©*Proc. Indian natn. Sci. Acad.* **52**, A, No. 1, 1986, pp. 135–158.
Printed in India.

ELECTRICAL TRANSPORT AND MAGNETIC PROPERTIES OF OXIDES WITH K_2NiF_4 STRUCTURE*+

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(*Received 4 December 1985*)

A brief review of the structural features including some new results on the accommodation of oxygen non-stoichiometry is presented. The electrical transport and magnetic properties have been reviewed with the following considerations : properties of La_2BO_{4+d} (B = Co, Ni, Cu) and other Ln_2CuO_4 compounds; comparison of the properties of $LaSrBO_4$ compounds with that of the corresponding $LaBO_3$ compounds; influence of percolation effects.

Key Words : Electrical Transport and Magnetic Properties of Oxides; K_2NiF_4 Structure; Perocolation Effects; Three-dimensional Perovskites; $La_2B_4O_4$ Compounds

INTRODUCTION

A_2B_4X halides (A = alkali metal ion, B = $3d$ transition metal ion, X = halide ion) are well known to serve as magnetic model systems, especially when X is a fluoride ion and they have the K_2NiF_4 structure.[1] The ionic nature of the bonding renders the $3d$-electrons localised so that the magnetic interactions in these systems may be described by the Heisenberg Hamiltonian. Moreover, for these halides charge-balance constraints impose a formal divalent state on the B-ion so that the range of metal-halogen covalency or transfer integral is restricted. In the A_2BO_4 oxides[2,3,4] with the K_2NiF_4 or related structures some of the constraints on the formal oxidation state of the B-ion is removed. The counter A-cations may have formal oxidation states between + 1 and + 3. The average oxidation state of the A-ion (typically La^{3+} and Sr^{2+}) may be varied between + 2 and + 3 so that the average oxidation state of the B-ions may be varied between + 2 and + 4. The B—O—B transfer integral or the d-electron bandwidth may then be varied over a wide range so that in the limits we may have localised or itinerant (or nearly itinerant) electrons. In addition, the absence of close-packing in these systems allows strains to be accommodated so that solid solutions not normally accessible in the entire range for three-dimensional perovskite oxide systems (such as $LaAl_{1-x}Ni_xO_3$ or $LaAl_{1-x}Fe_xO_3$) may easily be prepared in the layered perovskite oxides (such as $LaSrAl_{1-x}Ni_xO_4$ and $LaSrAl_{1-x}Fe_xO_4$). The oxides with the K_2NiF_4 or related structure, therefore,

*Communication No. 344 from the Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore.

+Presented at the INSA Golden Jubilee Symposium on Solid State Chemistry held at INSA, New Delhi during December 4–6, 1985.

provides unique opportunity not only to serve as model systems for magnetic interactions in low dimensions but also as model systems for the study of influence of lower dimensionality on the magnetic and electrical transport properties in transition-metal oxides.

The three-dimensional perovskites ABO_3 (B = 3d transition metal ion, A = La^{3+}, Sr^{2+} etc.) show a range of interesting properties.[2,5] The important properties from the view-point of this article are the magnetic and electrical transport properties with special emphasis on the metal-insulator (MI) transitions.[6] Composition-controlled MI transitions in systems such as $La_{1-x}Sr_xBO_3$ (B = Co, Mn, V) are well known.[7] Recently, the composition-controlled MI transitions in the $LaNi_{1-x}B_xO_3$ systems (B = Cr, Mn, Fe, Co) have been studied.[8] $LaNiO_3$ is metallic with a room-temperature resistivity $\sim 10^{-3}$ ohm cm and a positive temperature coefficient of resistance (TCR) at all temperatures studied so far (between 4–800 K). The $LaBO_3$ compounds are insulators. In all these systems a maximum value of the resistivity ρ_{max} ($\sim 2 \times 10^{-3}$ ohm cm) may be defined such that compositions with $\rho > \rho_{max}$ are semi-conducting in the sense that TCR is negative while these with $\rho < \rho_{max}$ are metallic with TCR being positive.[6] This value of ρ_{max} corresponds fairly closely to the value of minimum metallic conductivity σ_{min} proposed by Mott for such concentrated systems.[9] We shall refer to σ_{min} in an experimental sense as the value of the conductivity at which TCR change sign for a composition-controlled MI transition.

In this article we shall examine the changes in the electrical transport and magnetic properties of three-dimensional perovskite oxides on reducing the dimensionality. Special attention will be paid to the systems exhibiting MI transitions in three dimensions. For a proper understanding of these studies we have discussed in brief some of the structural aspects and the electrical transport and magnetic properties of some La_2BO_4 compounds (B = Co, Ni, Cu). In two recent communications the aspects of crystal structure and some unusual effects of anisotropic bonding have been more extensively discussed.[4,10]

Crystal Chemistry

In the A_2BO_4 oxides with the ideal tetragonal (T) K_2NiF_4 structure (Fig. 1) there is 180° B–O_I–B interactions in the basal ab plane while along the c-axis there are B–O_{II}–O_{II}–B interactions, the B–O_{II}–O_{II} angle being close to 135°. Magnetic interactions along the c-axis are therefore expected to be much weaker than the interactions in the basal plane. This gives rise to the low-dimensional magnetic behaviour.

