Rao (reproduced with permission from ref. 8)].

clearly of different kinds, the difference being caused by the difference in $<r_A>$.

The occurrence of two types of CO states can be understood qualitatively in terms of the variation of the exchange couplings, J_{FM} and J_{AFM}, and the single-ion Jahn–Teller energy (E_{JT}) with $<r_A>$. While J_{FM} and J_{AFM} are expected to decrease with a decrease in $<r_A>$, albeit with different slopes, E_{JT} would be insensitive to $<r_A>$. In the small $<r_A>$ regime, a cooperative Jahn–Teller effect involving long-range elastic strain would dominate charge ordering, while at moderate values of $<r_A>$ (when $J_{AFM}>E_{JT}$, J_{FM}), the e_g electrons which are localized magnetically lower the configuration energy by charge ordering. Such a CO state, as exemplified by $Nd_{0.5}Sr_{0.5}MnO_3$, would be sensitive to magnetic fields unlike the manganates such as $Y_{0.5}Ca_{0.5}MnO_3$ in the small $<r_A>$ regime. In $Nd_{0.5}Sr_{0.5}MnO_3$, the gain in Zeeman energy resulting from the application of a magnetic field stabilizes the ferromagnetic metallic state over the antiferromagnetic insulating state. The general phase diagram in the T–$<r_A>$ plane has been constructed by Kumar and Rao based on these considerations.[8] Although we understand the gross features of charge-ordering and associated properties in manganates, we do not have a proper theory or model to explain all the varied aspects of these fascinating materials.

The high sensitivity of charge ordering in manganates to $<r_A>$ cannot be understood on the basis of the variation of the Mn–O–Mn angle and the Mn–O distance. This is because these geometrical changes do not give rise to sufficiently large changes in bandwidth as are necessary to explain the significant changes in the charge ordering temperature and the Curie temperature with $<r_A>$. The study of the complex regime (region C in Fig. 9), has yielded fascinating results. Thus, $Nd_{0.25}La_{0.25}Ca_{0.5}MnO_3$ ($<r_A> = 1.19$ Å) undergoes a reentrant transition from an incipient charge-ordered state to a FMM state on cooling, driven by a first order phase transition.[22] The charge-ordering gap collapses at the transition. Charge ordering in the manganates needs to be pursued further, especially regarding the marked effects of electric fields and chemical substitution. The role of the A-site ion mismatch on CO and FM states also needs attention.

Porous solids

Porous inorganic materials have many applications in catalytic and separation technologies. The subject has grown explosively with 8000 or more literature citations. The synthesis of microporous solids with connectivities and pore chemistry different from zeolitic materials has attracted considerable attention. A variety of such open framework structures, in particular Al and Ga phosphates as well as many other metal phosphates prepared in the presence of structure directing agents, have been characterized. The work of Cheetham, Ferey, Flanigen, Stucky and Thomas in this direction is noteworthy.[23a] Zeolites and zeolite-like materials[23,24] with micropores in the 5–20 Å range have contributed much to the advances in catalysis. There have been many break-throughs in the design and synthesis of these molecular seives with well defined crystalline architecture and there is a continuing quest for extra-large pore molecular sieves.[24] Several types of new materials including tunnel and layer structures of porous manganese oxides have been reported.[25] The progress has resulted mainly from our understanding of the role of structure-directing agents. The discovery of mesoporous silica (pore diameter 20–100 Å) by Mobil chemists added a new dimension to the study of porous solids. The synthesis of mesoporous materials also makes use of structure-directing surfactants[24,26] (cationic, anionic, and neutral) and a variety of mesoporous oxidic materials (*e.g.* ZrO_2, TiO_2, $AlPO_4$, aluminoborates), have been prepared and characterized.[26,27] In Fig. 10, the X-ray diffraction patterns of the three forms of $CaAlBO_4$ are shown.

