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Virtues of marginally metallic oxides

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Transition-metal oxides at the metal–insulator boundary, especially those belonging to the perovskite family, exhibit fascinating phenomena such as insulator–metal transitions controlled by composition, high-temperature superconductivity and giant magnetoresistance (GMR). Interestingly, many of these marginally metallic oxides obey the established criteria for metallicity and have a finite density of states at the Fermi level. The perovskite manganates exhibiting GMR, on the other hand, are unusual in that they possess very high resistivities in the 'metallic' state and show no significant density of states at the Fermi level. Marginal metallicity in oxide systems is a problem of great complexity and contemporary interest and its understanding is of crucial significance to the diverse phenomena exhibited by these materials.

Properties of conventional metals such as gold and copper are familiar to most of us. One of these properties is the low electrical resistivity of metals. Some transition-metal compounds, in particular the oxides, exhibit low electrical resistivities just like conventional metals. The resistivity behaviour of the oxides such as ReO_3 and RuO_2 is indeed comparable to that of copper (Fig. 1). Metal oxides, however, exhibit a very wide range of electrical resistivity, anywhere between 10^{20} to 10^{-10} ohm cm, probably representing the widest range in any physical property known to date.[1] Besides the oxides with metallic resistivities and those with insulating properties, there are oxides which exhibit transitions from the insulating state to the metallic state. The insulator-to-metal (I–M) transition in V_2O_3 is well known for the unparalleled 10 or 100 million-fold jump in resistivity at 150 K; it is as if wood becomes copper at the transition temperature. The I–M transition in oxides can be brought about by changing the temperature, pressure or composition.[1,2] The perovskite oxides which exhibit compositionally controlled I–M transitions are especially noteworthy.[3] $La_{1-x}Sr_xCoO_3$ is an example of an oxide system which becomes metallic at a particular Sr concentration, the parent $LaCoO_3$ ($x = 0.0$) being an insulator at ordinary temperatures. $LaNi_{1-x}Mn_xO_3$ is an example of an oxide system which becomes insulating as x is increased, $LaNiO_3$ ($x = 0.0$) being metallic. I shall discuss briefly the nature of such metal oxides to point out how the I–M transition occurs across a state which can be considered as barely metallic and yet obey the known criteria for metallicity.†

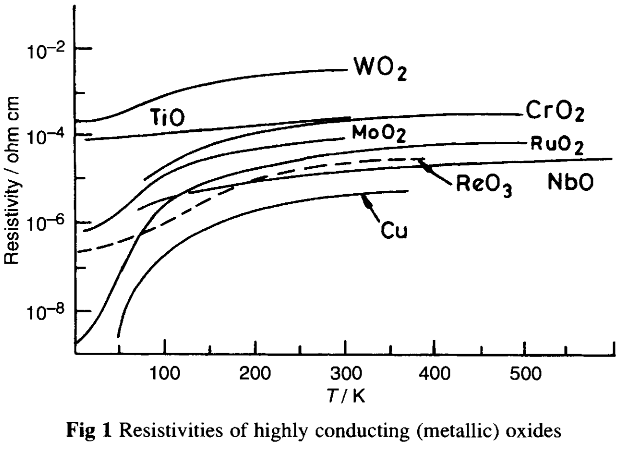

Fig 1 Resistivities of highly conducting (metallic) oxides

The cuprates which exhibit high-temperature superconductivity[4,5] are marginally metallic in the normal (non-superconducting) state and exhibit certain anomalous properties. What is even more interesting is that perovskite manganates of the general formula $La_{1-x}A_xMnO_3$ (Ln = rare earth, A = divalent ion such as Ca, Sr, Ba or Pb) exhibit high resistivities in what is considered to be the metallic state and do not seem to obey the criteria for metallicity. Marginal metallicity seems to be generally associated with all the oxides exhibiting giant magnetoresistance.[6,7] Thus, marginal metallicity of metal oxides is closely linked to three of the most important aspects of present-day solid-state science, namely insulator–metal transitions, superconductivity and giant magnetoresistance. In Fig. 2 we compare the temperature variation

