Account/Revue

Strongly correlated electron systems: From chemistry to physics

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ABSTRACT

Transition metal oxides represent a vast field for the study of strongly correlated electron systems, at the interface of crystal chemistry and physics. We describe herein the factors which govern the magnetic and transport properties of several families of oxides, which are promising functional materials: high T_C superconductive cuprates, colossal magnetoresistance (CMR) manganites, thermoelectric cobaltites and multiferroic perovskites.

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Numerous studies have been carried out these last two decades on strongly correlated electron systems due to their great ability to exhibit magnetic and transport properties susceptible of various applications as functional materials. In this respect, transition metal oxides present a great potential, due to the mixed valence, and to the various coordinations of the transition elements. These characteristics are at the origin either of the delocalisation of charge carriers or of charge ordering, and of the great flexibility of the structures, of numerous transition metal oxides. Among these materials, the high T_C superconductivity cuprates, the colossal magnetoresistance (CMR) manganites, the high thermoelectric power cobaltites and the very recently explored multiferroic oxides, have been extensively studied for these promising applications.

The high T_C superconducting cuprates have been the object of thousands of publications since the discovery of their properties in 1986. At the present time, three of these oxides, $YBa_2Cu_3O_7$, called "YBCO", $Bi_2Sr_2CaCu_2O_7$ and $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10}$, called Bi2212 and Bi2223 respectively, are considered for applications, due to their zero resistance and magnetic levitation properties above 77 K,

allowing liquid nitrogen to be used as refrigerant for electrotechnical applications such as distribution and connecting cables, transformers, magnets, generators, magnetic bearings and ship propulsion systems, but also in electronic devices, such as mobile phone filters, SQUID detectors in medical imaging, fault current limiters. In fact, these oxides belong to various systems: Y-Ba-Cu-O, La-Ba-Ca-Cu-O, Bi-Sr-Ca-Cu-O, Tl-Ba-Ca-Cu-O and Hg-Ba-Ca-Cu-O. One important condition for the appearance of superconductivity in these oxides deals with the fact that they exhibit the mixed valence Cu^{2+}/Cu^{3+}. This characteristic makes that the positive carriers (holes) provided by Cu^{3+} species, can be delocalized over the "copper-oxygen" framework leading to a semi-metallic or metallic type conductivity. However, this property is not sufficient to induce superconductivity, a second condition must be fulfilled, which deals with the bidimensionality of the structure. In fact, the structure of superconductive cuprates should consist of layers of "CuO_4" square planar units sharing corners as schematized in Fig. 1. Such $[CuO_2]_\infty$ layers are superconductive, i.e. contain the delocalized holes and are separated from each other by hole reservoir layers (of Bi, Pb, Sr, La, Y oxides). It is this anisotropy which hinders strong magnetic interactions between the copper-oxygen layers and is necessary for the
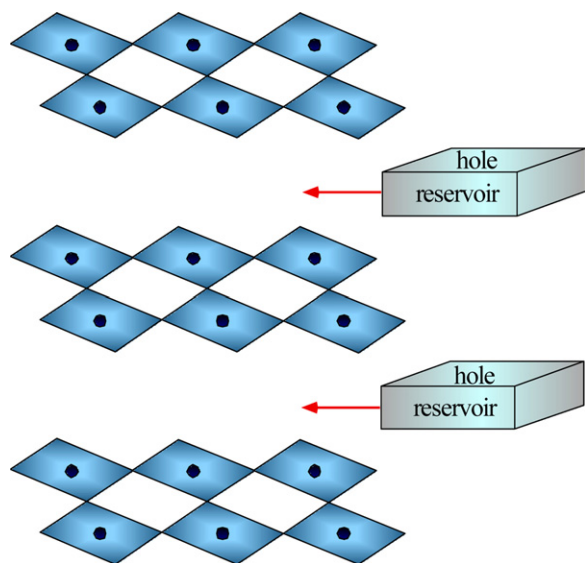
Fig. 1. Schematic representation of the $[CuO_2]_\alpha$ layers in superconductive cuprates built up of corner-shared CuO_4 square planar groups. Between these layers, rock salt layers (SrO, BaO, TlO, BiO...) play the role of hole reservoirs.

appearance of superconductivity at high temperature in oxides. This bidimensionality of the structure is strongly favoured in cuprates, owing to the Jahn Teller effect of copper which allows an elongation of the Cu–O bonds corresponding to the d_z^2 orbitals of copper. As a result, copper can accommodate various coordinations, as illustrated for the bismuth cuprates superconductors (Fig. 2), which consist of quadruple hole reservoir layers "$Bi_2Sr_2O_4$" stacked with superconductive copper oxygen layers, built up either of elongated CuO_6 octahedra like in $Bi_2Sr_2CuO_6$, or CuO_5 pyramids like in $Bi_2Sr_2CaCu_2O_8$, or of CuO_5 pyramids and CuO_4 square planar groups like in $Bi_2Sr_2Cu_3O_{10}$. In this way, the critical temperature T_C increases with the number of coupled copper layers from 22 K for $Bi_2Sr_2Cu_2O_6$ ($n = 1$) to 110 K for $Bi_2Sr_2Ca_2Cu_3O_{10}$ ($n = 3$). Thus, the key factors which govern the superconducting properties of the cuprates are mainly the mixed valence Cu^{2+}/Cu^{3+} and the associated hole carrier density which needs to be optimized, the Jahn-Teller effect of copper and the bidimensionality of the structure. Importantly, these superconductors exhibit a short coherence length, which makes that their utilisation as polycrystalline materials is limited by grain boundary effect, so that numerous investigations have been carried out for the texturation of these materials in order to enhance their performances in the form of ribbons or films or wires with a preferred orientation.