As in perovskites a tolerance factor t ($= r_{A-O}/\sqrt{2}r_{B-O}$) may be defined.[11] The T structure has been observed in the range $1.02 \leqslant t \leqslant 0.85$.[11,12,4,13] In most oxides t is considerably less than 1 and the following constraints are imposed. In the basal plane the B–O_I–B distance is shortened and the A–O_{II}–A distance is lengthened relative to the distance calculated from ionic radii considerations. The in-plane pressure on B–O_I becomes larger as t becomes smaller. This strong

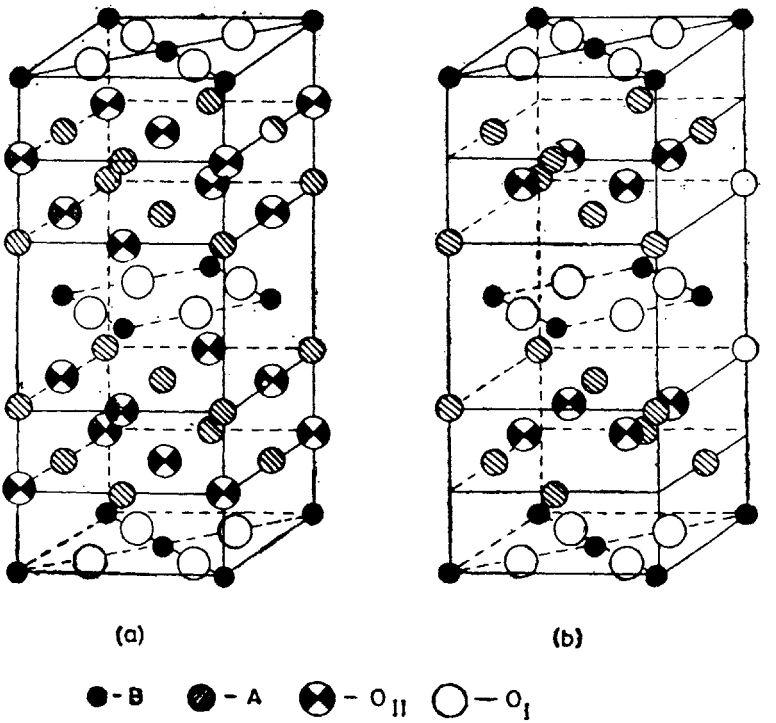

FIG 1 (*a*) the K_2NiF_4 (*T*) and (*b*) the *T'* Pr_2CuO_4 structure in A_2BO_4 oxides.

internal pressure on the *B*–O_I bond is reflected in a fairly large increase in the infrared *B*–O stretching frequency in the layered perovskites compared to that in three-dimensional perovskites. This is especially apparent in the changes in the stretching frequency in $GdSrAlO_4$ compared to that in $GdAlO_3$.[14] Such large changes are consistent with the assumption[4] that the two-dimensional K_2NiF_4 structure imposes a rigidity to the corner-shared sheets of BO_6 octahedra. The strain due to a low tolerance factor cannot be relieved by a buckling of the octahedral network as is possible in the three-dimensional perovskite oxides.

In order to maintain the mean metal-oxygen distance the *A*–O_{II} and *B*–O_{II} distances along the *c* axis has to be adjusted. The *A*–O_{II} distances are expected to be shortened and the *B*–O_{II} distances to be lengthened.[4,10] In fluorides such as K_2NiF_4 itself the tolerance factor is more than 1. The NiF_6 octahedra are accordingly compressed along the *c* axis. However, compounds such as Sr_4NdTaO_8 have very low tolerance factors,[13] and unusually small *c*/*a* ratio ($\sim$ 3.00 compared to $\sim$ 3.25 in La_2NiO_4). Thus the elongation of the BO_6 octahedra along the *c* axis seems to depend on the ratio of the formal oxidation states of the *A* and *B*-ions. In La_2BO_4 with trivalent *A*-cations and divalent *B*-cations, the *A*–O_{II} interaction competes favourably with the *B*–O_{II} interaction along the *c*-axis. The *A*–*A* electrostatic repulsion between *c*-axis near-neighbours is also expected to be more

important for trivalent A-ions which will tend to shorten the A–O_{II} bond. These factors could lead to short A–O_{II} distances.

The importance of short A–O_{II} bonds in accounting for the spectral features in the far infrared region has been stressed.[14] It is observed that in compounds such as La_2NiO_4 and La_2CuO_4 there is a band of considerable intensity appearing at a frequency which is much higher than that encountered in B-O monoxides or in La_2O_3. From a systematics of the changes in the frequency of this band a correlation was found with the A–O_{II} distance. Hence this band was attributed to La–O_{II} stretching. This was substantiated by the fact that this band is absent in compounds such as Nd_2CuO_4 in which there is no such short Nd-O_{II} distances. These results and conclusions were based on studies with La_2NiO_4 which has slight oxygen excess. It is now known that stoichiometric La_2NiO_4 has a monoclinic distortion.[15] Further studies are now necessary to ascertain whether the high frequency band could be due to the lower symmetry in these compounds.

One intriguing aspect of the K_2NiF_4 structure is that oxides[16] such as $La_2Li^{+}_{0.5}M^{3+}_{0.5}O_4$ or $Sr_2M^{3+}_{0.5}(Nb, Ta)^{5+}_{0.5}O_4$ show no X-ray evidence for ordering of the B-cations despite fairly large charge-difference potential for such ordering.[13] The B-cations with different charges may be looked upon as pseudo-spins with opposite orientations so that an ordering of the B-cations will be analogous to antiferromagnetic ordering. The $I\,4/mmm$ symmetry of the K_2NiF_4 structure imposes an inherent frustration when all the possible antiferromagnetic interactions between the spins in different layers are considered.[17] The same reason may be responsible for the absence of cationic ordering in three dimensions although there be two-dimensional ordering is seen by electron-diffraction studies[18] in $La_2Li_{0.5}Co_{0.5}O^{1}_{4}$[7]. This frustration may be looked upon as an inability to convey coherently information regarding structural changes or strains in layers containing O_I ions through layers containing O_{II} ions, especially when the tolerance factor is far from the limits of stability of the tetragonal (T) structure. This may account for the stability of solid solutions such as $LaSrAl_{1-x}B_xO_4$ (B = Ni, Fe) for all values of x in contrast to the situation in the corresponding three-dimensional $LaAl_{1-x}B_xO_3$ compounds.