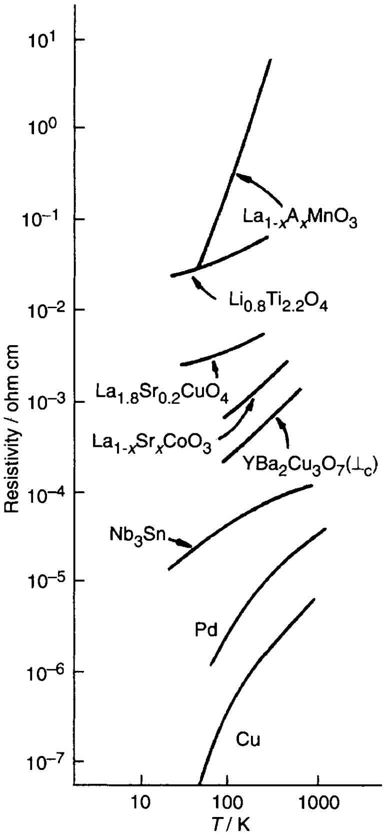

Fig 2 Resistivities of some of the oxides exhibiting marginal metallicity. Data on metallic Nb_3Sn, Pd and Cu are shown for comparison.

of resistivity of cuprates and other oxides to give an indication of the resistivity ranges encountered in marginally metallic oxides. In this article, I examine the nature of marginal metallicity encountered in transition-metal oxide systems after a brief discussion of the criteria for metallicity.

Operational criteria for metallicity

An important criterion for metallicity is the existence of the Fermi surface or the presence of a finite density of states at the Fermi level.† Two of the successful criteria for metallicity derived from theories of electron transport in solids are due to Mott.[8] Several years ago, Mott[9] pointed out how a material would be metallic at high charge carrier (electron) densities or small interparticle distances; in this state, the material would have a finite electrical conductivity at $T = 0$ K. On the other hand, at low carrier densities or large interparticle distances, the material would be an insulator with zero conductivity at 0 K. A discontinuous transition from the metallic state to the insulating state (Mott transition) can occur at a critical distance or a critical carrier concentration. At the transition, $n_c^{1/3}a_H \approx 0.25$, where n_c is the critical carrier concentration and a_H is the Bohr orbit radius of an isolated centre. A large number of systems, including doped semiconductors and metal–ammonia solutions, obey this relation.[2] The metallicity criterion as defined by this expression is essentially a manifestation of electron interactions or Coulomb correlation resulting in an energy gap at low densities.

Another criterion for metallicity arises from electron localization induced by disorder proposed by Anderson.[10] Electrons diffuse when the disorder is small, but at a critical disorder they do not diffuse (giving rise to zero conductivity). A transition from the metallic to the insulating state occurs as the disorder increases. Mott[11] proposed that there exists a minimum metallic conductivity, σ_{min}, or maximum metallic resistivity, ρ_{max}, for which the material may still be viewed as being metallic, prior to the localization of electrons due to disorder. The σ_{min} is given by $\rho^2/h\pi^3 l$, where l is the mean free path of the electrons. Mott's σ_{min} criterion assumes that the disorder-driven metal–insulator transition is discontinuous, but the scaling theory[12] predicts it to be continuous. It is, however, found that σ_{min} or ρ_{max} is a useful experimental criterion and represents the value of conductivity where the temperature coefficient of resistance changes sign from metal-like (+) to insulator-like (−) behaviour.[2,3] The value of Mott's ρ_{max} is around 1–10 mohm cm in oxide systems.

