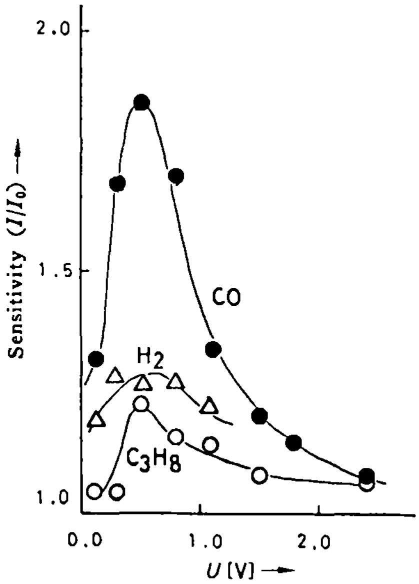

Fig. 3. Tuning of the sensitivity to carbon monoxide by bias in the CuO/ZnO contact type gas sensor [5]. ●: with CO, △: with H_2, ○: with C_3H_8; gas concentrations: 8000 ppm; temperature: 260°C.

reaction between carbon monoxide adsorbed on the positively charged copper oxide surface and oxygen adsorbed on the negatively charged zinc oxide surface, giving rise to carbon dioxide, is enhanced when the bias is greater than 0.5 V. If this explanation is correct, we have here an electric field controlling a chemical reaction.

A difficulty in applying control voltages is the need to connect leads. If the tuning is achieved by optical or magnetic means, the materials can be regarded as being more intelligent.

3. Conclusion

Intelligent materials can be developed through learning about the mechanisms in living organisms. However, we require materials that can be used in environments not tolerated by living organisms. Intelligent materials perform better than living organisms from the durability standpoint. Key functions for intelligent materials are self-recovery, self-adjustment or control, self-diagnosis, stand-by capability, and ability to be externally tuned. Some examples of intelligent materials have been discussed here. One example in which we can see self-recovery and stand-by capabilities, and ability to externally tune the behavior, is the p/n (CuO/ZnO) contact structure. Research and development on intelligent materials has only just begun. It is one of the most challenging frontiers of materials science.

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From Electronic/Ionic Conductors to Superconductors: Control of Materials Properties

**High T_c Perovskites
Electron/Ion Transfer
Topotactic Reactions**

By Robert Schöllhorn*

1. Introduction

Modern materials science may be defined in analytical terms as the effort to understand the macroscopic properties of solids by considering their structure on the microscopic (atomic) level. The term "structure" comprises here the geometrical/crystallographic aspects, the total of electronic interactions between the atoms which constitute the material, and the lattice dynamics. In synthetic terms one major approach in materials science is the aim of "tailoring" materials with a given set of particular properties on the basis of analytical knowledge in order to meet optimally and economically the needs of specific applications. The thermal synthesis of solid compounds is usually related to a substantial structural reorganization at high temperatures. However, the properties of the products are not

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determined solely by thermodynamics, but are frequently strongly dominated by kinetic phenomena leading to non-equilibrium states. One interesting alternative route for preparing new materials that makes use of the consequences of kinetics is low temperature synthesis, which exploits the fact that metastable intermediate states can be stabilized at lower temperatures. A particular case here is the synthesis of solids at or close to ambient temperature; under specific conditions such reactions can be carried out as reversible processes. One most attractive aspect of these "topotactic" reactions is the fact that they can be used for the *modification and control of physical properties* of solid materials by isothermal chemical reactions at ambient temperature. We shall briefly outline here the principles of this concept, and illustrate through a few selected examples the potential and the problems encountered.

2. Concepts

In terms of charge carrier transport properties, solid materials can be classified by a simple scheme in three groups: 1) electronic conductors, 2) ionic conductors, and 3) mixed electronic/ionic conductors, the latter being able to transport electrons as well as ions simultaneously. A large number of solids [H] (binary or multinary phases) which have electronic conductivity together with an appropriate band structure for the uptake of additional electrons and a system of interconnected vacant lattice sites may react with mobile ions A^+ according to the following scheme:[1-3]

$$\underset{\text{electronic conductor}}{[H]} + xe^- + xA^+ \rightleftharpoons \underset{\text{electronic/ionic conductor}}{A^+[H]^{x-}} \qquad (1)$$

This electron/ion transfer process can be performed by chemical or electrochemical techniques. The electrons are taken up into the upper band level (conductivity band) of the host matrix [H] (Fig. 1), while the guest ions A^+ fill up the vacant sites in [H]. Reactions of this type are usually reversible and proceed at or close to ambient temperature while retaining the structure of the rigid matrix [H] (topotactic process). In terms of composition, inorganic host materials are mainly binary or multinary compounds of non-metals with redox-active transition metals, e.g. oxides (WO_3, MoO_2, V_2O_5 etc.), chalcogenides (TiS_2, Mo_6S_8, $NiPSe_3$ etc.) or halides ($RuCl_3$, $RuBr_3$, FeOCl etc.). Similarly a large number of organic conducting polymers (e.g. polyacetylene, polypyrrole, polyaniline etc.) have been found to undergo electron/ion transfer reactions. Non-crystalline inorganic materials with electronic conductivity, such as amorphous MoS_3, TiS_2 and V_2O_5 have also been shown to be able to act as host lattices for these reversible topotactic processes.