Structures Related to K_2NiF_4

Several structures can result from a rearrangement of the oxygen ion positions. Three of these give rise to monoclinic distortions with $\gamma \neq 90°$. Of the monoclinically distorted phases, there are two structures with $a = b$ so that the unit-cell may be indexed on the basis of an orthorhombic unit-cell. Two types of orthorhombic structures have been distinguished.[19–21] In the O structure the conditions for the allowed reflections are $h + k = 2n$, $k + l = 2n$, $l + h = 2n$ while for the O′ structure the condition is $k + l = 2n$. The distortion to orthorhombic symmetry has been discussed in terms of two components.[4,10] The first component involves the cooperative displacement of one half of the A and O_{II} ions along the c-axis thus reducing the A–O_{II} distance and increasing the B–O_{II} distance along the c-axis

for half the *A* and *B* ions. This is the O structure proposed for Sm_2CoO_4 there being two distinguishable *B* (and *A*) cations.[19] In this structure the orthorhombic *b'*-parameter is smaller than the *a'*-parameter. The second component of the orthorhombic structure involves a rotation of the BO_6 octahedra about the orthorhombic *b'*-axis. This leads to a decrease in the *a* parameter of the O' cell. The first component is not ruled out in the O' structure. The O and O' phases and their relationship have been nicely demonstrated in the system $Ca_{1+x}Y_{1-x}CrO_4$.[20] The temperature-dependent study on $CaYCrO_4$ showed that with increasing temperature the sequence is $O' \rightarrow O \rightarrow T$.

The monoclinic *M* structure in which $a = \text{or} \neq b$ and $\gamma \neq 90°$ has been reported for Pr_2NiO_4 and[10] Nd_2NiO_4 and for[15] stoichiometric La_2NiO_4. An $a \neq b$ is possible only when the BO_6 octahedra are rotated about the *a* or *b* axis of the tetragonal cell. The B-O_{II}-B angle along the *a* or *b*-axis may therefore be different and this may introduce a one-dimensional component in the magnetic interactions.

There are two other structures which may be considered to be derived from the K_2NiF_4 structure. These are the *T'* tetragonal structures encountered in Ln_2CuO_4 compounds (Fig. 1*b*) (Ln = Pr, Nd, Sm, Eu, Gd)[21,23] in which the O_{II} ions in the K_2NiF_4 structure having the coordinates, O, O, *z*, are shifted to the coordinates 0.5, 0.0, 0.25, (referred to later as O'_{II} ions). In such a structure, the Ln ions have an eight-fold coordination and the Cu^{2+} ions have a four-fold coordination. A second structure derived from K_2NiF_4 are found in Ca_2CuO_3 and Sr_2CuO_3 in which half the O_I anions (the anions on the *a* axis) are missing the Cu^{2+} ions again having a four-fold square-planar coordination.[22]

Accommodation of Non-Stoichiometry

Oxides with the K_2NiF_4 structure are known to accommodate considerable amount of oxygen non-stoichiometry. It is new known that in La_2NiO_{4+d}, *d* can be as high as .12.[24,25] In La_2CoO_{4+d} prepared under different conditions *d* can be as high as .25.[26,27] $La_{1-x}Sr_{1+x}MnO_4$ has also large oxygen excess non-stoichiometry especially for small values *x*.[28] Such large oxygen excess is unusual. Drennan *et al.*[28] have proposed that intergrowths of Ruddlesdon-Popper phases such as $La_3Ni_2O_7$ and $La_4Ni_3O_{10}$ may account for the observed non-stoichiometry. However, recent resolution electron-microscope studies on powdered single crystals[25] as well as well-sintered air-fired ceramic samples[24] show that there is no intergrowth although there is considerable oxygen excess. *A*-site deficiencies have been suggested for lanthanum cobalt oxides to account for the oxygen excess.[30] Such *A*-site vacancies should give rise to a decrease in the density. Recent density measurement[27] on single crystals of $La_2NiO_{4.10}$ has shown that the density is actually higher (by about 1 per cent) than that calculated from X-ray lattice parameters. This is unusual and suggests that the excess oxygen enters the lattice as 'interstitials'. A complex polyoxygen anionic species $O_m^{-(2m-2)}$ may therefore exist. The simplest of these is the peroxide ion O_2^{2-}. Accurate X-ray studies could possibly indicate the

exact location of the excess oxygen. On examining the structure of the T and T' phases (Fig. 1) we note that for the given lattice parameters of La_2NiO_4 the distance between the O_{II} and O'_{II} ion positions is roughly 2.3 Å which is much too small for these sites to be simultaneously occupied by two oxide (O^{2-}) ions. However, this distance is sufficiently large to accommodate two oxygen atoms belonging to a peroxide-like species. It will be interesting to study whether the accommodation of excess oxygen by the formation of peroxide-like species is peculiar to the low-dimensional systems or may be found in three-dimensional systems also. More corroborative work is necessary before a peroxide-like species is to be accepted. Oxygen-deficient non-stoichiometry as in Ca_2MnO_{4-d} has been attributed to the loss of O_I oxygens.[31]

La_2BO_4 Compounds

La_2NiO_4

Quite early in the literature it was noticed that the TCR of the compound with the nominal composition La_2NiO_4 changed sign around 550K.[32,33] This was taken as an instance of a metal-insulator transition. It was proposed that anisotropic bonding in the basal plane gives rise to a strong metal oxygen overlap in the basal plane. At low temperature the $d_{x^2-y^2}$ electrons of the Ni^{2+} ions were considered to be antiferromagnetically coupled. The so-called metal-insulator transition was then thought to be due to the breaking up of antiferromagnetic order. The gradual MI transition was attributed to the persistence of short range magnetic order ateclevated temperatures in these low-dimensional systems.[5,10] The shorter Ni—O_I distance in La_2NiO_4 ($\sim$ 1.93Å) compared to that in NiO ($\sim$ 2.05Å) is consistent with a strong Ni–O overlap in the former and nearly itinerant electrons in broad bands.[5,33] The compounds with the nominal composition Pr_2NiO_4 and Nd_2NiO_4 also show similar 'metal-insulator' transition.[10,33] These compounds have a monoclinic distortion and it was observed that the temperature at which TCR changes sign corresponds fairly closely to the temperature at which the structure becomes tetragonal.[10] La_2NiO_4 itself is believed to have a superstructure indicative of lower symmetry even though X-ray diffraction may show it to have tetragonal structure.[15]