A useful way of describing and classifying transition-metal oxides in terms of their electronic properties is that due to Zaanen, Sawatzky and Allen (ZSA)[13] who consider the intra-atomic Coulomb strength, U, the ligand–metal charge-transfer energy, Δ, and the metal (d)–oxygen(p) hybridization strength, t_{pd}, to provide a electronic phase diagram (with U/t_{pd} plotted against Δ/t_{pd}). This diagram has been modified by Sarma to account for magnetic properties and doping effects. Such a modified phase diagram[14] is shown in Fig. 3. In this phase diagram, region D corresponds to d-band metals with $U < \Delta$, and $U < W$ where W is the d-band width and region C represents mixed-valent or p-type metals with $U > \Delta$. Mott insulators with $\Delta > U > W$ wherein U essentially determines the band gap are in region B. Charge-transfer insulators with $U > \Delta$ wherein the band gap is mainly controlled by Δ are in region A. Covalent insulators in region E are those where t_{pd} plays a crucial role; this region had not been identified in the ZSA phase diagram. Amongst the binary oxides, NiO is a charge-transfer insulator (region A) while ReO_3 is a d-band metal (D). Amongst the ternary oxides, $LaTiO_3$ is best described as a Mott insulator (B) while $LaNiO_3$ is a metal in the C region. Both $LaCoO_3$ and $LaMnO_3$ have mixed-valent ground states, but $LaCoO_3$ is closer to A than B, probably on the borderline, while $LaMnO_3$ is closer to B than A. La_2CuO_4, which is the parent cuprate for the numerous superconductor families, is described as a charge-transfer insulator with $\Delta \ll t_{pd}$.

Compositionally controlled metal–insulator transitions in perovskite oxides

In Fig. 4 we show typical compositionally controlled I–M transitions in two perovskite oxide systems. In $La_{1-x}Sr_xCoO_3$, the material becomes metallic as x is increased beyond a critical composition. A similar behaviour is seen in $La_{1-x}Sr_xVO_3$. Metallicity arises in these oxides because of fast hopping of

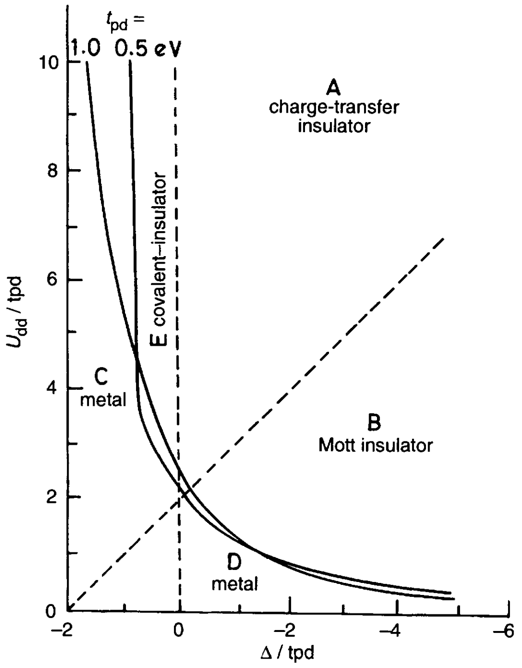

Fig. 3 ZSA phase diagram as modified by Sarma.[14] The solid lines separate the metallic and insulating regimes.

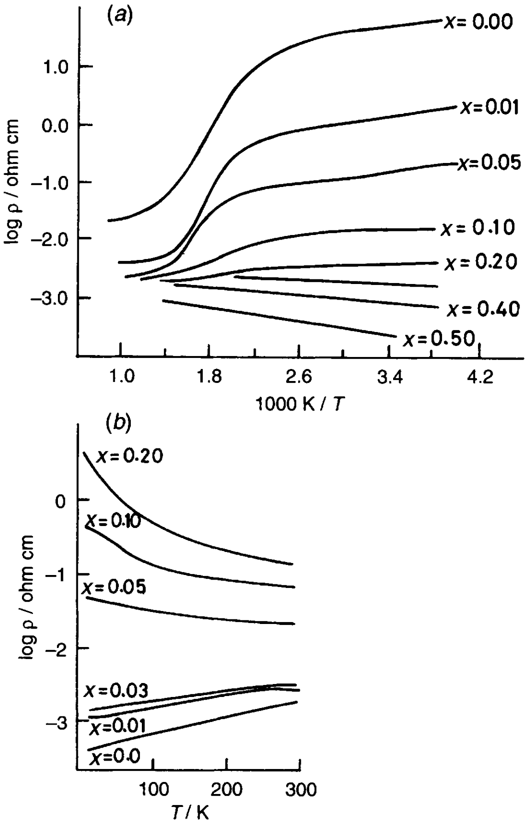

Fig. 4 Compositionally controlled insulator metal transitions in (a) $La_{1-x}Sr_xCoO_3$ and (b) $LaNi_{1-x}Mn_xO_3$ (from the author's laboratory)