The CMR manganites have also been the subject of numerous investigations since 1995, due to their ability to exhibit a decrease of their resistivity by several orders of magnitude by applying a magnetic field. In fact, these manganese oxides belong to the perovskite family with the generic formulation $Ln_{1-x}A_xMnO_3$, where Ln is a lanthanide element and A is a divalent cations (Ca, Sr, Ba). The

introduction of a bivalent cation, A = Ca, Sr, Ba, into the cages of the perovskite structure of $LaMnO_3$ (Fig. 3) induces the mixed valence Mn^{3+}/Mn^{4+}, according to the formula $Ln_{1-x}A^{II}_xMn^{III}_{1-x}Mn^{IV}_xO_3$. Like for the cuprates, the existence of this mixed valence of manganese is absolutely crucial for the appearance of CMR properties. Indeed, the appearance of magnetoresistance in such oxides corresponds to the transition from an insulating or semi-conducting state to a semi-metallic or metallic state by applying a magnetic field. This is illustrated, as an example for the oxide $Pr_{0.7}Ca_{0.25}Sr_{0.05}MnO_3$ (Fig. 3), whose resistivity is decreased by 15 orders of magnitude at 30 K under a magnetic field of 5 T. Thus, the possibility of existence of a semi-metallic state requires, here again a delocalisation of the holes provided by the Mn^{4+} species over the $[MnO_3]_\infty$ framework of the perovskite. The mechanism of the CMR effect can easily be understood by considering the orthorhombic perovskite $Pr_{0.5}Ca_{0.5}MnO_3$ (Fig. 4), which in the absence of magnetic field exhibits charge and orbital ordering, i.e. rows of Mn^{3+} species alternating with rows of Mn^{4+} species. The former exhibits a distorted perovskite structure with an elongation of the Mn^{3+} octahedra along the direction of the d_z^2 orbitals, whereas the Mn^{4+} octahedra remain practically regular. As a consequence, the lack of orbital overlapping along the Mn^{3+}–O–Mn^{4+} bonds makes that this oxide is an antiferromagnetic insulator. By applying a high magnetic field (> 25 T), the distortion of the structure tends to disappear leading to a practically cubic perovskite (Fig. 4). It results in a complete overlapping of the Mn-O-Mn orbitals which are oriented at $180°$, so that charge ordering disappears, through double exchange phenomena. It is this double exchange which is responsible for the appearance of metallic conductivity and ferromagnetism. In other words, the CMR effect corresponds to the transition from an antiferromagnetic insulating (AFMI) to a ferromagnetic metallic (FM) state. Starting from this point, it can be seen that the magnetic field value of 25 T is much too high to be used for CMR application. In order to decrease the value of the applied magnetic field, we have to decrease the value of the applied magnetic field, i.e. to decrease dramatically the Jahn-Teller effect of Mn^{3+}, so that the AFMI phase becomes metastable, and concomitantly the charge-orbital ordering on the manganese sites would be destroyed. For this purpose, the doping of the Mn^{3+} sites with a non Jahn-Teller cation is of great interest since it destroys locally the elongation of the octahedra and favours a $180°$ overlapping of the d orbitals (Fig. 5a). Such a doping of the Mn^{3+} sites by trivalent cations (1 to 5%) such as Ga^{3+}, Al^{3+} has indeed allowed to decrease the H value to less than 4 T. Importantly, the doping with a magnetic cation such as Cr^{3+} is still more efficient, since additionally it expands the ferromagnetic state through an antiferromagnetic coupling of Cr^{3+} with surrounding Mn species (Fig. 6). Thus, in such systems a new physics appears, which deals with magnetic and electronic phase separation, as illustrated schematically on Fig. 7. Around each doping cation (Ga^{3+}, Cr^{3+}) FM clusters are formed within the AFMI matrix (Fig. 7a). The crystal symmetry of these FM islands is higher than that of the AFMI matrix, developing strains at the interfaces. Then the FM regions grow, by increasing the magnetic field (Fig. 7b),
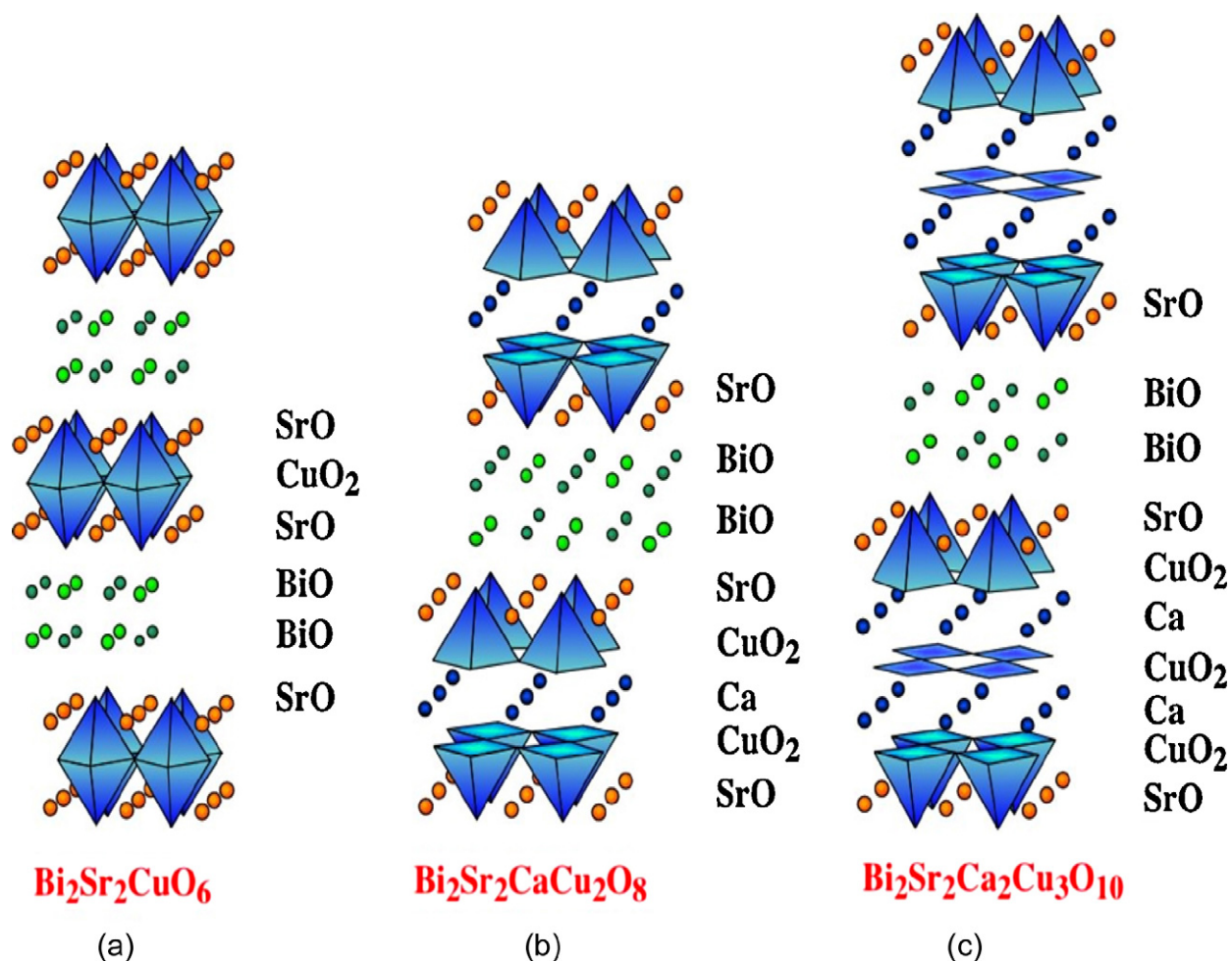
Fig. 2. Structures of the high T_C superconductive cuprates, where the Jahn-Teller effect of copper allows single octahedral copper layers (a) or double pyramidal copper layers (b) or triple pyramidal/square planar layers (c) to be formed.