The anisotropic nature of electrical conduction is seen in single-crystal studies.[15,25] A sharp decrease in the resistivity around 550 K when mersured parallel to the basal plane and the absence of such a feature in the resistivity measured perpendicular to it seemed to support the early models. These studies, however, highlighted the fact that La_2NiO_4 may accommodate considerable oxygen-excess non-stoichiometry and special annealing procedures were necessary to render it stoichiometric. The properties of La_2NiO_{4+d} is critically dependent on the value of d and the earlier studies lose most of their significance as far as the intrinsic properties of La_2NiO_4 is concerned as the value of d has not been specified. Recent studies seem to show that stoichiometric samples of La_2NiO_4 has a much higher resistivity than reported so far. The fairly low value of the resistivity of the air-

fired samples therefore seems to be due to excess oxygen. We have observed that samples prepared in air at 1470 K and then cooled slowly to room temperature shows a value of d close to $0.125 \pm .005$.[24] Such samples show susceptibility and resistivity behaviour similar to that reported earlier.

Magnetic susceptibility studies on samples prepared in air show some unusual features. Below 200 K there is a deviation from the Curie-Weiss law which at higher temperatures gives a μ_{eff} corresponding closely to that expected for Ni^{2+} ions.[31] Between 4 and 100 K the Curie-Weiss law is obeyed[10,34] with no evidence for long-range magnetic ordering despite a high paramagnetic Curie temperature θ in this range. The μ_{eff} value calculated from the low-temperature region corresponds to that of an $S = \frac{1}{2}$ system. This $S = 1$ to $S = \frac{1}{2}$ transition below 200 K was attributed to antiferromagnetic coupling of the $d_{x^2-y^2}$ electrons in the basal plane. Around 200 K a change in the activation energy for electrical conduction was also observed. (Fig. 2). Studies on $La_2Ni_{1-x}Cu_xO_4$ and $La_{2-2x}Sr_{2x}Ni_{1-x}Ti_xO_4$ confirmed this behaviour.[10] This behaviour must new be attributed to the excess oxygen in the sample. The electrical resistivity and magnetic susceptibility behaviour is reminiscent of properties of $Na_{0.33}V_2O_5$ (Fig. 3).[36] It may be worth exploring how non-stoichiometry

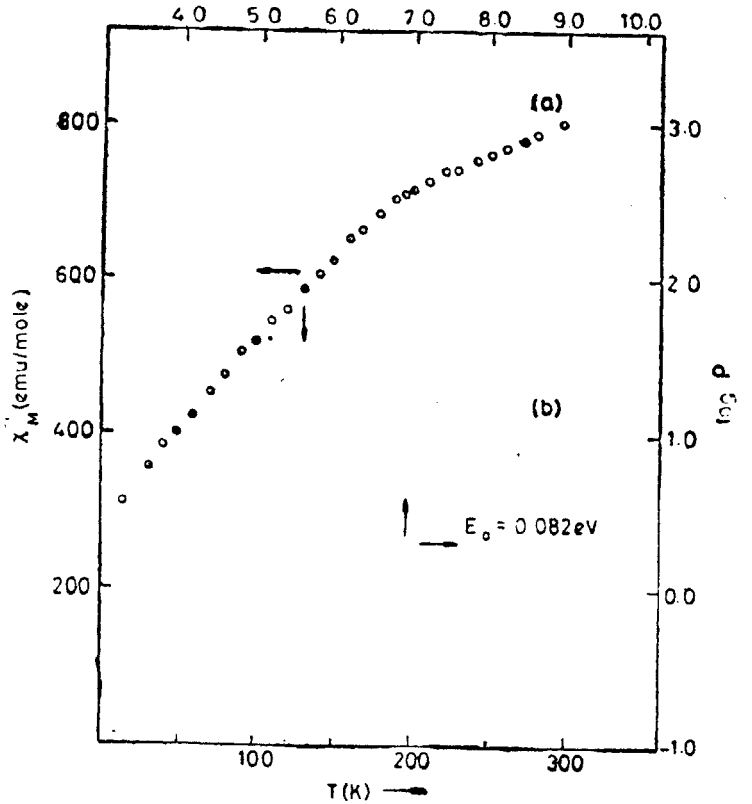

FIG 2 χ_M^{-1} *vs* T and log ρ *vs* $1/T$ plot of and air-fired sample of La_2NiO_4.[10]

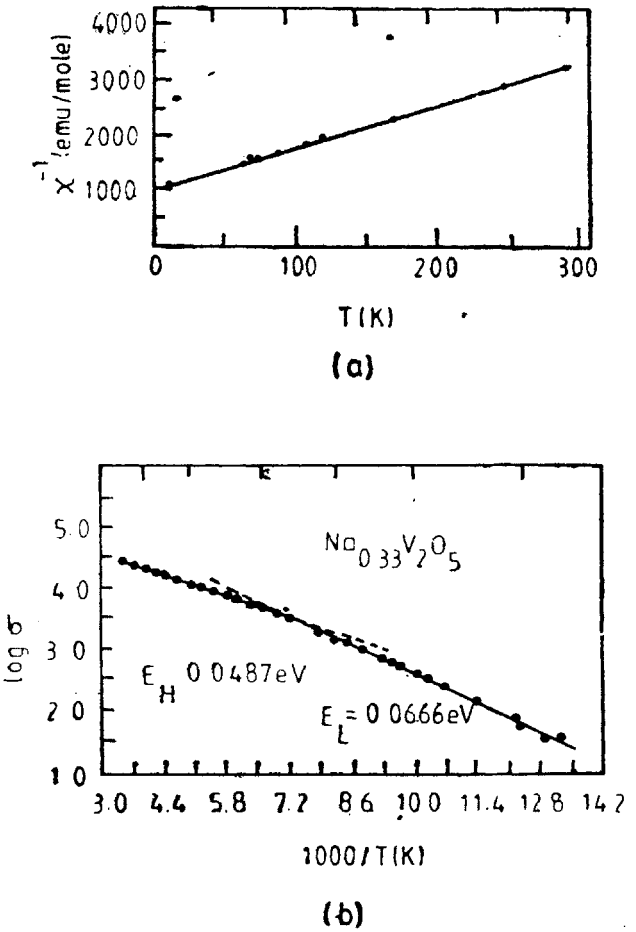

FIG 3 χ_M^{-1} *vs* T plot (*a*) and log σ *vs* $1/T$ plot of $Na_{0.33}V_2O_5$.[36]