electrons between the 3+ and 4+ states of the transition metal. It is noteworthy that the temperature coefficient of resistance changes sign around a resistivity value close to Mott's maximum resistivity, ρ_{max}. In $LaNi_{1-x}Mn_xO_3$ where the material becomes insulating with increasing x, the change from the metallic to the insulating state occurs again around Mott's ρ_{max}. The value of ρ_{max} or σ_{min} is known to scale with the critical carrier concentration,[15] n_c, as shown in Fig. 5 where log ρ_{max} is plotted against log n_c for a variety of systems including doped semiconductors. The points corresponding to the metal oxides exhibiting compositionally controlled metal–insulator transitions fall in line with the other electronic materials at the threshold of metallicity. It is noteworthy that these oxides obey the ρ_{max} or the σ_{min} criterion as well as the $n_c^{1/3}a_H \approx 0.25$ criterion. Although the oxides obey the σ_{min} criterion, it is possible that some of them may show a departure from this behaviour and become insulating at very low temperatures (say <50 K), with the resistivity increasing with decreasing temperature[16] (*i.e.* conductivity is zero at 0 K). If so, σ_{min} serves as the high-temperature limit for the conductivity of these marginal metals.

Photoelectron spectroscopic studies[14] of $La_{1-x}Sr_xCoO_3$ in the valence band region show the presence of a finite density of states at the Fermi level in these marginally metallic oxides (Fig. 6). The oxygen K-absorption spectra of $La_{1-x}Sr_xCoO_3$ show a feature increasing in intensity and width with increasing x, suggesting a progressive creation of doped hole states with substantial oxygen p-character as expected of a charge-transfer insulator. These states overlap the top of the valence band above a critical concentration. A finite density of states at the Fermi level is seen in $LaNi_{1-x}Mn_xO_3$ as well, even slightly beyond the critical x value above which the material is insulating.

Cuprate superconductors

Most of the cuprates which exhibit high-temperature superconductivity exhibit metallic resistivity (with the resistivity decreasing with temperature) before they become superconducting (Fig. 7). The values of resistivities in the metallic regime before they become superconducting is in the range 2–5 mohm cm, not far from Mott's ρ_{max}. Interestingly, the cuprates conform to the $n_c^{1/3}a_H \approx 0.25$ relation (Fig. 8) and also follow the linear log ρ_{max}–log n_c plot (Fig. 5). Although these observations would suggest that the cuprates are similar to $La_{1-x}Sr_xVO_3$ and such oxides showing I–M transitions, they exhibit certain anomalous properties[18] in the metallic state, one of them being the linear variation of resistivity with temperature in the metallic state (see Fig. 7). High-energy spectroscopic studies[19] of the cuprates show that the oxygen 2p contribution in the hole doped states near the Fermi level is significant. The cuprates have strong correlation effects and there is as yet no unanimous view as to the best way of describing the marginally metallic state.

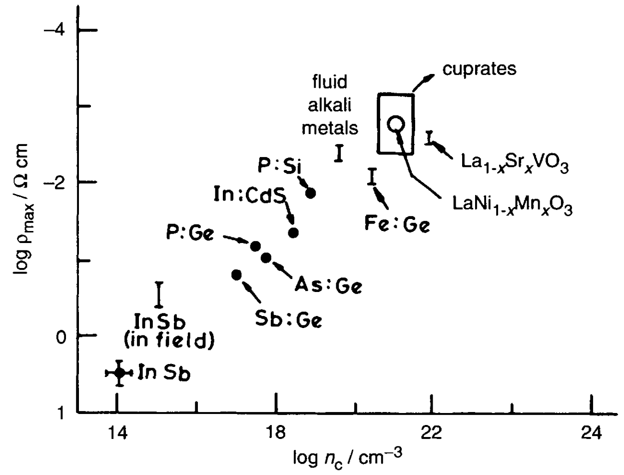

Fig. 5 A log–log plot of the maximum metallic resistivity, ρ_{max}, against the critical carrier density, n_c, at the insulator–metal transition