leading to percolation so that the material becomes FM. This transformation which has been shown to be martensitic, requires a doping with only some percents of M^{3+} cations. Note that a similar effect can be obtained by doping the A sites of the perovskite structure with large divalent cations, such as Ba^{3+} or Sr^{2+}. This is illustrated on Fig. 5b which shows that for small cation like Ca^{2+}, the perovskite cage is distorted favouring the Jahn-Teller effect of Mn^{3+}, whereas introducing a larger cation like Ba^{2+} tends to make the cage more symmetric and favours the formation of more symmetric domains around Ba^{2+}, and consequently tends to destroy locally the Jahn-Teller effect of Mn^{3+}. Thus the mixed valence Mn^{3+}/Mn^{4+} and the Jahn-Teller of manganese are, similarly to cuprates, key factors which play a capital role in the CMR effect of manganese. However differently, there are several other parameters, namely charge-orbital ordering and nanoscale phase separation which must be taken into consideration to tune the CMR properties of these oxides. Though they appear as very promising materials for magnetic recording and storage, and as actuators and sensors, the performances of the CMR manganites remain still far from the

application, requiring a magnetic field of 500 mT to reach a magnetoresistance of ∼8% at room temperature, i.e. far from the giant magneto resistance thin films discovered by A. Fert, and already commercially available.