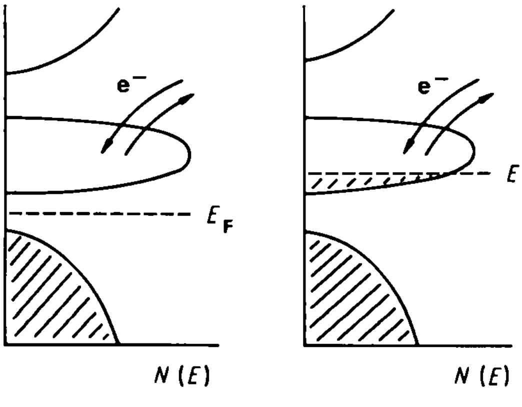

Fig. 1. Electron/ion transfer scheme for semiconducting (left) and metallic (right) materials (E_F = Fermi energy, $N(E)$ = density of states.

The structural dimensionality of the host compounds may range from three-dimensional to one-dimensional (Fig. 2), and strongly affects the reactivity in geometrical terms. Framework hosts with vacant "lattice channels" can accept only atomic guest ions (metal ions, protons) up to a critical diameter determined by the geometry of the channel system. Layered host lattices are flexible and can easily adapt to the geometry of the guest species; they may also

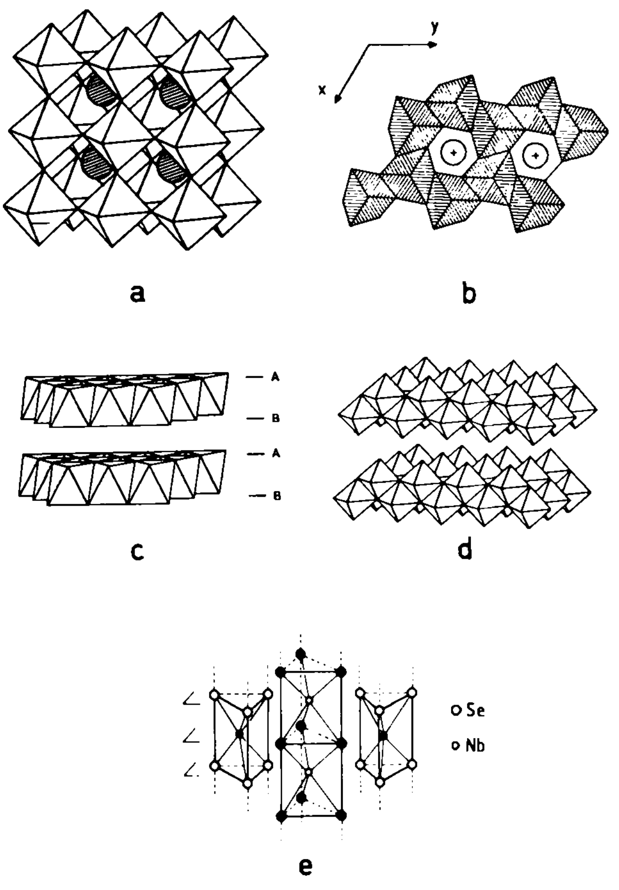

Fig. 2. Host lattices with different structural dimensionality. Framework structures: a) WO_3, b) Nb_3S_4; layered structures: c) TiS_2, d) MoO_3; chain structure: e) $NbSe_3$ (spheres in a) and b) indicate guest positions on lattice sites) [19].

intercalate organic and organometallic ions with or without neutral solvate molecules. The tremendous variety of the latter phases represents an interesting area in which molecular chemistry and solid state chemistry are closely associated. Reactions of layered host systems exhibit a number of structural peculiarities such as "staging" (partial occupation of the van der Waals gaps between the layers in an ordered sequence), "stacking" (different layer order sequence perpendicular to the basal planes), order/disorder transitions of guest or host sublattice, incommensurate phases, cooperative exchange reactions and hysteresis. Similar phenomena are observed for one-dimensional host lattices.

Reaction (1) describes the electron/ion transfer process for an "empty" conductor host lattice. Many ternary phases $A_xM_yX_z$ (M = transition metal, X = non-metal) with electronic conductivity are known, however, which are characterized by a rigid lattice framework (M_yX_z) and cations A^+ selectively mobile at ambient temperature. Many of these phases have an appropriate band structure that allows the following (reversible) electron/ion transfer process:

$$A_x^+[M_yX_z]^{x-} \rightleftharpoons M_yX_z + xA^+ + xe^- \qquad (2)$$

A few examples may illustrate the reaction principles outlined above. Niobium disulfide is a metal with a layered structure related to that of the CdI_2 type, which may intercalate Li^+ ions, for example, according to equation (3). For $x = 1$ the lithium ions occupy all octahedral

$$x\mathrm{Li}^+ + xe^- + \mathrm{NbS}_2 \rightleftharpoons \mathrm{Li}_x^+[\mathrm{NbS}_2]^{x-} \qquad (3)$$

sites in the van der Waals gap between the NbS_2 layer units which themselves have a negative excess charge $[NbS_2]^{1-}$ (macroanions). The intercalation of solvated ions or molecular ions (Cp_2Co^+ = cobaltocenium ion) is similarly illustrated by equations (4) and (5). An example for

$$x\mathrm{Na}^+ + y\mathrm{H_2O} + xe^- + \mathrm{NbS}_2 \rightleftharpoons \mathrm{Na}_x^+(\mathrm{H_2O})_y[\mathrm{NbS}_2]^{x-} \qquad (4)$$

$$x\mathrm{Cp_2Co}^+ + xe^- + \mathrm{NbS}_2 \rightleftharpoons (\mathrm{Cp_2Co}^+)_x[\mathrm{NbS}_2]^{x-} \qquad (5)$$

$$\mathrm{Cu}^+[\mathrm{Ti_2S_4}]^- \rightleftharpoons \mathrm{Cu}^+ + e^- + \mathrm{Ti_2S_4} \qquad (6)$$

the deintercalation of a ternary phase with a selectively mobile cation species (Cu^+) is the reaction of the metallic copper chalcogen spinel $CuTi_2S_4$ [equation (6)] that leads to the formation of $Ti_2S_4 = TiS_2$, i.e. a new modification of titanium disulfide with cubic structure (Table 1).