A novel feature of the cuprates is that they exhibit compositionally controlled metal–insulator transitions in the normal state ($T > T_c$) as can be seen in Fig. 9(*a*), (*b*). It is indeed curious that the insulating state transforms directly to the superconducting state in some compositions [Fig. 9(*b*)]. Such an insulator–metal transition is found in $La_{2-x}Sr_xCuO_4$ as well. The question that arises is whether there can be insulating and superconducting ground states without a metallic ground state in between. A careful comparison[20] shows that the Hall coefficients and other properties of such cuprate compositions are different from those of oxide systems such as $La_{1-x}Sr_xTiO_3$ which exhibit insulator–metal transitions. Clearly, the superconducting cuprates are associated with a unique kind of a marginal metallic state.

Perovskite manganates exhibiting GMR

Of all the oxide systems considered here, the manganates of the general formula $Ln_{1-x}A_xMnO_3$ (Ln = La, Pr, Nd; A = Ca, Sr, Ba, Pb) possessing the perovskite structure are most unusual in

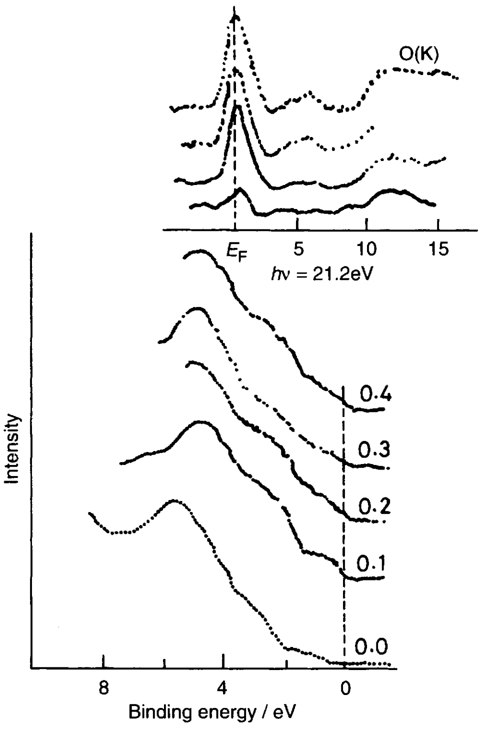

Fig. 6 Photoelectron spectra of $La_{1-x}Sr_xCoO_3$ in the valence region. The inset shows the oxygen K-absorption spectra (from ref. 14).

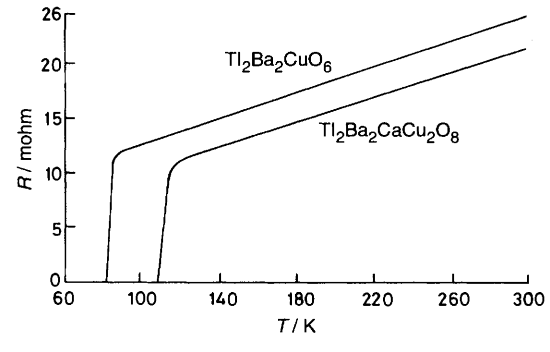

Fig. 7 Resistivity behaviour of cuprates showing linear temperature variation of resistivity in the normal (metallic) state. The linearity can be extended down to 0 K.

that they possess high resistivities in the metallic state which cannot be accounted for or explained on the basis of the criteria discussed earlier. Let us briefly examine the nature of the metallic state in these materials. In $La_{1-x}A_xMnO_3$, the Mn^{4+} content increases with x (when $x = 0.0$, Mn will be nominally in the 3+ state).‡ The Mn^{3+}–O–Mn^{4+} interaction is ferromagnetic, unlike the Mn^{3+}–O–Mn^{3+} and Mn^{4+}–O–Mn^{4+} interactions which are antiferromagnetic. The manganates become ferromagnetic above a critical concentration of Mn^{4+} (or value of x) and simultaneously exhibit metallic conductivity.§ The primary process involved is the hopping of a charge carrier as described by,