gives rise to the unusual magnetic susceptibility behaviour reminiscent of valence fluctuation systems[37] such as $CeCu_2Si_2$. Nearly, stoichiometric samples of La_2NiO_4 have always shown so far a weak field dependence which in most samples disappears around 580 K. It is yet to be ascertained whether this is due to the presence of metallic Ni or due to canting of spins in an ordered antiferromagnet. The reduced symmetry of the stoichiometric support samples could support a Dzialoshinskii vector. Neutron diffraction studies should be helpful in resolving the problem.

It has been observed that samples close to stoichiometry show a higher resistivity than that reported for both single crystals and powders. Moreover, samples which are close to stoichiometry have a tendency to be oxidised even at low partial pressures of oxygen at moderate temperatures so that studies on such samples without a proper control of the atmosphere should be interpreted with some caution.

Despite the recent studies on the influence of non-stoichiometry much of the recent work[38] does not pay attention to this problem.

The electrical properties of the air-fired samples as well as single crystals show some interesting features. The value of the conductivity in the so-called metallic phase in all the samples studied so far is much lower than that in other systems which exhibit metal-insulator transition or other systems which exhibit a composition-controlled MI transition.[6] As we shall see later this may be due to the two-dimensional character. Another interesting observation is that the so-called MI transition in the air-fired samples at a temperature T_{min} at which the resistivity is a minimum may be explained by a classical diffusion equation for the conductivity of the forms $\sigma = (\sigma_0/T) \exp(-E_a/kT)$ since it is observed that $E_a \simeq kT_{min}$.[10]

La_2CuO_4 and Ln_2CuO_4 (Ln = Pr, Nd)

La_2CuO_4 shows at high temperatures a fairly low resistivity (10^0–10^{-1} ohm cm).[33] The nearly temperature-independent resistivity was attributed to metallic behaviour.[5,33] However, low-temperature studies on La_2CuO_4 showed it to be semiconducting.[10] The Ln_2CuO_4 compounds on the other hand showed a semiconducting behaviour with a marked increase in the activation energy at high temperatures. Studies on $La_{2-x}Ln_xCuO_4$ as a function of x showed an abrupt increase in volume on going from the O structure of La_2CuO_4 to the T' structure of the Ln_2CuO_4 compounds. This is accompained by an abrupt increase in the resistivity so that structure dominates the electrical transport properties. The large increase in the volume in the semiconducting T' phase suggests that application of

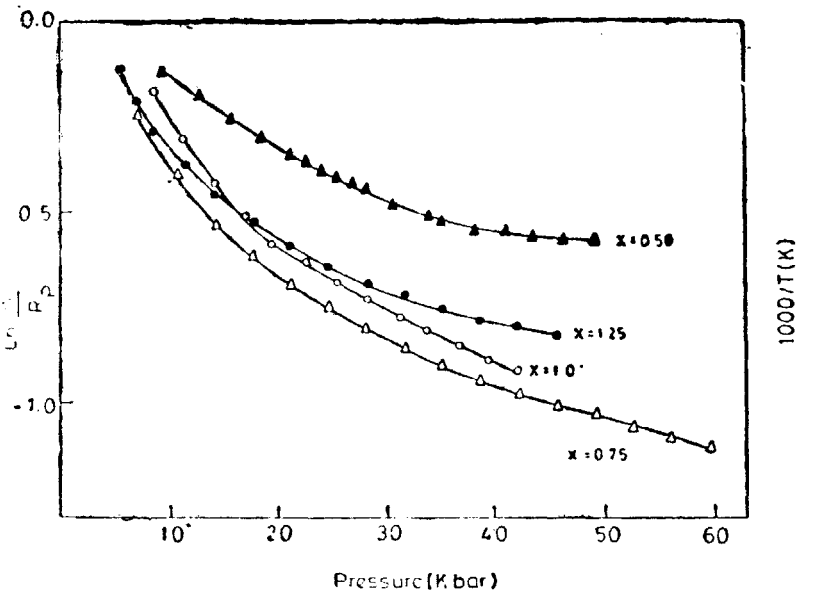

FIG 4 Variation of the resistance (R_p) of $La_{2-x}Pr_xCuO_4$ samples as a function of pressure at 300 K. R is the resistance at atmospheric pressure.

pressure could induce a first-order 'semiconductor-metal' transition. This, however, was not observed[28] in studies upto 60kbar (Fig. 4).

The low magnetic susceptibility of La_2CuO_4 has been attributed to antiferromagnetic interaction persisting at high temperature.[39] Interpretations based on Pauli paramagnetism is hardly convincing because of the fairly high resistivity and the low-temperature semiconducting behaviour. As we shall see later, however, there is some reason to believe that the system may be metallic as far as magnetic properties are concerned although electrical resistivity behaviour may not indicate it to be so. The susceptibility results of Singh *et al.*[10] has been correlated with the changes in the electrical resistivity at low temperatures (Fig. 5). The number of free Cu^{2+} ions as determined from magnetic susceptibility studies starts decreasing at the temperature at which the resistivity starts increasing sharply. The magnetic susceptibility studies on Nd_2CuO_4 and Pr_2CuO_4 also showed that there is no contribution from copper ions at low temperatures indicating that there could be antiferromagnetic interactions between the copper ions.[35,36] In this context, the break in the log ρ *vs* $1/T$ plots at high temperatures may be relevant as it is known that similar breaks are observed across antiferromagnetic ordering temperatures.