Table 1. Metastable binary transition metal chalcogenides prepared from ternary phases via electron/ion transfer reactions. A^+ = mobile lattice ion, D = structural dimensionality of the product.

Ternary Phase	A^{n+}	Binary Phase	D	Ref.
$Fe_2Mo_6S_8$	Fe^{2+}	Mo_6S_8	3	[5]
$K_xTi_3S_4$	K^+	Ti_3S_4	3	[6]
$CuTi_2S_4$	Cu^+	c-TiS_2	3	[7, 8]
Na_xWS_2	Na^+	o-WS_2	2	[9]
$LiVS_2$	Li^+	VS_2	2	[10]
$KCrSe_2$	K^+	$CrSe_2$	2	[11]
$TlMo_6Se_6$	Tl^+	Mo_6Se_6	1	[12]

The reactions considered above represent electron/cation transfer processes. Only a few host lattices able to undergo the symmetrical reaction of electron/anion transfer [equation (7), [H] = host lattice] have been found so far. Examples are graphite and conducting polymers, which are

$$[\mathrm{H}] + x\mathrm{A}^- \rightleftharpoons (\mathrm{A}^-)_x[\mathrm{H}]^{x+} + xe^- \qquad (7)$$

redox amphoteric systems accessible to electron/cation as well as to electron/anion transfer. Layer charge sign transition $[H]^- \rightarrow [H]^+$ and electron/anion transfer reactions have been reported recently, however, for a series of layered transition metal hydroxide oxide phases,[4] and we shall discuss below in more detail an example of an electron/oxide ion transfer.

3. Control Functions and Potential Application

The primary chemical properties of solids that can be controlled by electron/ion transfer processes are changes in composition (type of guest species), stoichiometry (concentration of guest species), redox state, and structure. Since these reactions are performed at low temperatures the influence of kinetics becomes dominant. For this reason the reaction products are frequently metastable new phases that cannot be prepared by conventional thermal synthesis techniques. Table 1 presents a few examples of binary chalcogenides which have been obtained from ternary compounds by electrochemical or chemical oxidation. None of these phases can be synthesized from the elements with the stoichiometry or structure indicated. The (reversible) structural changes within the host matrix elements are always rather small (0.01-0.1 Å); for low dimensional host lattices with flexible matrix units (layers, chains) the geometrical separation between these units can, however, be controlled between ca. 6 and 60 Å, e.g. by intercalation of large or anisometric guest species. Lattice defect concentration and order/disorder transitions in the guest or host sublattice can be strongly influenced by the kinetics of the reaction. In layered solvated compounds significant changes in the interlayer spacing can be controlled by minor changes in the equilibrium electrolyte concentration, due to structure induced selectivity resulting from cooperative transitions.[2-4]

One most important aspect is the possibility of inducing and controlling changes in the *physical* properties of a given solid by reversible chemical reactions at ambient temperature. These changes concern in particular the electronic properties (i.e. electronic transport, metal/semiconductor and metal/superconductor transitions, charge density waves, magnetic ordering phenomena), optical properties and ionic transport. Mechanical properties can similarly be strongly affected: the layered chalcogenide NbS_2 is a highly elastic compound with lubricant properties, whereas after intercalation even of small amounts of copper (Cu_xNbS_2) a brittle material results.

In terms of applications, electron/ion transfer reactions are of interest from various aspects. As already discussed above, they provide a wide base for the low temperature synthesis of new materials. A quite obvious application in energy storage is their use as reversible electrodes, e.g. in high energy density secondary batteries with aprotic electrolytes.[13] Galvanic cells for this purpose have been designed not only with inorganic materials but also with conducting organic polymers.[14] Changes in optical properties with the redox state have been used for the construction of passive display systems, with the advantage that the information stored is retained in the absence of an external voltage.[15] Recently a rear mirror with dimmer function for automobiles has been developed with a thin film galvanic cell around the reflector plane[16] (Fig. 3). Mixed conductor materials with redox properties can be used as sensor systems (e.g. ion-sensitive field effect transistors) and in microelectronic devices.[17] Further applications relate to the use of electronic/ionic conductors in heterogeneous catalysis, electrocatalysis, in photoelectrochemical systems[18] and for the controlled release and uptake of reagents by host solids.

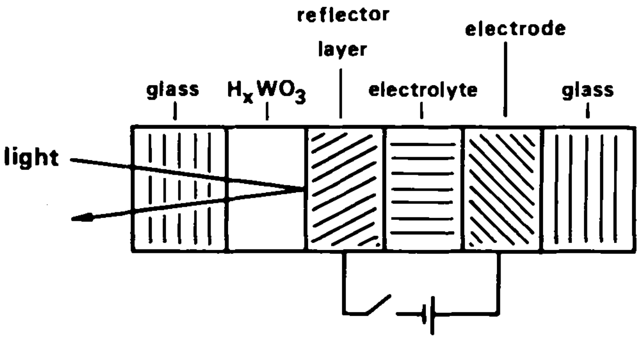

Fig. 3. Scheme of the design of a rear mirror for automobiles (cross section) with dimmer function based on the reversible formation of H_xWO_3 (see section 4) [19].