$$Mn^{3+}(i)\text{–O–}Mn^{4+}(j) \rightarrow Mn^{4+}(i)\text{–O–}Mn^{3+}(j)$$

where i and j are nearest neighbours. Zener[22] suggested that a paramagnetic to ferromagnetic transition should occur with a transition temperature T_c according to the relation $k_BT_c \approx x_htZ$, where x_h is the Mn^{4+}(hole) concentration, t is the hopping amplitude and Z is the number of nearest neighbours. These materials exhibit a transition from an insulating to a metallic state as the temperature is lowered, the transition occurring close to the ferromagnetic Curie temperature, T_c. The material is insulating at $T > T_c$ because thermal fluctuations of the magnetic moments impede the motion of holes. The I–M transition in an $La_{1-x}Ca_xMnO_3$ composition is shown in Fig. 10. The resistivity peak in this figure arises from the I–M transition, with the temperature variation of resistivity being metal-like at $T < T_c$ (T_{IM}) and insulator-like when $T > T_c$ (T_{IM}).

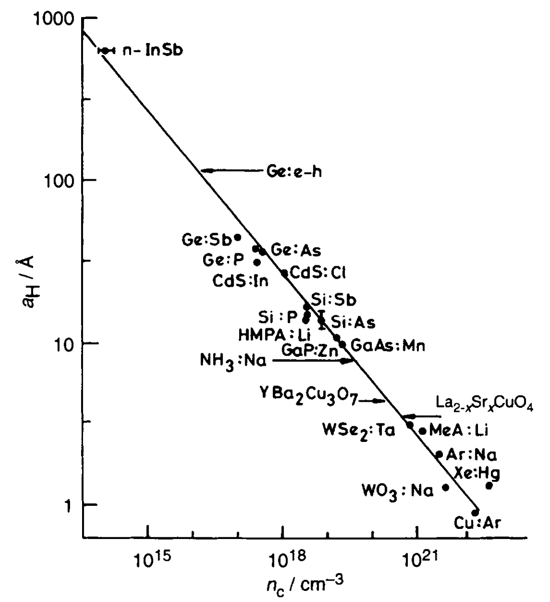

Fig. 8 Relation between the critical carrier concentration, n_c, and the Bohr radius, a_H. The solid line represents $n_c^{1/3}a_H = 0.26$ (from ref. 17).

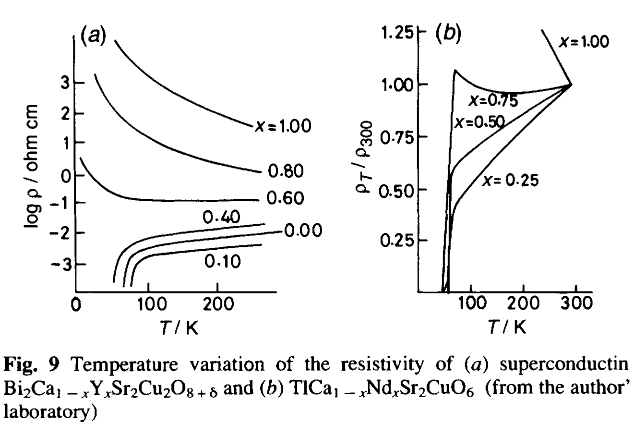

Fig. 9 Temperature variation of the resistivity of (*a*) superconducting $Bi_2Ca_{1-x}Y_xSr_2Cu_2O_{8+\delta}$ and (*b*) $TlCa_{1-x}Nd_xSr_2CuO_6$ (from the author's laboratory)

When a magnetic field is applied to such a material the resistivity decreases enormously[23] (Fig. 10). This phenomenon, called giant magnetoresistance (GMR), is of great importance in magnetic recording and other technological applications. GMR-related aspects of the manganates are not within the scope of this article¶ and I shall restrict myself to the metallic state of these materials.