There may be other mechanisms by which the moments on the copper ions may be reduced. In CuO itself it is known that the moments on Cu^{2+} are reduced

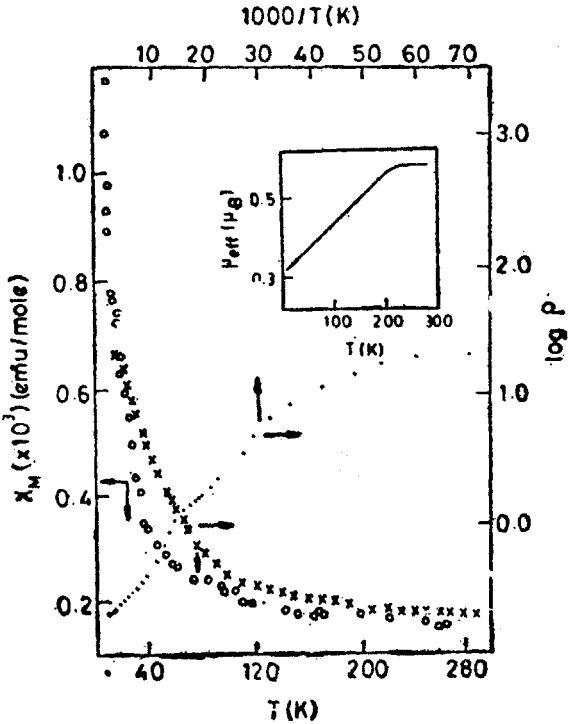

FIG 5 log ρ *vs* $1/T$, log ρ *vs* T, χ_M *vs* T and μ_{eff} *vs* T (inset) plots of La_2CuO_4.[10]

although the system is insulating.[41] We have studied the XPS spectra of Nd_2CuO_4 and compared it to that in CuO (Fig. 6). The binding energy of the $2p_{3/2}$ line is comparable to that in CuO so that the copper ions are formally in the divalent state. The satellite intensity of $2p_{3/2}$ level is much reduced in Nd_2CuO_4 compared to that in CuO. Such a reduction in the satellite intensity would indicate a marked reduction in the number of unpaired electrons on Cu^{2+}. This could be attributed to :—

(*i*) A disproportionation of Cu^{2+} to Cu^{+} and low-spin Cu^{3+} (usually stabilised in square-planar configuration). This could be dynamic or there could be a mixing of such excited configuration into the ground state tending to reduce the moments.

(*ii*) A strong covalent Cu–O bonding with transfer of electron from oxygen to copper.

Compounds such as Sr_2CuO_3 and Ca_2CuO_3 in which there are 180° Cu–O–Cu interactions also exhibit very low susceptibilities which are comparable to that of La_2CuO_4.[42] In the case of Ca_2CuO_3 the susceptibility decreases with decreasing temperature indicating antiferromagnetic coupling of the spins. Whether this is due to long-range antiferromagnetic coupling or dimerisation of copper pairs is not certain. More interestingly, the ESR susceptibility of these compounds shows entirely different temperature independence. The ESR susceptibility in both cases increases markedly with temperature the χ_{ESR}^{-1} *vs* T plot showing a large ferromagnetic intercept. This behaviour is similar to that reported for $TiCl_3$ in which there is also one-dimensional antiferromagnetic interactions. This has been attributed to end-chain effects.[43] However, in our studies we find that at low temperatures the ESR susceptibility may be actually larger than the static susceptibility.

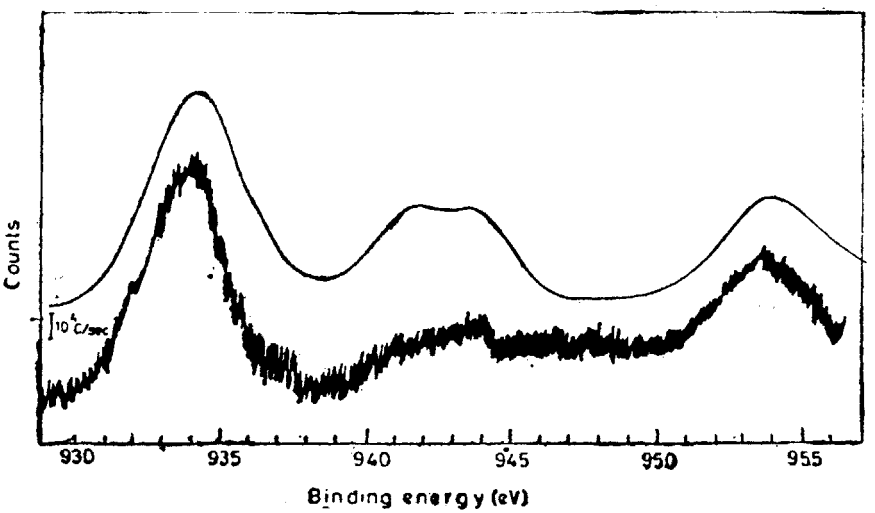

FIG 6 XPS spectra in the Cu $2p_{3/2}$ region for CuO smooth line and Nd_2CuO_4.

In La_2CuO_4 there may be other factors which could favour such a disproportionation. The tolerance factor in La_2CuO_4 is very close to the lower range of stability of the tetragonal (T) structure. A disproportionation improves the tolerance factor as the average radius of Cu^+ and Cu^{3+} is less than that of Cu^{2+}. The pseudo-tetragonal lattice parameters of La_2CuO_4 is close[5] to that of $La_2Li^+_{0.5}Cu^{3+}_{0.5}O_4$.[5] Since the Cu^{3+} ions are in the diamagnetic state and the Li^+ ionic radii similar to that of Cu^+ a disproportionation would not change much the lattice parameters. The orthorhombic O structure of La_2CuO_4 can also accomodate two distinguishable copper ions as mentioned earlier.