A major requirement in setting out to exploit the potential of electron/ion transfer reactions for the control of the physical properties of solid materials is the understanding of the reaction mechanism and the changes in structure and bonding with the redox state. We shall discuss in the following a few examples of systems which have recently been studied in more detail; for simplicity we will restrict the scope to atomic species as the guest ions.

4. Electron/Proton Transfer: Mechanism, Kinetics, Anisotropic Dynamics

The intercalation of hydrogen via electron/proton transfer into electronically conducting solids with the formation of hydrogen bronzes is a well known phenomenon.[1,2] These systems can be used as battery electrodes, for passive displays, for hydrogen storage, and as heterogeneous catalysts. An instructive example for the reversible changes in composition, structure and physical properties is the reaction of tungsten trioxide WO_3 (ReO_3 type framework structure, Fig. 2a):

change in stoichiometry:	$WO_3 + xH^+ + xe^- \rightleftharpoons H_x[WO_3]$
change in structure:	monoclinic $\rightleftharpoons$ tetragonal
change in electronic transport:	semiconductor $\rightleftharpoons$ metal
change in optical properties:	yellow transparent $\rightleftharpoons$ blue metallic

Similar reactions are observed for the layered binary molybdenum oxide MoO_3 (Fig. 2d). Five different phases have been identified for H_xMoO_3: I, blue orthorhombic, $0.25 \leqslant x \leqslant 0.4$; II, blue monoclinic, $0.6 \leqslant x \leqslant 0.8$; III, blue monoclinic, $0.95 \leqslant x \leqslant 1.05$; IV, red monoclinic, $1.55 \leqslant x \leqslant 1.72$ and V, green monoclinic, $x = 2.0$. The H_xMoO_3 system displays a characteristic strong kinetic influence: 1) IV and V are metastable phases with potentials lying below the equilibrium potential of H_2/H^+, 2) the reaction cycle exhibits strong hysteresis, phases II and III appear only in the oxidation cycle, which has been explained by the large changes in unit cell volume;[19] 3) the complete transformation of $H_{0.25}MoO_3$ (lower limit of phase I) back to MoO_3 is not possible at equilibrium potentials due to an electron transport threshold. MoO_3 is a wide gap semiconductor (insulator), which at first sight is in conflict with the requirement of electronic conductivity for host lattices as stated above. However, upon reduction the first phase $H_{0.2}MoO_3$ formed at the triphase boundary electronic lead/electrolyte/MoO_3 is a metal, and is thus able to transport electrons. On the way back (anodic oxidation) in the two phase region from $H_{0.2}MoO_3$ to MoO_3, the latter forms a thin layer (metal/insulator transition) blocking the electron transport across the phase boundary. Similar characteristic kinetic phenomena are frequently found in electron/ion transfer reactions of other systems.[2,19]

A further characteristic is the observation of anisotropy effects in low-dimensional host lattices, not only with respect to electronic transport but also regarding the dynamics of the mobile guest species. It is surprising to find that this applies also to proton mobility, since protons are the smallest mobile ions, and could be expected to show isotropic motion independent of the host lattice dimensionality. An interesting example that has been thoroughly studied by solid state ^{1}H-NMR is provided by the layered H_xMoO_3 phases. At low hydrogen concentration ($x \approx 0.25$) hydrogen shows quasi-one-dimensional mobility between the zigzag chains of edge sharing MoO_6 octahedra that constitute the MoO_3 layer units. At intermediate hydrogen concentration ($x \approx 1$) a quasi-two-dimensional motion in the *a/c* layer planes is observed, while at high concentration ($x = 2$) three-dimensional mobility appears. The motional dimensionality of hydrogen can thus be controlled via the redox state and the corresponding stoichiometry.[20]

Early use was made of hydrogen bronzes for galvanic cells, although the reaction mechanisms were established only later. The nickel/hydroxide electrode in the Ni/Cd and Ni/Fe battery is basically an electron/proton transfer process [equation (8)]. The accessible range is $0.2 \leqslant x \leqslant 1.4$;

$$H_2NiO_2 \rightleftharpoons H_{2-x}NiO_2 + xe^- + xH^+ \qquad (8)$$

the lower limit corresponding to $Ni(OH)_2$ cannot be reached in electrochemical systems for kinetic reasons, since nickel(II) hydroxide is an insulator (electron transport threshold, see above). Equation (8) represents a simplified version of the overall process; investigations on the solid state chemistry of layered hydroxide oxides have shown that the real process is far more complex.[4,21]

The first discharge region of the MnO_2 electrode in the Leclanché cell [equation (9)] is reversible and corresponds

$$MnO_2 + xH^+ + xe^- \rightleftharpoons H_xMnO_2 \qquad (9)$$

to the insertion of protons into the vacant lattice channels of the rutile structure of MnO_2; however, further reduction leads to irreversible lattice transformations. Replacement of H^+ by Li^+ and the use of aprotic electrolytes have led to the development of secondary batteries (reversible cells) of the Leclanché type with higher energy density.