An appropriate integration of hydrogen bond interactions at the inorganic–organic interface and the use of sol–gel and emulsion chemistry has enabled the synthesis of a large class of porous materials.[28a] Today, we have a better understanding of the structure, topology and phase transitions of mesoporous solids. Thus, block copolymers have been used to prepare mesoporous materials with large pore sizes[28a] (>30 nm). There is also some understanding of the lamellar–hexagonal–cubic phase transitions in mesoporous oxides[28b] (Fig. 11). Derivatized mesoporous materials have been explored for potential applications in catalysis and other areas.[29a] It has been found recently that transition metal complexes encapsu-

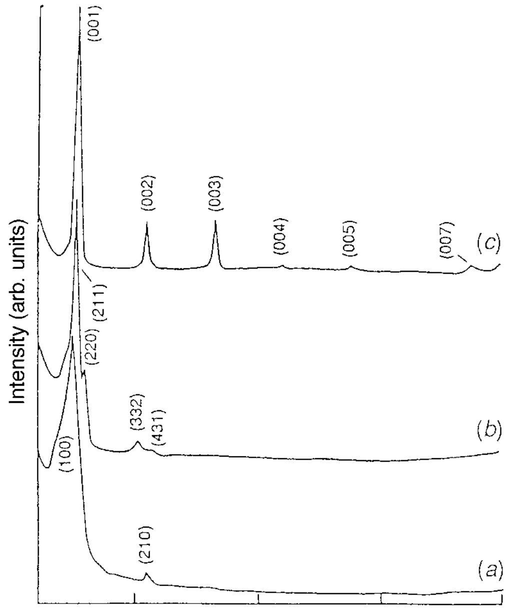

Fig. 10 X-Ray diffraction patterns of (*a*) hexagonal, (*b*) cubic and (*c*) lamellar forms of mesoporous calcium aluminoborate (from Ayyappan and Rao[27]).

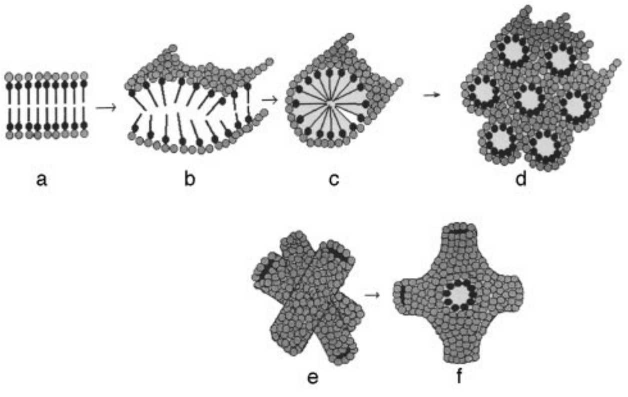

Fig. 11 Phase transitions in mesoporous solids: a–d, lamellar–hexagonal; e–f, hexagonal–cubic. The circular objects around the surfactant assemblies are the metal-oxo species (from Neeraj and Rao[28b]).

lated in cubic mesoporous phases show high catalytic activity in oxidation reactions.[29b]

Organic inclusion compounds and clathrates have been known for a long time. While these compounds are still being investigated, there have been efforts to synthesise novel organic structures by supramolecular means.[30] A recent example in this direction is the noncovalent synthesis of a novel channel structure formed by trithiocyanuric acid and bipyridine.[30b] The channels can accommodate benzene, xylenes and other molecules (Fig. 12) and the process is reversible.

Synthesis of inorganic materials

Although rational design and synthesis have remained primary objectives of materials chemistry, we are far from achieving this goal universally. There are many recent instances where rational synthesis has worked (*e.g.*, porous solids), but by and large the success has been limited. Thus, one may obtain the right structure and composition, but not the properties. There are very few instances where both the structure and properties of the material obtained are as desired. The synthesis of $ZrP_{2-x}V_xO_7$ solid solutions showing zero or negative thermal expansion is one such example.[31] The synthesis of $HgBa_2Ca_2Cu_3O_8$ with the highest superconducting T_c (*ca.* 160 K under pressure) is another example.[15,32] The preparation of modulation free bismuth cuprate superconductors by the substitution of Bi by Pb is also a good example.[33] One may also cite examples of the synthesis of ionic conductors and other materials. Most inorganic materials are still discovered accidentally, the cases of high T_c cuprates and CMR manganates being well known. What is noteworthy is the development of new strategies for synthesis, particularly those involving soft chemical routes. The subject has been reviewed adequately in the recent literature.[16,34,35]