The resistivity of the manganates at the I–M transition is generally high, anywhere from 10 mohm cm to several ohm cm (see Fig. 2). No metal can have such resistivities, the observed values being much higher than Mott's ρ_{max}. Furthermore, the resistivity in the metallic regime ($T < T_c$) in some of the manganates is comparable to or even higher than that in the insulating state ($T > T_c$).‖ Residual resistivities at low temperatures (*ca.* 4 K) are also very large (several mohm cm), larger than in disordered metals. While the effects of the lattice and of magnetic polarons may contribute to such high resistivities, we note that electron correlation would play a major role in a Mott insulator such as $LaMnO_3$. What is curious is that photoelectron spectra in the valence-band region[14] of $La_{1-x}Sr_xMnO_3$ show the absence of any significant density of states in the 'metallic' compositions at ordinary temperatures as can be seen from Fig. 11. The oxygen K-absorption spectra show a progressive formation of hole states with the increase in x *ca.* 1 eV above the Fermi level (Fig. 11).

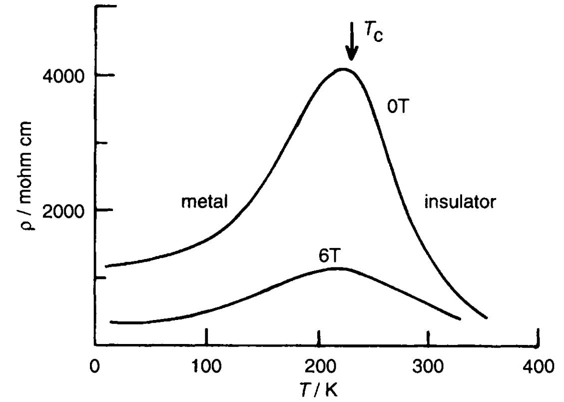

Fig. 10 Resistivity behaviour of $La_{0.9}Ca_{0.1}MnO_3$ at zero field (0 T) and in a magnetic field (6 T) (from ref. 23)

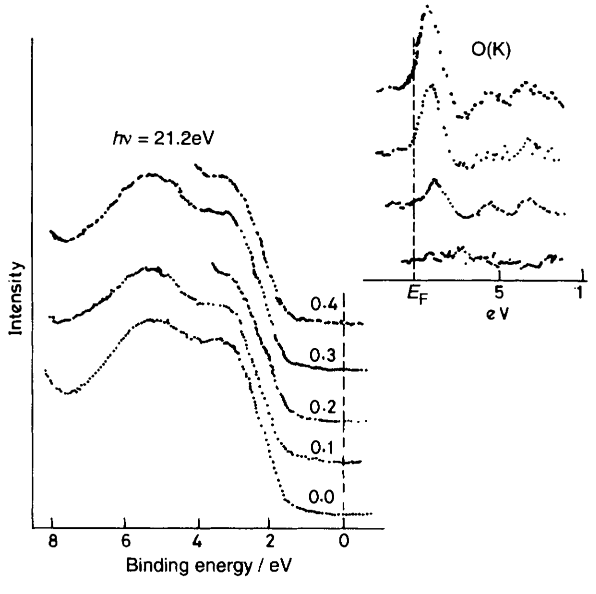

Fig. 11 Photoelectron spectra of $La_{1-x}Sr_xMnO_3$ in the valence region. Inset shows the oxygen K-absorption spectra (from ref. 14).

Concluding remarks

I have discussed three types of complex metal oxides which are marginally metallic. The first category of oxides exhibiting compositionally controlled insulator–metal transitions have a finite density of states at the Fermi level in the metallic state and obey the known criteria for metallicity. The second category involves the superconducting cuprates. They are marginally metallic in the normal state, obey the criteria for metallicity and undergo unusual insulator–metal and insulator–superconductor transitions, besides exhibiting certain anomalous properties in the metallic state. The first two categories of oxides seem to obey both the criteria of Mott arising from considerations of electron interactions (correlation) and of disorder. It is obvious that both these factors should be considered in describing these oxides. The importance of disorder in these oxides is also indicated by the fact that the phenomena are dependent on a critical concentration of one of the component species. Correlation is certainly important in all the systems considering that the parent oxides, $LaCoO_3$, $LaMnO_3$ and La_2CuO_4, all have mixed-valent ground states and fall in the category of Mott or charge-transfer insulators (Fig. 3). Yet, those who work on electron correlation models of oxides ignore disorder and *vice versa.* Unlike the two categories of oxides mentioned above, the manganates exhibiting giant magnetoresistance have high resistivities beyond the range of all known metallic oxides and show no evidence for any significant density of states at the Fermi level in the so-called 'metallic' state. The metallicity of the manganates is clearly of an entirely different category, not encountered hitherto in any other oxide system.