Topotactic electron/proton transfer reactions have also been found to occur in molecular solids, e.g. planar transition metal complexes with columnar structures and cluster halides.[22] In the latter phases long-range electron/proton transfer across insulator barriers occurs, as in certain organized biological cell components; the mechanism of this process is not yet understood.

5. Stoichiometry: Electronic and Geometrical Thresholds

An important point in the control of stoichiometry is the question of the upper intercalation limit, which can be governed either by electronic (band structure) or by steric factors. We will briefly demonstrate these aspects by using the molybdenum cluster chalcogenide Mo_6S_8 as an example.[23,24] The structure of Mo_6S_8 can be described as consisting of sulfur cubes surrounding Mo_6 octahedra. These units are interconnected via Mo-S bonding to a framework which contains "channels" of vacant sites along the rhombohedral axes. The simple valence electron counting scheme shows that the Mo_6 clusters have a deficit of four electrons in terms of metal-metal two-electron cluster bonds. This is in agreement with band structure calculations. We can now predict easily that the maximum number of electrons that can be taken up into the valence band is four [equation (10)], corresponding to an intercalation limit of four monovalent or two bivalent guest ions. This prediction on electronic grounds has turned out to be valid for all cations with small ionic radii.

$$Mo_6S_8 + 4e^- \rightleftharpoons [Mo_6S_8]^{4-} \qquad (10)$$

A steric threshold appears for guest ion radii >0.9 Å: $Cd_1Mo_6S_8$ can be obtained easily, while $Cd_2Mo_6S_8$ does not form, although the system is not saturated in electronic terms. Physical properties change significantly with stoichiometry as is shown, e.g., by the electronic transport characteristics of the lithium system:

Mo_6S_8	$Li_1Mo_6S_8$	$Li_3Mo_6S_8$	$Li_4Mo_6S_8$
metal	superconductor	metal	semiconductor

After a transfer of $4e^-$ the band is filled and the compound becomes a semiconductor.

In spite of this simple and consistent scheme, detailed investigations revealed that these transitions can be more complex. ^{7}Li-NMR studies have recently shown that in the lithium system $Li_xMo_6S_8$ at $x = 3$ partial charge transfer is observed, which has been explained by the formation of Li_3^{2+} guest ion clusters with one-electron three-center bonding; after a transfer of four electrons and transition to the semiconductor state, however, normal NMR shift values and quantitative charge transfer are found.[24]

6. Control of Isothermal Magnetic Phase Transitions: Critical Valence States

An interesting specific example of the modification of electronic properties of solids by electron/ion transfer reactions is the possibility of isothermal control of magnetic ordering states which has been observed recently for copper chromium chalcogen spinels $CuCr_2X_4$ (X = S, Se, Te).[25] The structure of these phases can be described schematically by a cubic close-packed anion lattice with Cr ions on octahedral lattice sites and Cu ions on tetrahedral sites. In terms of electron transport properties these phases are metals; the copper ions are mobile at ambient temperature. These spinels are able to intercalate additional copper ions according to equation (11). As shown in Figure 4, this reaction corresponds, e.g. for the selenide, to a one phase region with $x_{max} = 1$ (i.e. $Cu_2Cr_2Se_4$) and a contin-

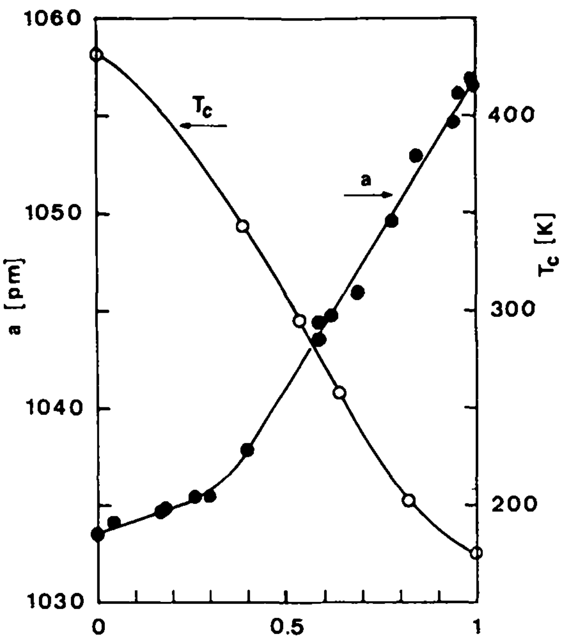

Fig. 4. $Cu_{1+x}Cr_2Se_4$: change of the cubic lattice parameter a (300 K) and Curie temperature T_c with the stoichiometry [25].

uous change in lattice parameters. $CuCr_2Se_4$ is a ferromagnetic metal at 300 K with a rather high Curie temperature T_C. Figure 4 shows the change in T_C with increasing copper content. Reaction (11) corresponds to the 300 K isotherm in Figure 4: it can be seen that at a critical value x_c an isothermal phase transition [equation (12)] from the spin-ordered magnetic state to the disordered system is observed. The reaction is reversible and represents the first example of the control of isothermal magnetic order-disorder transitions by chemical reactions at ambient temperature. In principle, this process can be used to design chemically operated magnetic switches or magnetic sensor systems indicating the redox state of a chemical reaction.

$$\underset{\substack{x=0\\ \text{ferromagnetic}\\ \text{metal}}}{CuCr_2Se_4} + xCu^+ + xe^- \rightleftharpoons \underset{\substack{x=1\\ \text{paramagnetic}\\ \text{semiconductor}}}{Cu_{1+x}Cr_2Se_4} \qquad (11)$$

$$\text{ferromagnetic ordered state} \underset{x<x_c}{\overset{x>x_c}{\rightleftharpoons}} \text{paramagnetic state} \qquad (12)$$