The growing needs in energy have incited to consider the wasted heat as a possible source for producing electricity, since a great part of energy is wasted in incinerators, factories, but also in cars and trucks. For instance, in a car only ∼25% of the gasoline is used for the mobility, whereas ∼40% is lost as heat at the exhaust pipe and ∼30% for cooling (Fig. 8). For this reason, thermoelectric oxides were recently revisited in view of discovering new materials susceptible to be used for the conversion of heat into electrical energy. Indeed, by coupling p-type and n-type semi-conductors, a thermogenerator can be set up based on the Seebeck effect and involving a temperature gradient between a hot and cold surface (Fig. 9). In order to be efficient, such thermoelectric oxides should exhibit a high thermoelectric power (S), a low resistivity (ρ) and a low thermal conductivity (k) according to the figure of merit $ZT = (S^2/\rho k) T$, where T is the temperature. Moreover, these thermoelectric materials should work at high
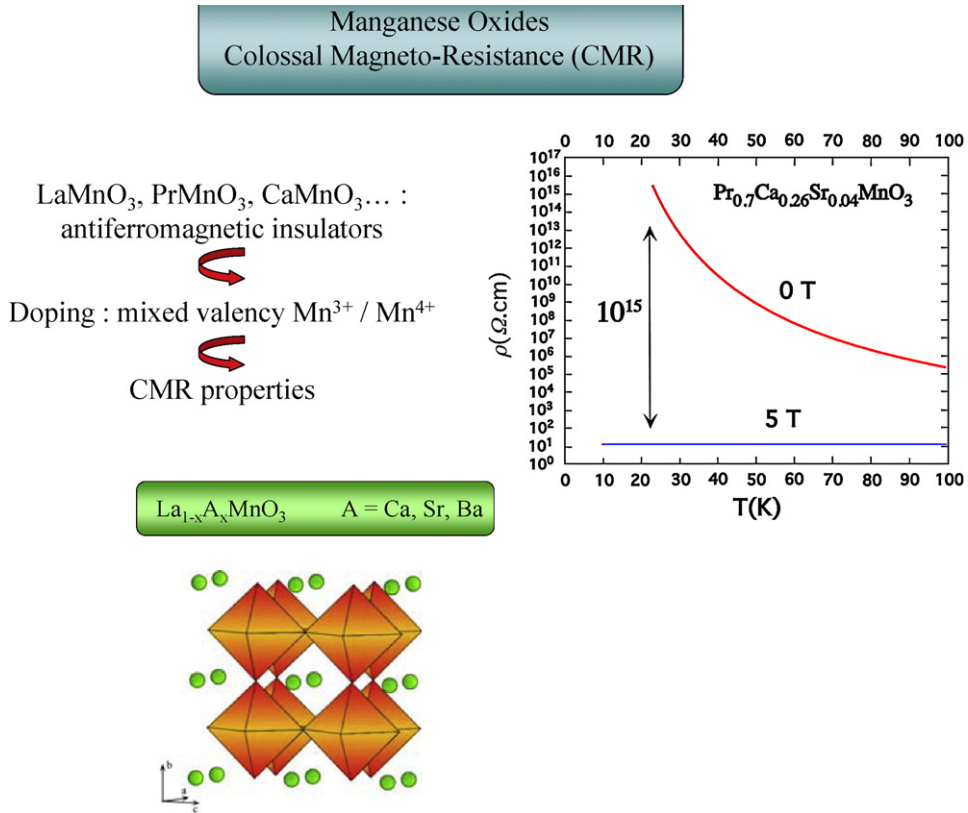
Fig. 3. Example of ρ(T) curves in zero magnetic field (0 T) and under 5 T for a perovskite $Pr_{0.7}Ca_{0.26}Sr_{0.04}$, showing a large magneto resistance effect at low temperature.
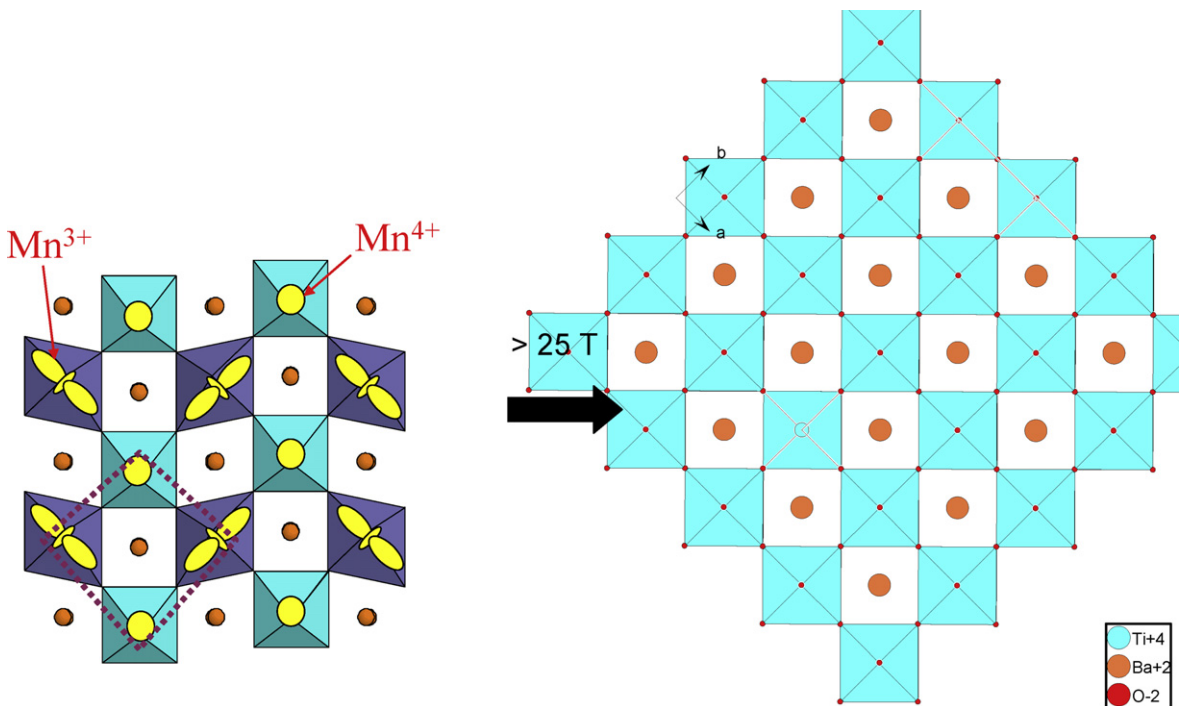

Fig. 4. $Pr_{0.5}Ca_{0.5}MnO_3$ perovskite: transition from the distorted orthorhombic structure, involving charge orbital ordering in the form of Mn^{3+} and Mn^{4+} rows to a cubic or pseudo cubic perovskite characterized by a delocalisation of the manganese charges, by applying a magnetic field larger than 25 T.
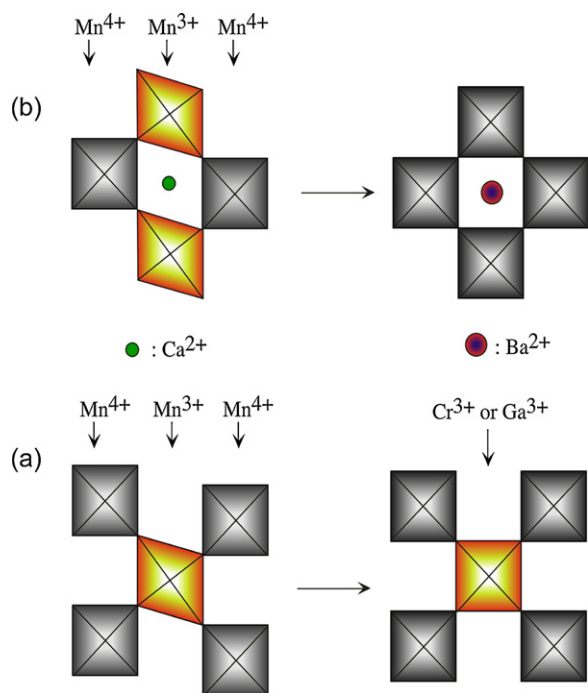
Fig. 5. Local destruction of the Jahn-Teller effect of Mn^{3+} by local doping: (a) of the Mn^{3+} sites by non Jahn-Teller cations (Ga^{3+}, Cr^{3+}), (b) of the Ca^{2+} sites by larger Ba^{2+} cations.