La_2CoO_{4+d}

The susceptibility of a $d = 0.03$ sample is shown in (Fig. 7).[48] There is clear evidence for low-dimensional magnetic ordering in terms of a broad maximum at high temperatures. In addition, there is a sharp maximum around 400 K. This feature is observed also for powdered single crystals. DSC studies on powdered single crystals as well as ceramic samples shows two transitions around 400 K. One of these is reversible with respect to temperature while the other shows a thermal hysteresis. CoO also shows a reversible transition in the DSC which is associated with antiferromagnetic ordering. The reversible DSC transition in La_2CoO_4 may therefore be associated with antiferromagnetic ordering. Neutron diffraction studies

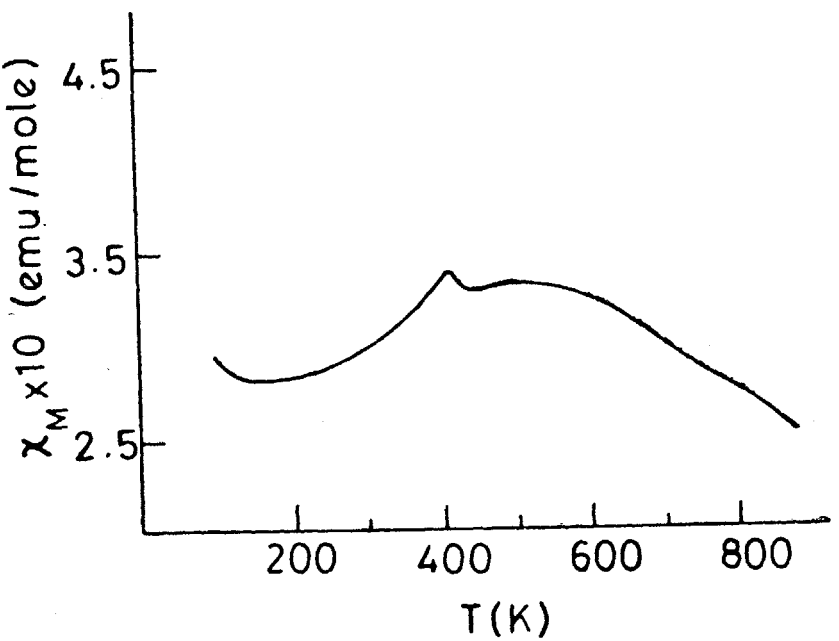

FIG 7 χ_M *vs* T plot of $La_2CoO_{4\cdot03}$.[44]

or Co^{57} Mössbauer source studies would be useful in confirming the presence of antiferromagnetic interactions. Changes in d have a small but definite influence on these transitions, the transition temperature decreasing with increasing d. Just as in La_2NiO_4 stoichiometric samples of La_2CoO_4 also shows a strong field dependence in the susceptibility which persists to high temperatures.

Influence of Dimensionality

Magnetic Properties

The three-dimensional ABO_3 perovskites and the corresponding layered perovskites $ASrBO_4$ ($SrO.ABO_3$) show similar magnetic properties. In Figs. 8–10 we have compared the magnetic susceptibility behaviour of the three-dimensional perovskites $LaNiO_3$, $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.5}Sr_{0.5}MnO_3$ with their two-dimensional analogues, respectively. We see that the magnetic susceptibilities are comparable. There is a small decrease in the paramagnetic Curie temperature for the ferromagnetic samples in two-dimensions which is consistent with their smaller nearest-neighbour spin coordination number. Similarly, $LaSrFeO_4$ and $LaSrCrO_4$ are antiferromagnet[45] just as their three-dimensional counterparts $LaFeO_3$ and $LaCrO_3$ although with reduced Neel temperatures.[2]

In the $La_{1-x}Sr_{1+x}CoO_4$ systems it was noticed[28] that the μ_{eff} values calculated from the slopes of the χ_M^{-1} *vs* T plots just above the Curie temperature corresponds

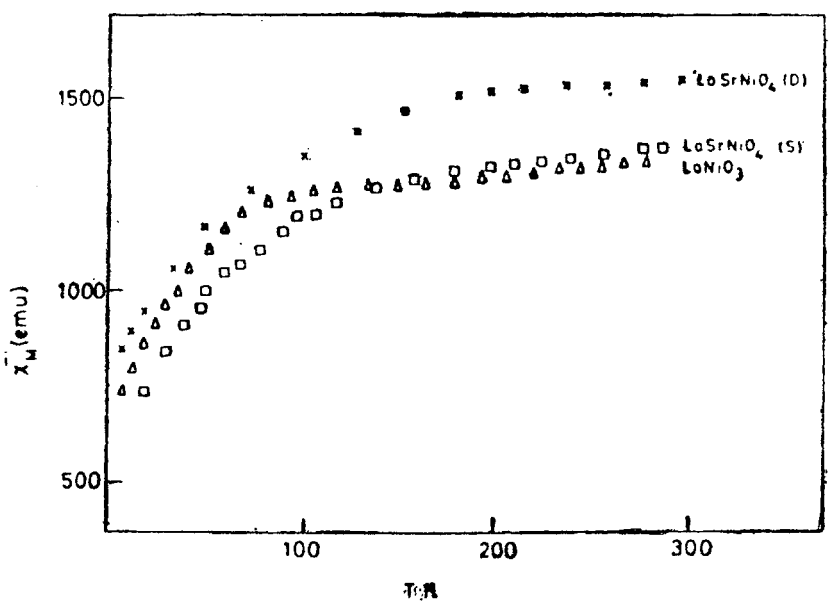

FIG 8 χ_M^{-1} *vs* T plots of $LaNiO_3$ and $LaSrNiO_4$ $LaSrNiO_4$(S) is data of Mohan Ram *et al.*[48] and $LaSrNiO_4$(D) is data from Demazeau *et al.*