Clearly, there is need for models which include both electron interactions and disorder to describe marginally metallic oxides. This is not an easy task and requires new ideas. The problem does not end here. Besides electron interactions and disorder, other factors such as electron–lattice interactions, magnetic effects and the effect of finite temperature would have to be taken into account depending on the situation as shown schematically in Fig. 12. The theoretical complexity of the marginally metallic state is truly formidable, a proper description of either one of the factors alone (*e.g.* pure correlation or pure disorder) being fraught with many difficulties. Some workers have considered simple models which essentially assume the coexistence of localized and itinerant electrons to describe insulator–metal transitions[25,26] and superconductivity[26] in oxides. For example, Burdett[26] makes use of the interaction or crossing of two diabatic potential-energy curves for the insulating and metallic states to describe the two phenomena. Although educative, such models do not throw light on the nature of marginal metallicity. An effort to combine both electron interactions and disorder has been made recently by Logan *et al.*[27] Whether the metallic state has a universal minimum (electron) diffusity and hence minimum conductivity[28] due to localized states (in addition to extended electron states) is another question that needs to be explored.

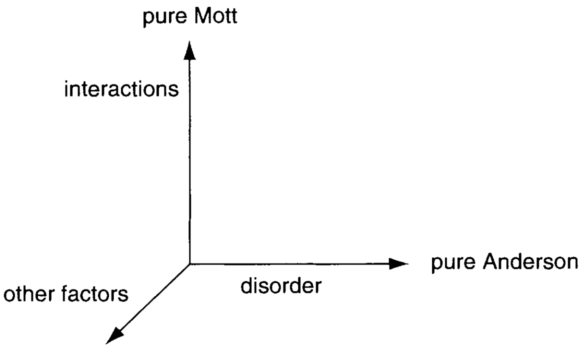

Fig. 12 Complexity of the problem of marginal metallicity (adapted from ref. 27). The oxides discussed in this article fall somewhere in the three-dimensional space indicated here. The 'other factors' include electron–lattice interaction, magnetic polaron and finite temperature effects.

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Footnotes

† An important experimental criterion for metallicity is the presence of a finite density of states at the Fermi level, which is readily established by photoelectron spectroscopy in the valence region and other high-energy spectroscopic techniques. Two of the most useful operational criteria for metallicity are those due to Mott discussed in the next section.

‡ $LaMnO_3$ as prepared in the laboratory by the solid-state reaction of the oxides and carbonates of the component metals at high temperatures, generally contains around 10% Mn^{4+}. The origin of Mn^{4+} is the presence of cation vacancies in both the A(La) and B(Mn) sites in roughly equal proportions. It cannot be due to oxygen excess since the perovskite structure cannot accommodate excess oxygen.[21]

§For small x, the material is an antiferromagnetic insulator; the same is true for large x ($x \geqslant 0.5$).

¶ The ferromagnetic T_c in $Ln_{1-x}A_xMnO_3$ increases markedly with the increase in the average radius of the A-site cations, $\langle r_A \rangle$; accordingly, T_{IM} also increases with $\langle r_A \rangle$. The magnitude of GMR as well as the peak resistivity at the I–M transition decrease with the increase in $\langle r_A \rangle$. Increasing $\langle r_A \rangle$ in these perovskites is analogous to increasing pressure.[24] It should also be noted that GMR is not confined to perovskites or manganates.[7]

|| The magnitude of GMR itself increases with an increase in the peak resistivity (at T_{IM}). In other words, one needs a bad metal to observe good GMR. Furthermore, even formally antiferromagnetic compositions ($x > 0.5$) show GMR because of the presence of ferromagnetic clusters.

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