temperature, i.e. in the range 900–1200 K in oxidizing atmosphere. Very few compounds, except transition metal oxides, can be used in such conditions without encapsulation. In this respect, the cobaltite Na_xCoO_2 and the recently discovered misfit cobaltites of the systems Ca-Co-O, Tl-Sr-Co-O, Bi-Sr-Co-O and Pb-Sr-Co-O are quite remarkable and are promising p-type thermoelectric materials. Again, the existence of rather high conductivity of these oxides, requires the mixed valence Co^{3+}/Co^{4+} to be fulfilled, the positive carriers being provided by Co^{4+} species. The structure of these cobaltites consists of $[CoO_2]_\alpha$ layers built up of edge-sharing CoO_6 octahedra similar to the CdI_2-type structure, as exemplified for $Na_{0.5}CoO_2$ (Fig. 10) and for the misfit oxide $(Bi_{0.87}SrO_2)_2(CoO_2)_{1.82}$ (Fig. 11). The triangular geometry of such layers favours magnetic frustration and allows in this way better electronic conductivity. The Na^+ layers in $Na_{0.5}CoO_2$ (Fig. 10), as well as the quadruple oxygen deficient rock salt layers $[(Bi_{0.87}SrO_2)_2]_\alpha$ (Fig. 11) weaken the magnetic interactions between the layers, and may also contribute to the decrease of thermal conductivity due to a partial disordering of their cations and anions. For these reasons $Na_{0.5}CoO_2$, exhibits a rather high thermoelectric power, $S \cong 100\,\mu V/K$, much larger than for a normal metal, in spite of its rather low resistivity, $\rho \sim 2.10^{-4}\,\Omega cm$. The value of the thermoelectric power is even substantially increased for the bismuth based misfit cobaltites up to $\sim 140\,\mu V/K$ (Fig. 12), for rather low resistivity values, which are so far not completely optimized. Thus, these cobalt oxides appear as promising thermoelectric materials, showing that the mixed valence
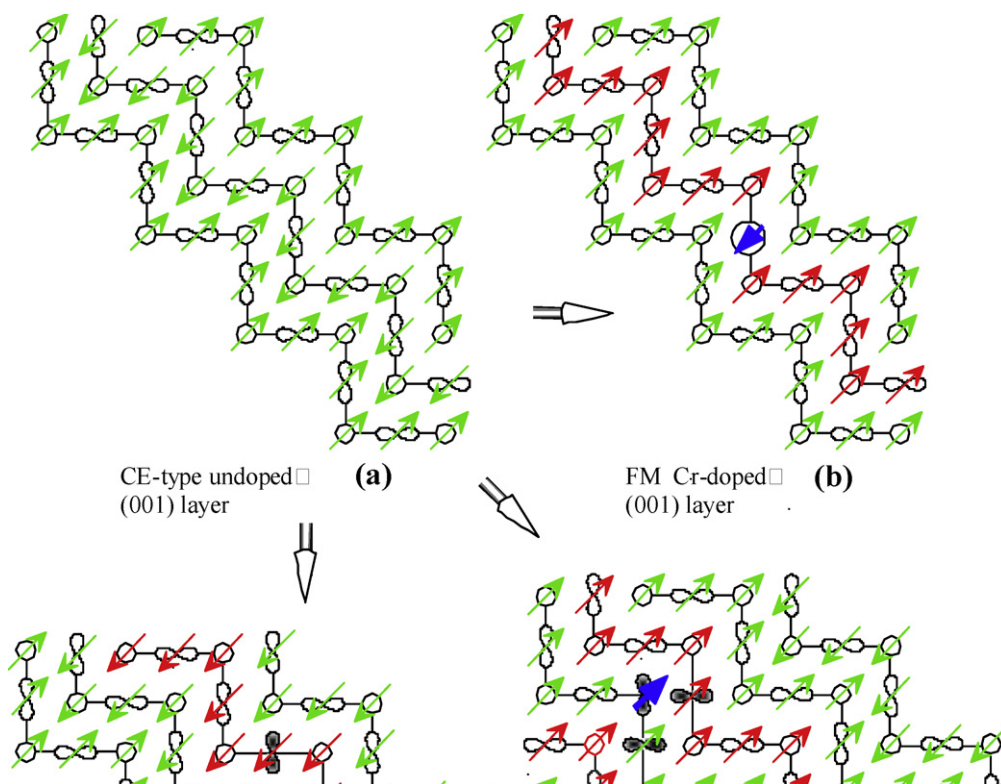

Fig. 6. Effect of doping Mn^{3+} sites with a magnetic cation such as Cr^{3+} (blue arrow). The latter induces a local antiferromagnetic coupling with its Mn neighbours, which induces spin reversal and creates locally ferromagnetic domains, even in the absence of applied magnetic field.
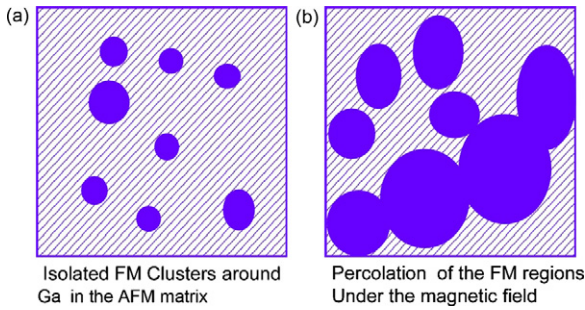
Fig. 7. Magnetic phase separation scenario showing: (a) ferromagnetic clusters (FM) formed around each non Jahn-Teller cation such as Ga within the antiferromagnetic (AFM) matrix (hatched) and, (b) expansion of these clusters under a magnetic field leading to percolation of the FM regions.
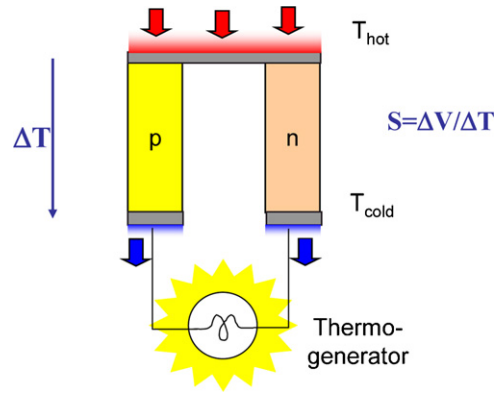

Fig. 9. Principle of Seebeck effect of a thermogenerator.