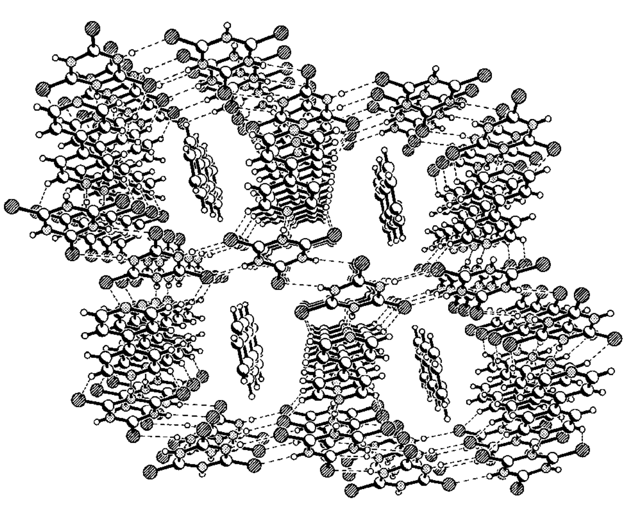

Fig. 12 Noncovalent synthesis of a layered network with large cavity based on hydrogen bonding between trithiocyanuric acid and bipyridine. Three-dimensional channels with benzene molecules can be seen [from Pedireddi *et al.* (reproduced with permission from ref. 30(*b*))].

The methods of soft chemistry include sol–gel, electrochemical, hydrothermal, intercalation and ion-exchange processes. Many of these methods are employed routinely for the synthesis of ceramic materials.[36,37] There have been recent reviews of the electrochemical methods,[38] intercalation reactions,[39] and the sol–gel technique.[40] The sol–gel method has been particularly effective with wide-ranging applications in ceramics, catalysts, porous solids and composites[41] and has given rise to fine precursor chemistry. Hydrothermal synthesis has been employed for the synthesis of oxidic materials under mild conditions[42] and most of the porous solids and open-framework structures using organic templates are prepared hydrothermally.[43] The advent of supramolecular chemistry has started to make an impact on synthesis,[16] mesoporous solids being well known examples.[43]

Many of the traditional methods continue to be exploited to synthesise novel materials. In the area of cuprates, the synthesis of a superconducting ladder cuprate and of carbonato- and halocuprates is noteworthy. High pressure methods have been particularly useful in the synthesis of certain cuprates and other materials.[36,44] The combustion method has come of age for the synthesis of oxidic and other materials.[45] Microwave synthesis is becoming popular[46] while sonochemistry has begun to be exploited.[47]

In the oxide literature, there are several reviews specific to the different families, such as layered transition metal oxides[48] and metal phosphonates.[49] Synthesis of metal nitrides has been discussed by Di Salvo.[50] Precursor synthesis of oxides, chalcogenides and other materials is being pursued with vigour.[16,36] Thus, single-molecule precursors of chalcogenide containing compound semiconductors have been developed.[51] Kanatzidis[52] has reviewed the application of molten polychalcophosphate fluxes for the synthesis of complex metal thiophosphates and selenophosphates.

In our own work over the years,[53] we have found the use of precursor carbonates to be effective in the synthesis of many oxide materials. Electrochemical techniques have been useful in oxidation reactions (*e.g.*, preparation of $SrCoO_3$, ferromagnetic $LaMnO_3$ containing *ca.* 30% Mn^{4+}, $La_2NiO_{4.25}$, $La_2CuO_{4+\delta}$). Intercalation and deintercalation of amines can be used to produce novel phases of oxides such as WO_3 and MoO_3. Topochemical oxidation, reduction and dehydration reactions also give rise to novel oxide phases, which cannot be prepared otherwise. Thus, $La_2Ni_2O_5$ can only be made by the reduction of $LaNiO_3$. Special mention must be made of the simple chemical technique of nebulized spray pyrolysis of solutions of organometallic precursors, to obtain epitaxial films of complex oxide materials; this technique can also be used to prepare nanoscale oxide powders.[54] Epitaxial films of PZT, $LaMnO_3$, $LaNiO_3$ and other oxide materials have been prepared by this method. Good films of copper and other metallic systems have also been obtained.