In order to discuss the correlation between redox state, magnetic behavior and chemical bonding, we come back to equation (6) which concerns the reaction of the spinel $CuTi_2S_4$[7] that is obviously at variance with the chromium system. The titanium spinel can be oxidized to c-TiS_2, which is easy to understand in terms of the ionic formula [equation (13)].

$$Cu^+[Ti^{3+}Ti^{4+}(S^{2-})_4]^- \rightleftharpoons [(Ti^{4+})_2(S^{2-})_4] + Cu^+ + e^- \qquad (13)$$

Ti^{3+} is oxidized to Ti^{4+}. The formula is based on the well established fact that Cu ions in chalcogenides are invariably monovalent;[26] the metallic properties of $CuTi_2S_4$ are explained by cation mixed valence states with identical lattice positions. The equivalent reaction of the chromium spinels which should lead to cubic CrS_2 [equation (14)] is

$$Cu^+[Cr^{3+}Cr^{4+}(S^{2-})_4]^- \rightleftharpoons [(Cr^{4+})_2(S^{2-})_4] + Cu^+ + e^- \qquad (14)$$

not accessible, however. Instead, the chromium spinels may be reduced [equation (11)] with the uptake of one additional electron. Earlier polarized neutron diffraction studies[27] and recent XPS/UPS investigations[28] have now provided experimental evidence for the presence of holes in the anion p band of the copper chromium spinels $CuCr_2X_4$ and for the exclusive presence of chromium(III) in the reduced and oxidized state. The correct description of $CuCr_2Se_4$ by formal valence states is thus given by

$$Cu^+[(Cr^{3+})_2(Se^{2-})_3(Se^{\cdot-})]^-$$

This description explains the metallic properties of $CuCr_2Se_4$ by anion mixed valence. The ferromagnetic properties have been discussed in the original bonding model given above [equation (14)][29] in terms of super-exchange via excited anion states; however, this cannot easily explain the high Curie temperature. The revised model explains the strong spin coupling by super-exchange $Cr^{3+}/Se^{\cdot-}/Cr^{3+}$ via a high concentration of delocalized ground state anion holes in the valence band. The reaction mechanisms of the titanium and chromium spinels are thus quite different in terms of bonding changes. The oxidation of $CuTi_2S_4$ to c-TiS_2 is related to a conventional oxidation state change of the transition metal ions [equation (15)].

$$Ti^{3+}/Ti^{4+} \rightleftharpoons Ti^{4+}/Ti^{4+} + e^- \qquad (15)$$

The reduction of the chromium spinels is correlated with a new electron transfer mechanism via host lattice anion redox reactions equivalent to the annihilation and generation of anion p band holes:[30]

$$\begin{array}{lcl} & Cu^+[(Cr^{3+})_2(X^{2-})_3(X^{\cdot-})_1]^- & \text{anion mixed valence;} \\ & +xe^- + xCu^+ & \text{ferromagnetic metal} \\ \text{hole generation process} & \uparrow\downarrow & \text{hole annihilation process} \\ & (Cu^+)_2[(Cr^{3+})_2(X^{2-})_4]^{2-} & \text{integral valence;} \\ & & \text{paramagnetic semiconductor} \end{array}$$

The behavior of the chromium spinel phases has been rationalized recently in terms of a "critical valence state" (CVS) model.[28,30] The latter is defined for an internal redox couple M^{n+}/X^{m-} in a solid as the critical redox state, where the electron affinities E_A of the metal ion M^{n+} and the anion X^{m-} become equivalent

$$E_A(M^{n+}) \triangleq E_A(X^{m-})$$

The limiting states are given by equation (16); for low valent M^{n+} the left side is favored, with the upper band being

$$M^{n+}/X^{m-} \longleftrightarrow CVS \longleftrightarrow M^{(n-1)+}/X^{(m-1)-} \qquad (16)$$

dominated by cation states, while the anion retains a closed valence shell. For high-valent M^{n+} the metal ion becomes reduced to a lower valency by electron transfer from X^{m-} (right side). The upper band is now dominated by anion states with p band holes. In chemical terms the anion loses its closed valence shell and becomes a "radical". As in molecular chemistry, where radical ions are known to tend to dimerize so as to for complete the valence shell, anion holes are frequently "dimerized" also in the solid state. Well-known examples are pyrites MS_2 with S_2^{2-} ions. In some cases, however, delocalized hole systems with metallic properties occur, e.g. $CuS = (Cu^+)_3(S_2^{2-})S^{\cdot -}$, where localized hole dimers S_2^{2-} coexist with delocalized $S^{\cdot -}$ in different lattice planes.