Co^{3+}/Co^{4+} and the bidimensionality of the structure are key factors for the realisation of p-type thermoelectrics working at high temperature. Nevertheless, the ZT figure of merit remains still rather low, i.e. close to 0.4–0.5 and will require further investigations of mixed valent oxides for applications.

Transition metal oxides are also involved in the investigations performed these last years for the research of new multiferroic materials. In such systems, ferroelectricity and magnetism (antiferromagnetism or ferromagnetism) coexist within the same matrix of a single phase. Importantly, this coexistence is not sufficient to create multiferroism, i.e. a coupling between ferroelectricity and ferromagnetism or antiferromagnetism, called magneto-electric coupling is necessary. Thus, in a multiferroic material, the spontaneous magnetization can be switched by an electrical field, and reciprocally an electrical
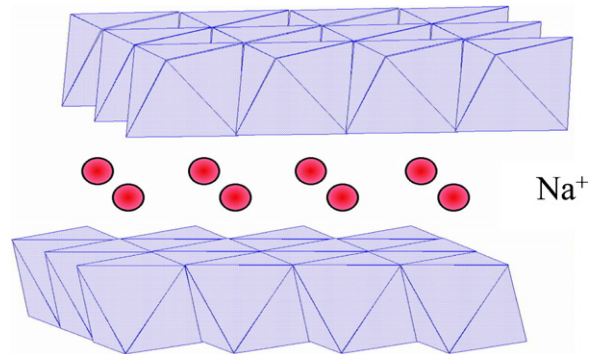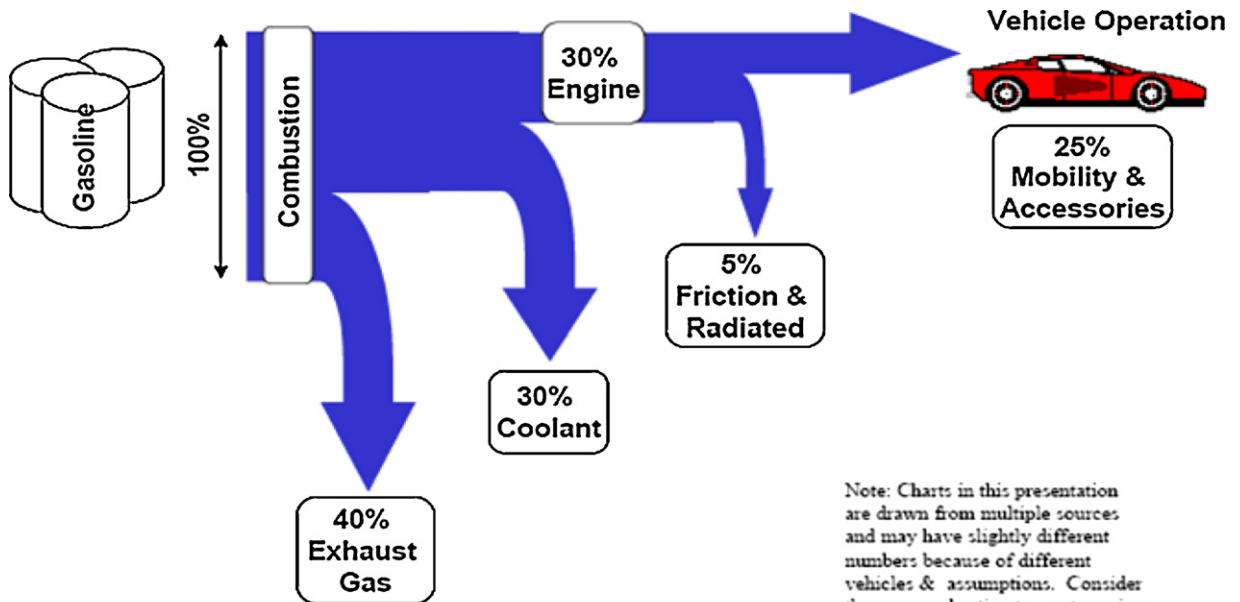

Fig. 10. Lamellar structure of $Na_{0.5}CoO_2$ built up $[CoO_2]_\infty$ triangular layers of edge-shared CoO_6 octahedra interleaved with Na^+ cations.

Note: Charts in this presentation are drawn from multiple sources and may have slightly different numbers because of different vehicles & assumptions. Consider them general estimates, not precise analysis.

Fig. 8. Typical energy path in gasoline fueled internal combustion engine vehicle.
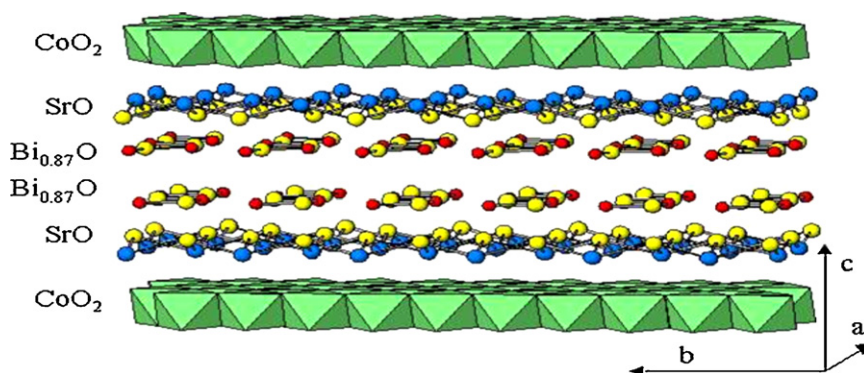
Fig. 11. Lamellar structure of the misfit cobaltite $(Bi_{0.87}SrO_2)_2$ $(CoO_2)_{1.82}$ built up of triangular $[CoO_2]_\alpha$ layers intergrown with $[Bi_{0.87}SrO_2]_2$ rock salt layers.