Molecular materials

Molecular materials, especially organic ones, have gained prominence in the last few years, with practical applications as optical and electronic materials already becoming possible. This rich area of research has benefitted from attempts to carry out rational design based on crystal engineering, including supramolecular chemistry[55,56] and the interest to investigate the structure and chemistry of the organic solid state.[57] The conventional areas of polymer research have become more

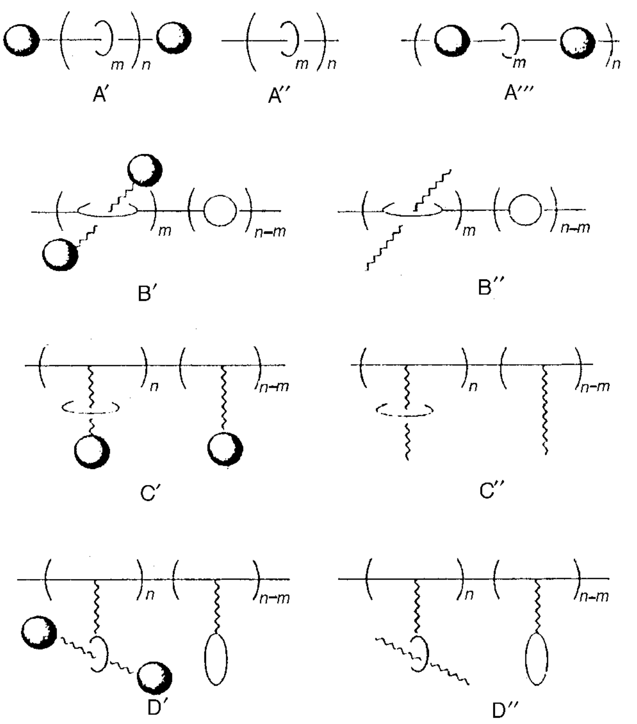

Fig. 13 Various types of main chain and side chain polyrotaxanes: blocking group (shaded circle); hollow circle (cyclic component); ellipses (cyclics threaded by linear species) [from Gong and Gibson (reproduced with permission from ref. 58)].

focussed on developing new synthetic methods and controlling polymerization. Since architecture and functionality at a molecular level control many of the properties of polymers, there are efforts to synthesise polymers with well defined topologies. Polymers involving rotaxanes, catenanes, rods, dendrimers and hyperbranched systems[58,59] are some recent examples of such efforts. Recognizing that hydrogen bonding is the driving force for the formation of crown ether based polyrotaxanes, mechanically linked polymers have been prepared, with the possibility of molecular shuttles at polymeric level (Fig. 13). Standard synthetic routes for dendrimers (Fig. 14) and hyperbranched polymers suggest many new possibilities.

Molecular magnetic materials constitute an interesting area of research, although practical applications may not be feasible in the short term. Synthesis and design of molecular ferromagnets, ferrimagnets and weak ferromagnets, providing permanent magnetization with fairly high T_c values are the main objectives of this effort. While purely organic ferromagnets have only reached modest T_cs below 2 K, materials incorporating transition metals have shown promise [*e.g.* V(TCNE)$_x$]. Molecular magnetic materials generally make use of free radicals such as nitroxides, high-spin metal complex magnetic clusters or a combination of radicals and metal complexes.[60,61] There has been a renaissance in spin-crossover materials with emphasis on active elements for memory devices and light-induced spin changes.[62] The study of diradicals and radical pairs has been strengthened by our understanding of how to stabilize the triplet state.[61] C_{60}–TDAE ($T_c \approx 16$ K) and related compounds have attracted some attention (TDEA = tetrakisdimethylaminoethylene). BEDT-TTF salts with magnetic anions have been discovered recently.[63] Organometallic materials based on neutral nitroxide radicals and charge-transfer (CT) complexes derived from the radicals have been examined in some detail.[64]

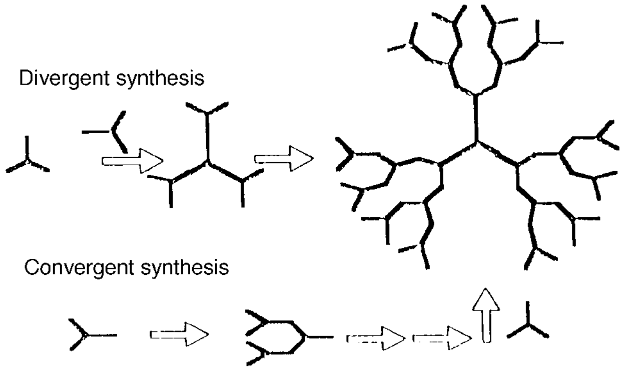

Fig. 14 Synthetic routes to dendrimers [from Hobson and Harrison (reproduced with permission from ref. 59)].