For the copper chromium chalcogen spinels the equilibrium is clearly above the critical valence state on the right side of equation (17). The fundamental difference in reactivity and reaction mechanism between the titanium spinel and the chromium spinels can thus be rationalized in terms of the model outlined above. An important aspect is that one can now make predictions of the reactivity of related phases.[30] To illustrate this we shall consider here only the case of a simple system. The pyrite FeS_2 is a semiconductor with a rock salt type lattice; Fe is located on the cation positions in a distorted octahedral environment, while the anisometric anions display statistical orientation so that the overall symmetry is cubic. In FeS_2 iron is above the critical valence state, i.e. $Fe^{2+}/S^{\cdot -}$. The anion holes are dimerized, resulting in $^{-}S{-}S^{-}$ units which explains the semiconducting properties. It should thus be possible to generate decocalized holes by electron/anion transfer, e.g. by intercalation of Li^+ ions according to equation (18) and to simultaneously achieve a semiconductor/metal transition.

$$Cr^{4+}/X^{2-} \rightleftharpoons Cr^{3+}/X^{\cdot -} \qquad (17)$$

$$Fe^{2+}S_2^{2-} + xLi^+ + xe^- \rightleftharpoons (Li^+)_x[Fe^{2+}(S_2^{2-})_{1-x}(S^{2-})_xS^{\cdot -}]^{x-} \qquad (18)$$

7. Control of the Transition Temperature of Defect Perovskite Superconductors

The concept of controlling physical properties of materials by intercalation reactions led at a relatively early stage to studies on the modification of the critical temperature T_c of superconducting phases.[1,31-33] It has been possible to verify this concept with a variety of systems; examples that have been studied in more detail are layered transition metal dichalcogenides (e.g. NbS_2, TaS_2, $NbSe_2$) and molybdenum cluster chalcogenides Mo_6X_8 (X = S, Se). The results show that T_c can be either increased or decreased depending upon the band structure of the host lattice. The accessible temperature range extends from ca. 0.8 K to ca. 12 K. The recent rapid development in the area of high temperature superconductors[34] has provided a series of new materials, whose properties are of major interest also in terms of the aspects under discussion here. We shall take the quaternary copper oxide $YBa_2Cu_3O_7$ as an example for the consideration of chemical reactivity, stoichiometry, reaction mechanism, and corresponding changes in superconducting behavior.

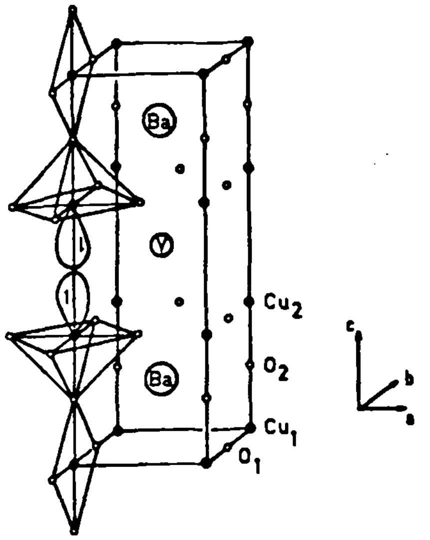

Fig. 5. Structure of the high temperature superconductor $YBa_2Cu_3O_7$ (schematic).

$YBa_2Cu_3O_7$ has a defect perovskite type structure[35] (Fig. 5) with copper ions in tetragonal pyramidal (sheets in the *a/b* planes) and in square planar (chains in *b/c* planes) coordination. The simple ionic formula may be described by

$$Y^{3+}(Ba^{2+})_2(Cu^{2+})_2(Cu^{3+})_1O_7$$

Obviously a part of the copper ions is present in the unusual valence state Cu^{III}. Interatomic distances based on refined structural data suggest that Cu^{III} is primarily located in chain positions along the *b* axis, while Cu^{II} occupies positions in the *a/b* plane.

Investigations on the synthesis conditions revealed a significant influence of oxygen partial pressure and annealing temperature on the superconducting properties of $YBa_2Cu_3O_7$. Similar observations were made earlier on several ternary perovskite systems which show temperature and $p(O_2)$ dependent changes in oxygen stoichiometry correlated with high defect concentrations.[36] Detailed studies have shown that $YBa_2Cu_3O_7$ may react according to equation (19) with a rather broad nonstoichiometric range $(0 \leqslant x \leqslant 0.9)$.[37-39] This reaction is clearly a topotactic process which is fully reversible in the range indicated. $YBa_2Cu_3O_7$ is a metal at ambient temperature, but transforms into an electronic/ionic conductor at a rather low temperature (ca. 300°C), where the oxygen ions become selectively mobile. Reaction (19) can similarly be performed in a galvanic cell; the oxygen intercalation and deintercalation thus correspond to an electron/anion transfer process [equation (20)]. The oxygen ions are selectively removed from the copper/oxygen chains in the basal planes of the unit cell.

$$YBa_2Cu_3O_7 \rightleftharpoons YBaCu_3O_{7-x} + x/2\,O_2 \qquad (19)$$

$$YBa_2Cu_3O_7 + 2x\mathrm{e}^- \rightleftharpoons YBa_2Cu_3O_{7-x} + xO^{2-} \qquad (20)$$

The reaction discussed in equation (20) can be used to control the superconducting transition temperature of $YBa_2Cu_3O_{7-x}$ as is shown in Figure 6, which illustrates the correlation between oxygen stoichiometry and T_c. By topotactic oxygen intercalation/deintercalation the transition temperature can be varied continuously between 93 K and 30 K. From $x=0$ to $x=0.5$ the lattice parameters a and b vary simultaneously with the oxygen loss such that a transition from orthorhombic to tetragonal is attained at $x=0.5$. This structural transformation is accompanied by an electronic metal/semiconductor transition: at $y=0.5$ the oxide displays semiconductor properties. In terms of chemical bonding this effect can be explained by the correlated valency changes [equation (21)]. For $x=0$ the metallic properties are related to the mixed valence system Cu^{2+}/Cu^{3+}, while at $x=0.5$ all Cu ions are bivalent, which results in semiconductor behavior.