polarization can be switched by a magnetic field. It results that multiferroics have potential applications for memory storage, since they can exhibit additional degree of freedom in device design compared to pure magnetic materials involved in spintronics. Therefore, it should be possible to design multiple-state memory elements, by storing the data in both magnetic and electrical polarizations, and novel memory media should be considered by writing of ferroelectric data and reading of the magnetic field generated by association. Attention must be drawn on the fact that, for applications, it is absolutely necessary to control the magnetoelectric coupling by a magnetic field. Consequently, among all the multiferroics that can be discovered, only those which are ferromagnetic are of interest for such applications. The magnetoelectric properties of oxides, mainly perovskites, are known since more than 30 years, but most of the compounds are

antiferromagnetic (Table 1) if one excepts $BiMnO_3$, which can only be obtained under high pressure of several kbars. Several strategies have been used to discover new multiferroic oxides, considering to date mainly perovskites. The first strategy which consists in doping a ferroelectric matrix, such as $BaTiO_3$ at Ti sites by magnetic cations (such as Fe, Mn, Co) is, as expected inappropriate since it involves both magnetic dilution and ferroelectricity destruction. In the same way, the doping of a ferromagnetic matrix, such as (Ln, Sr)MnO_3 at Mn site with ad d^0 "ferroelectric" element (such as Ti, or Nb) is inefficient since it leads to a destruction of ferromagnetism. A second strategy was proposed which can be described as the macroscopic association of a ferrimagnetic spinel such as Fe_3O_4 (for instance in the form of rods) within a ferroelectric matrix such as $BaTiO_3$. An interesting effect described as multiferroism was observed, but these results were not confirmed subsequently. The third strategy which is realized in the case of thin films, is so far the most fruitful. It consists of the stacking of ultrathin layers of a ferroelectric material (e.g. $BaTiO_3$) with a ferromagnetic material (e.g. (La, Ca) MnO_3) as schematized in Fig. 13. In this way, numerous superlattices can be constructed, whose multiferroic properties can be tuned by varying the thickness of the layers, the thickness of the film and the distribution of the cations. These compounds offer a vast field of investigation, where the role of the interfaces between the layers, of the strains and of the charge distribution are still not completely understood. Finally, a fourth direction of research has been started recently, which is based on the association of one ferroelectric sublattice, with one ferromagnetic sublattice
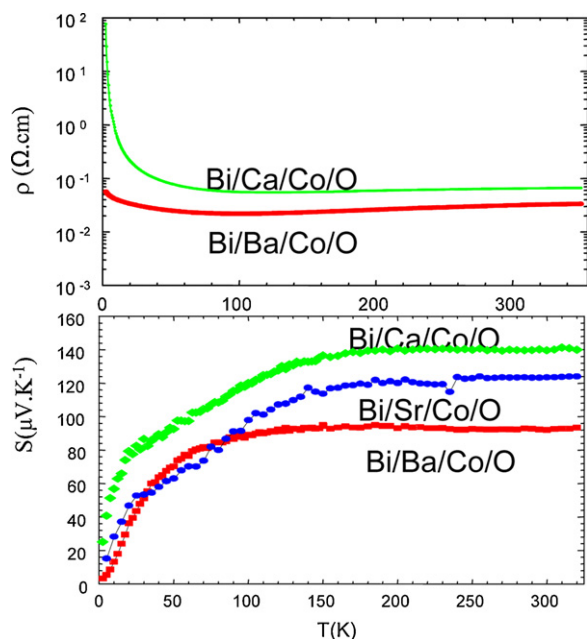

Fig. 12. Some S(T) and ρ(T) curves obtained for the misfit cobaltites of the Bi-A-Co-O systems with A = Ca, Sr, Ba.

Table 1
Some multiferroic oxides.

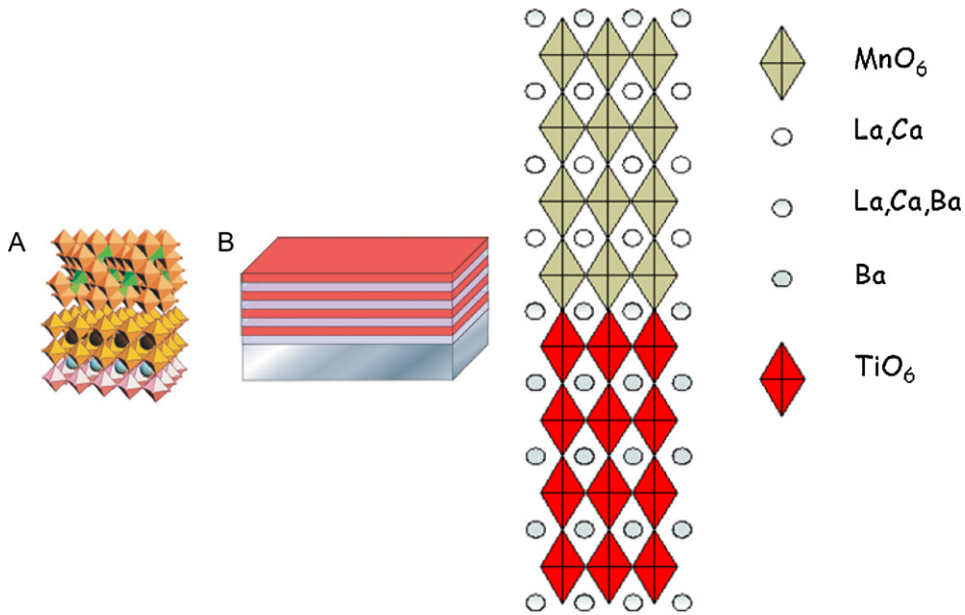|	Ferroelectric order	Magnetic order	T_c (K)	T_N (K) or T_c (K)
$Pb(Fe_{2/3}W_{1/3})O_3$	FE	AFM	178	363
$Pb(Fe_{1/2}Ta_{1/2})O_3$	FE	AFM	233	180
$Pb(Fe_{1/2}Nb_{1/2})O_3$	FE	AFM	387	143
$BiFeO_3$	FE	AFM	1123	650
$BiMnO_3$	FE	FM	773	103
$YMnO_3$	FE	AFM	913	80
$HoMnO_3$	FE	AFM/WFM	873	76