Semiconducting, metallic and superconducting molecular materials have been investigated by several workers in the last two decades. New types of TTF type molecules, transition metal complexes with elongated π ligands, neutral radicals and Te-containing π donors have been synthesized and an organic superconductor with an organic anion, β″-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$, has been discovered.[65] Cation radical salts of BEDT-TTF and similar donors as well as BEDT-TTF salts are still a fertile ground for the production of new materials.[63,65] Synthesis of linearly extended TTF analogues[66] as well as of new TCNQ and DCNQ acceptors[67] have been reported. The use of organic semiconductors as active layers in thin films holds promise, α-sexithiophene being an example.[68,69]

High performance photonic devices have been fabricated from conjugated polymers such as poly(*p*-phenylenevinylene), polyaniline and polythiophene.[70] The devices include diodes, light-emitting diodes, photodiodes, field effect transistors, polymer grid triodes, light emitting electrochemical cells, optocouplers and lasers. The performance levels of many of these organic devices have reached those of the inorganic counterparts. The high photoluminescence efficiency and large cross section for stimulated emission of semiconducting polymers persist upto high concentrations (unlike dyes). By combination with InGaN, hybrid lasers can now be fabricated. It is gratifying that plastic electronics is moving rapidly from fundamental research to industrial applications.

The area of molecular nonlinear optics has been rejuvenated by efforts to investigate three-dimensional multipolar systems, functionalized polymers as optoelectronic materials, near infrared optical parametric oscillators and related aspects.[71] There have been some advances in chromophore design for second-order nonlinear optical materials;[72] these include one-dimensional CT molecules, octopolar compounds and organometallics. Some of the polydiacetylenes and poly(*p*-phenylenevinylene)s appear to possess the required properties for use as third-order nonlinear optical materials for photonic switching.[73]

Increasing interest in molecular materials has made an impact on the direction of organic chemistry as well, giving rise to large-scale activity in this area. The discovery of fullerenes and fullerene-based materials has contributed to some interesting developments.[74–76] Organic–inorganic hybrids offer many interesting possibilities, with the composites exhibiting properties and phenomena not found in either component.[77a] Two types of materials have been classified, organic–inorganic units held together by weak bonds and organometallic polymers.[77b] Silicon based hybrids and related materials have been reviewed by Livage.[40] In Fig. 15, we show some examples of polyhedral oligomeric silsesquioxanes used as building blocks for the sol–gel synthesis of hybrid materials. It is indeed gratifying that organic molecular devices have become a reality. The concepts and directions suggested by Whitesides[78a] have been useful in designing devices. Special mention must be made of the devices developed by Willner[78b] making use of self-organized thiols and other molecular systems. In this connection, the device-related studies of functional polymers by Wegner and others are also relevant.

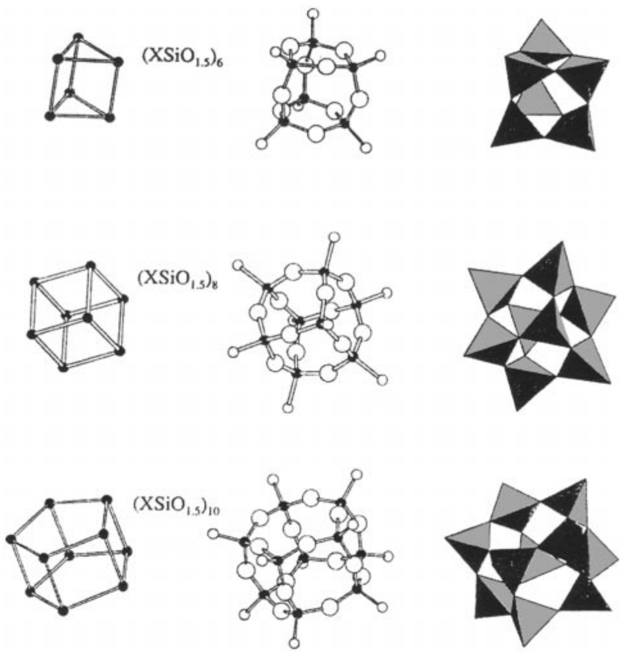

Fig. 15 Examples of silsesquioxanes used as building blocks for the sol–gel synthesis of hybrid materials [from Livage (reproduced with permission from ref. 60)].