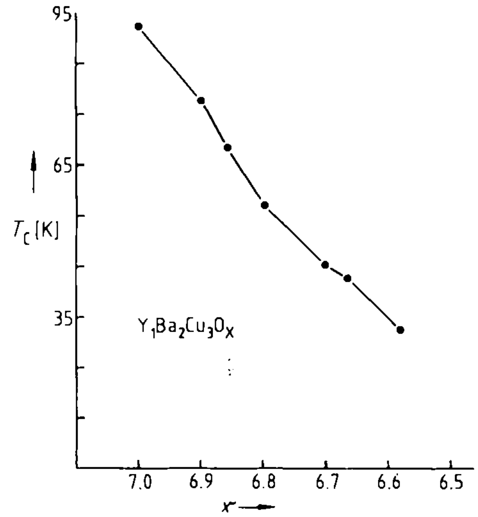

Fig. 6. Change of the superconducting transition temperature T_c of $YBa_2Cu_3O_x$ with the stoichiometry [39].

$$Y^{3+}(Ba^{2+})_2(Cu^{2+})_2(Cu^{3+})O_7 \rightleftharpoons Y^{3+}(Ba^{2+})_2(Cu^{2+})_3O_{6.5} + 1/4\,O_2 \qquad (21)$$

mixed valence metal superconductor (93 K)	integral valence semiconductor

One most interesting aspect of the $YBa_2Cu_3O_{7-x}$ system is the observation that the oxygen anions become mobile at an exceptionally low temperature, which is quite unusual for a ceramic oxide with high lattice energy. In order to explain this behavior a model has been proposed recently that suggests a critical valence state situation:[30,38,39]

$$Cu^{3+}/O^{2-} \rightleftharpoons Cu^{2+}/O^{\bullet -} \qquad (22)$$

i.e. the simultaneous presence of Cu^{3+} as well as $O^{\bullet -}$ (anion holes). This implies that the electron affinities of Cu^{3+} and O^{2-} are approximately equivalent; the upper band level must exhibit considerable anionic character. This model can explain the high oxygen mobility in terms of the lower activation energy of site change for a monovalent anion (Fig. 7), and the reduced effective size of $O^{\bullet -}$. As in the case of the chromium chalcogen spinels (see Section 6) the appearance of anion 2p band holes may result in strong super-exchange coupling between the Cu ions close to the Y planes inducing antiferromagnetic order (Fig. 5), which in turn would explain the absence of local magnetic moments in $YBa_2Cu_3O_7$.

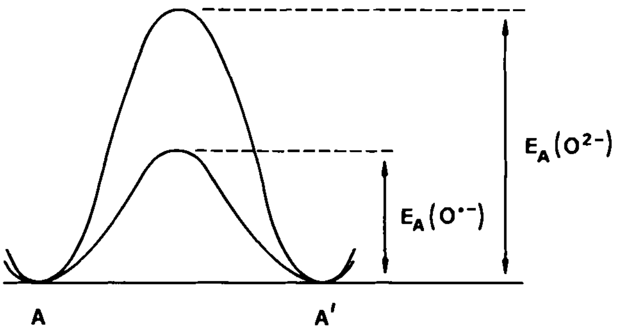

Fig. 7. Scheme of difference in activation energy E_A for site change between regular lattice sites A,A' for bivalent and monovalent oxygen anions.

With respect to the bonding situation, several other models have recently been proposed, some of them rejecting the presence of Cu^{III};[40–42] a decision in this controversial situation must await further experimental evidence.

8. Conclusions

The few examples presented in the foregoing focussed on the demonstration of the attractive potential for controlling major functional properties of solid materials by reversible chemical reactions at low temperature under isothermal conditions. One obviously critical point with respect to these systems is the level of understanding of the correlation between chemical reactivity, geometrical structure and chemical bonding, which in turn is a prerequisite for undertaking a systematic search for new systems. As shown in the preceding sections, even seemingly simple reactions may turn out to be rather complex at various levels of description. At the same time there is an evident trend in advanced materials—when specific requirements have to be met—towards an increasing degree of complexity in terms of stoichiometry. An illustrative example is the development of superconductor materials, where high transition temperatures are one particular objective for application purposes. The first superconductors were elements with an upper T_c limit of ca. 10 K under normal pressure. The investigation of binary and ternary alloys increased T_c to as high as 23 K. Ternary compound superconductors attained ca. 40 K, and only polynary phases containing four or more different elements were found to yield transition temperatures above the boiling point of liquid nitrogen. Obviously a large number of different atomic species is required for optimal "tuning" of these phases with respect to the property desired.

It is hard to see at present how materials science, as defined in the introductory paragraph of this article, can keep pace with the progress made via the predominantly empirical traditional approach. It is apparent that both lines will coexist in the near future; what we can expect from modern materials science is the development of firm qualitative guide lines indicating more economic routes to the tailoring of solids with defined functional properties.

One additional note should be made concerning bonding concepts in inorganic solid state chemistry. In the last decade major trends in studies on metal/non-metal systems M_nX_m have been the concentration on compounds with high n/m ratio, i.e. cluster phases with metal-metal bonding, and on compounds with low n/m ratio exhibiting anion homonuclear bonding. The example of the critical valence state discussed above demonstrates that, also in the intermediate n/m range of "classical" compounds, interesting bonding situations may arise which may be correlated with specific solid state properties.

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