Fig. 13. Stacking of $BaTiO_3$ (BTO) and $(La, Ca)_1MnO_3$ (LCMO) ultrathin layers for the realisation of multiferroic superlattices in thin films.

within the same crystals structure. This strategy can be applied to the perovskite structure ABO_3, where the B sublattice which forms the BO_6 octahedra can be occupied by magnetic cations (e.g. Fe, Co, Mn) forming the ferromagnetic sublattice, whereas the A sublattice can be occupied by lone pair cations such as Bi^{3+} or Pb^{2+}, which may induce ferroelectricity. This is the case of the perovskite $La_{0.5}Bi_{0.5}Mn_{0.5}Fe_{0.5}O_3$, which exhibits both a hysteresis loop characteristic of ferromagnetism (Fig. 14) and a reversal of its electric polarization in an applied electric field of 3.5 kV/ cm (Fig. 15). These results suggest strongly the magneto-electric character of this oxide, through the interaction between magnetism and ferroelectricity has to date not been proved. Finally, it is worth to emphasize that there remains a vast field for the investigation of this phenomenon, but that to date no result has been obtained at sufficiently high temperature for applications.
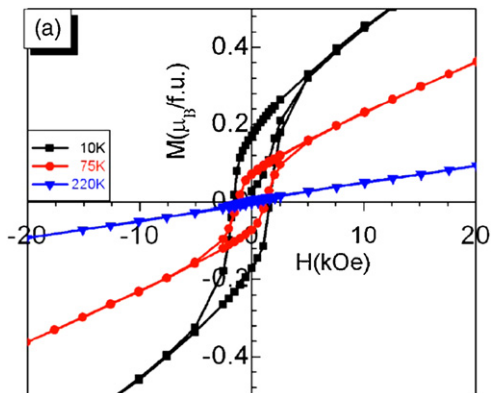
In conclusion, transition metal oxides represent an extraordinary rich domain for the exploration of strongly correlated electron systems. The study of their physics, especially magnetism and transport properties
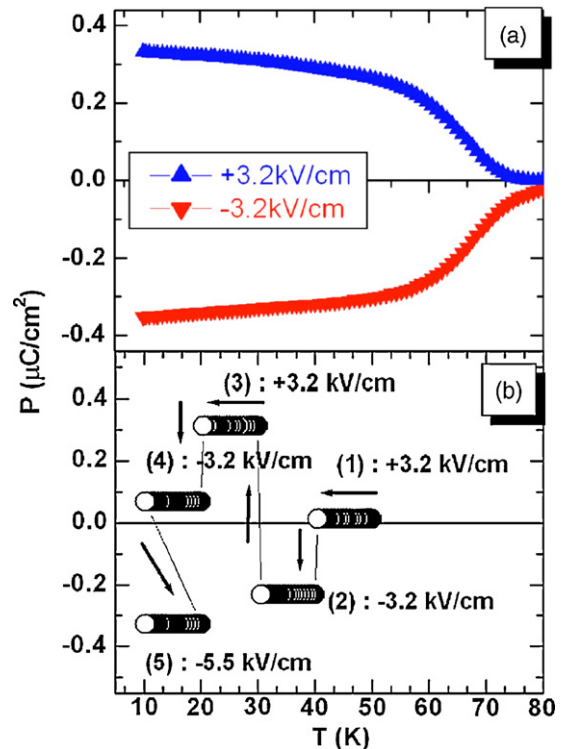

Fig. 14. Isothermal magnetization M(H) of $La_{0.5}Bi_{0.5}Mn_{0.5}Fe_{0.5}O_3$ perovskite registered at various temperatures.

Fig. 15. $La_{0.5}Bi_{0.5}Mn_{0.5}Fe_{0.5}O_3$: (a) temperature dependence of electric polarization in an applied field of 3.2 kV/cm. (b) Electric field-dependant reversal at low temperature on different applied field directions. The arrows and numbers indicate the way the measurement is made.

requires a simultaneous investigation of their crystal chemistry, bearing in mind that complex phenomena such as electronic or magnetic phase separation, or charge-orbital ordering may appear, and can be influenced by oxygen non stoichiometry, Jahn-Teller effect, order-disorder phenomena. Importantly such materials can be regarded as a source for various applications.

Further reading

B. Raveau, C. Michel, M. Hervieu, D. Groult, Crystal chemistry of high T_C superconducting copper oxides, Springer Verlag, 1991.

J.G. Bednorz, K.A. Müller (Eds.), Earlier and recent aspects of superconductivity, Springer Verlag, 1989.

C.N.R. Rao, B. Raveau (Eds.), Colossal magnetoresistance, charge ordering and related properties of manganese oxides, World Scientific, 1998.

Y. Tokura, Colossal magnetoresistive oxides, Gordon and Breach Science Publishers, New York, 1999.

A.C. Masset et al., Phys. Rev. B 62, 166 (2000).

A. Maignan et al., Crystal Eng. 5, 365 (2002).

I. Terasaki et al., Phys. Rev. B 56, R 12685 (1997); Nature 422, 53 (2003).

A. Maignan et al., Phys. Rev. Lett. 93, 026401 (2004).

N.A. Spaldin et al., Science 309, 391 (2009).

W. Prellier et al., J. Phys. Condens. Matter 17 R 803 (2005).

H. Zheng et al., Science 303, 661 (2004).

A. Kundu et al., Appl. Phys. Lett. 93, 052906 (2008).