Biomolecular materials

Biomolecular materials constitute a class of materials at the interface between biology and materials science. They not only provide an insight to Nature's ways, but also suggest new methods of synthesis and design of materials. Thus we can learn much from a study of the principles of structure–function relations in mineralized biological materials, the various forms of calcium carbonate forming the basis for many things that happen.[79,80] Some of the materials such as shells can, in principle, be considered to be part of traditional ceramic materials. The synthesis of mesoporous silica and related materials also owes its origins to biomineralization. Biomineralization has inspired the synthesis of nanocomposites, nanoparticles and nanoparticulate films.[81,82] Collagen fibrillar structure in mineralized and nonmineralized tissue, in particular the ultrastructure orientation of mineral crystals in bone relative to that of the collagen fibril, is an important problem receiving attention.[83]

Some of the recent developments in biomolecular materials include designed drug delivery systems consisting of self-assemblies of lipid and biocompatible lipids,[84] protein-based biological motors,[85] formation of new types of liposomes (*e.g.* spherical liposomes) and emulsions, tissue engineering, biogels, higher-order self-assemblies in biomaterials, and new methods of biopolymer synthesis.[86] Assembly of soft biofunctional and biocompatible interfaces of solids by the deposition of ultrathin soft polymer films, supported lipid–protein bilayers or membranes separated from solids by soft polymer cushions are other areas of vital interest.[87] The ability of polymer molecules attached at one end to a surface to prevent or enhance protein adsorption is being examined.[88]

Glasses and ceramics can bond to living tissues if there is bioactive layer. The development of a bioactive hydroxyapatite layer *in vivo* at body temperature is therefore an important problem.[89] Materials with the highest level of bioactivity develop a silica layer that enhances the formation of such a layer. Such sol–gel processes are used to produce bioactive coatings, powders and substrates which allow molecular control over the incorporation and behavior of proteins and cells with applications as sensors and implants. Sol–gel encapsulation of biomolecules within silica matrices has encompassed enzymes, metalloproteins, photoactive biomolecules and even whole cells.[78] Recently, interfacing electronic materials with lipids and proteins has shown promise in several fields, including biosensors.[90]

Nanomaterials

The synthesis, characterization and properties of nanomaterials have become very active areas of research in the last few years. In particular, nanostructured materials assembled by means of supramolecular organization offer many exciting possibilities. These include self-assembled monolayers and multilayers with different functionalities, intercalation in preassembled layered hosts and inorganic three-dimensional networks. The reader is referred to the special issue of *Chemistry of Materials*[91] for an overview of present day interests. There are many recent reviews on the varied aspects of nanomaterials. The work of Alivisatos[92] on the structural transitions, elec-

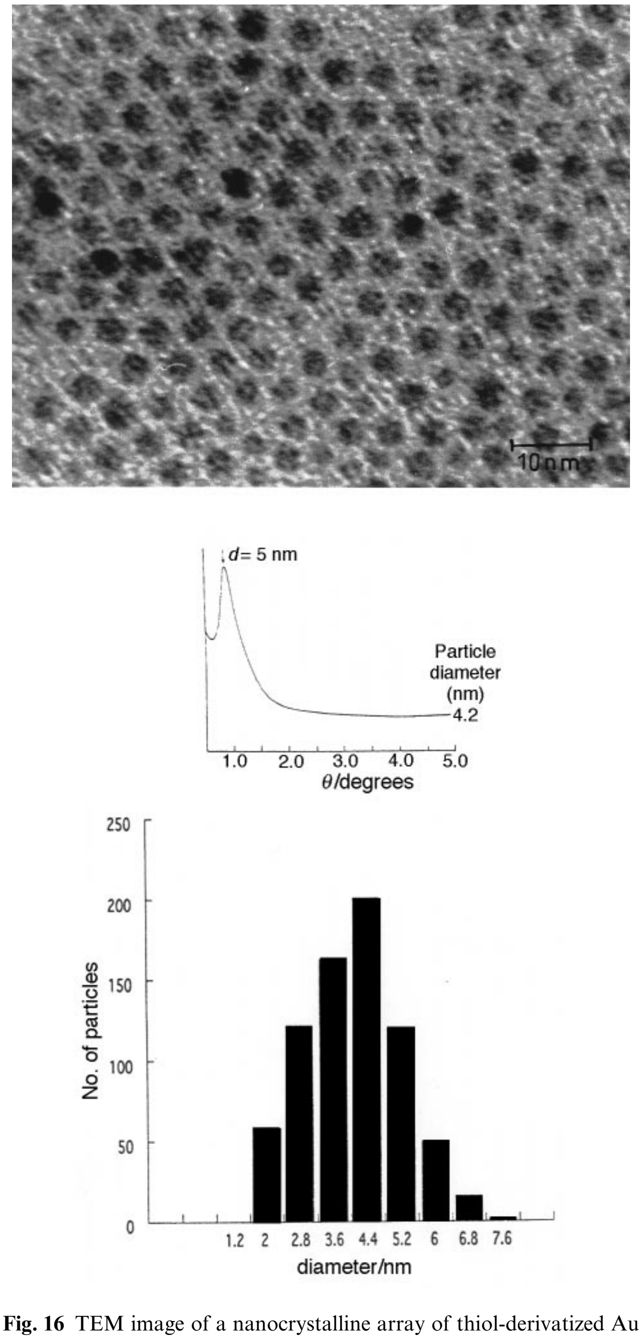

Fig. 16 TEM image of a nanocrystalline array of thiol-derivatized Au particles [from Sarathy *et al.* (reproduced with permission from ref. 96(*b*))].

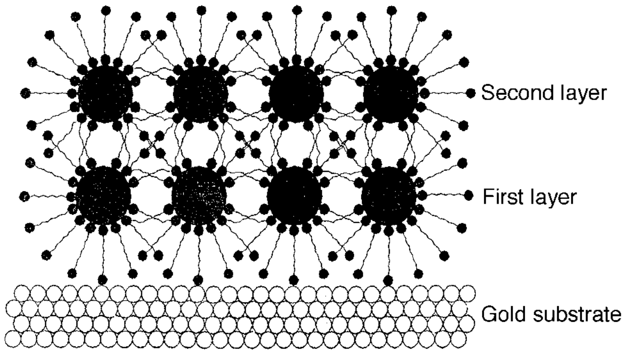

Fig. 17 Schematic representation of successive deposition of layers of metal (Pt or Au) nanoparticles and dithiols.

tronic properties and related aspects of nanoparticles of CdS, InAs and such materials is particularly noteworthy.

We have been interested in investigating the size-dependent electronic structure and reactivity of metal clusters deposited on solid substrates. Thus, we have shown that when the cluster size is small ($\lesssim 1$ nm), an energy gap opens up.[93a] Bimetallic clusters show additive effects due to alloying and cluster size[93b] in their electronic properties. Small metal clusters of Cu, Ni and Pd show enhanced chemical reactivity with respect to CO and other molecules.[94] Metal clusters and colloids, especially those with protective ligands, have been reviewed in relation to nanomaterials.[95] We have recently developed methods of preparing nanoparticles of various metals as well as nanocrystalline arrays of thiolized nanoparticles of Au, Ag and Pt.[96] In Fig. 16, we show the TEM image of thiol-derivatized Au nanoparticles forming a nanocrystalline array. More interestingly, by using dithiols, it has been possible to accomplish layer-by-layer deposition of dithiol–metal nanoparticle films (Fig. 17). This is somewhat similar to the layer-by-layer self assembly of polyelectrolyte–inorganic nanoparticle sandwich films.[97] Such superlattices involving vertical organization of arrays of metal quantum dots may have novel properties.

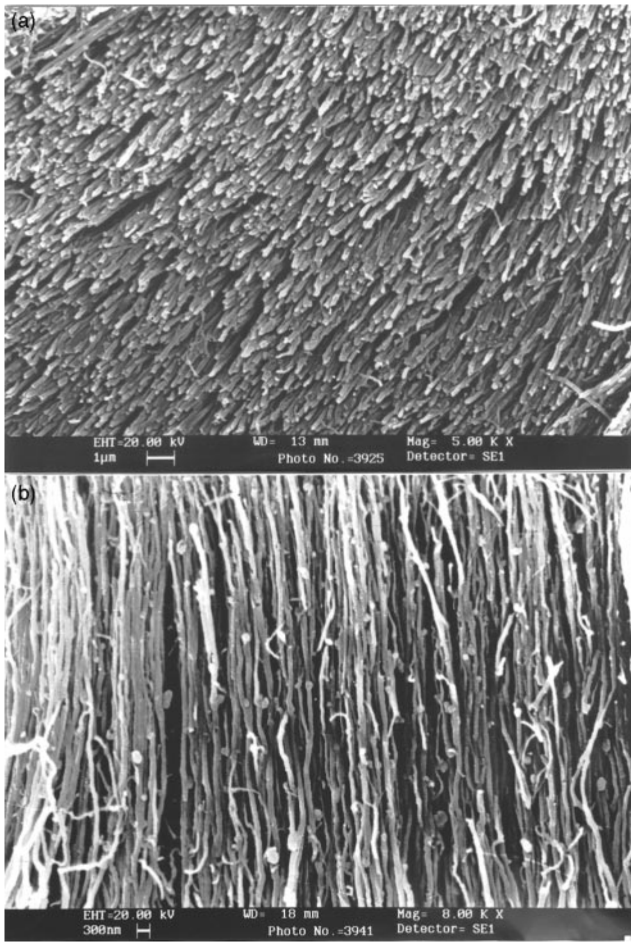

Fig. 18 SEM images of aligned-nanotube bundles obtained by the pyrolysis of ferrocene (from Rao *et al.*[99b]).

Unprecedented interest has developed in carbon science ever since the discovery of fullerenes and nanotubes. Solid state properties of C_{60} and C_{70} have been of interest to the author since 1991. Some of the aspects investigated in this laboratory include orientational phase transitions, amorphization and polymerization under pressure, molecular magnetism of the TDAE derivative *etc.*[74] We have been working on the synthesis and characterization of carbon nanotubes for some time.[74] Opening, filling, closing and functionalizing carbon nanotubes have been accomplished.[98] Since metal particles are essential as catalysts to prepare nanotubes by the pyrolysis of hydrocarbons, we have employed organometallic precursors to generate nanotubes.[99a] Single-wall nanotubes have been obtained by the pyrolysis of metallocene or $Fe(CO)_5$–hydrocarbon mixtures under controlled conditions. It has also been possible to obtain copious quantities of aligned-nanotube bundles by the pyrolysis of ferrocene (Fig. 18) precursors. C–N and B–C–N nanotubes have been prepared by precursor pyrolysis as well.[99a] By using acid-treated carbon nanotubes as templates, ceramic oxide nanotubes have been prepared.[100] The procedure involves coating the acid-treated nanotubes by metal alkoxides and such precursors, and burning off the carbon.

Concluding remarks

In a brief overview of this type, it has not been possible to do justice to the work of many leading practitioners of materials chemistry or cover all the known classes of materials and phenomena. Thus I have not covered chalcogenides, nitrides and the like. An area that has not been discussed is noncrystalline materials, especially glasses, which have been of vital interest to materials chemists for many years. The subject is growing rapidly because of the increasing number of applications. Amorphous carbon, amorphous silicon, fluoride glasses, superionic glasses and metallic glasses are some of the amorphous materials of great interest.[101] The glass transition continues to arouse interest.[102] It is an unusual phase transition indeed. The subject of phase transitions itself is of great importance in materials chemistry and a proper understanding of the subject is essential to appreciate many of the materials properties.[103] Ionic conductors, energy storage materials and dielectrics constitute important areas of vital technological relevance. Recent developments in solid state electrochemistry are nicely covered in the book edited by Bruce.[104] An aspect of materials chemistry that is being increasingly exploited is computer simulation and modelling of structures, surfaces, processes and mechanisms.[105] Simulation and modelling techniques are particularly useful in understanding phenomena and structures in situations where experimentation is difficult (*e.g.* molecular processes in zeolites). Another development that deserves notice is the atomic layer-by-layer synthesis of inorganic materials,[106] which suggests the possibility of making use of oxides and other materials in integrated circuits. In spite of the brevity, I trust that the article has succeeded in communicating the nature of present-day materials chemistry. I believe that the references to many of the recent reviews will be useful to students, teachers and practitioners of the subject.

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