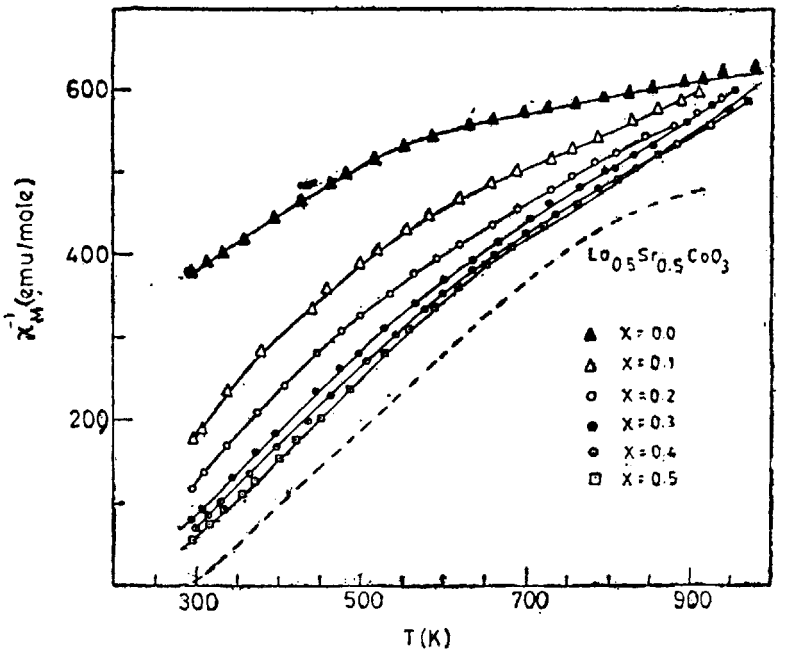

FIG 9 χ_M^{-1} *vs* T plots of $La_{1-x}Sr_{1+x}CoO_4$ and $La_{0.5}Sr_{0.5}CoO_3$ (dotted line).[32]

to an S value of about 0.75 or an average number of 1.5 unpaired electrons. This corresponds to half the cobalt ions being in the intermediate-spin (Co^{III}, t_{2g}^5, e_g^1) state and the other half is in the low-spin tetravalent (Co^{IV}, t_{2g}^5, e_g^0) state. At higher temperatures the μ_{eff} values corresponds to the trivalent ions being in the high-spin state (Co^{3+}, t_{2g}^4, e_g^2). Similar behaviour was observed in the three dimensional systems at high temperatures. In $LaSrCoO_4$ itself magnetic susceptibility studies[45,46] have been interpreted in terms of a low-spin to high-spin transition.

One of the surprising features in these systems is that the magnetic susceptibility of $La_{0.5}Sr_{0.5}MnO_4$ does not diverge at low temperatures despite the high paramagnetic Curie temperature (Fig. 10).[28,47,48] There is thus no long-range ferromagnetic ordering in two-dimensional system although there is such ordering in three dimensions. Similar behaviour was observed in $LaSrMn_{0.5}Ni_{0.5}O_4$ (Fig. 10)[28] although the three-dimensional compound is a true ferromagnet.[49,50] On the other hand $LaSrMn_{0.5}Co_{0.5}O_4$ shows (Fig. 10) a well-defined ferromagnetic ordering temperature just as[27] in $LaMn_{0.5}Ni_{0.5}O_3$.[28] This aspect has not been explained statisfactorily. It may be interesting to see whether systems such as $LaSrMn_{0.5}Ni_{0.5}O_4$ or $La_{0.5}Sr_{1.5}MnO_4$ show metamagnetic behaviour at low temperatures.

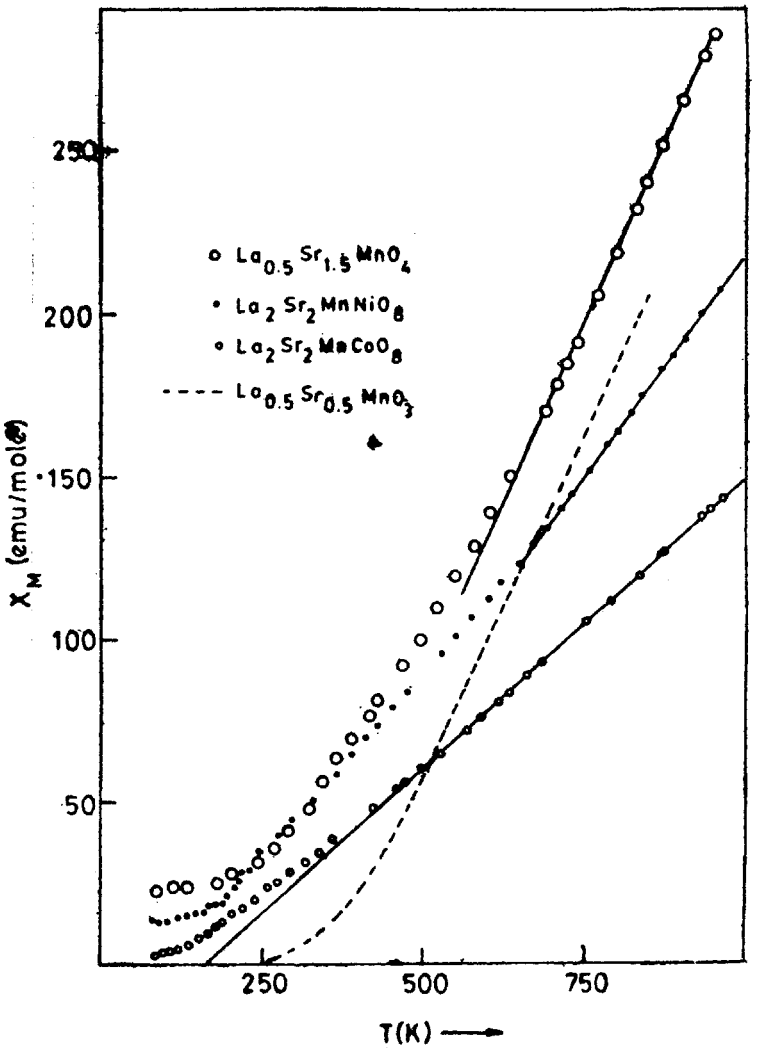

FIG 10 χ_M^{-1} *vs* T plots of $La_{0.5}Sr_{1.5}MnO_4$, $La_{0.5}Sr_{1.5}MnO_4$, $LaSrMn_{0.5}Ni_{0.5}O_4$ and $LaSrMn_{0.5}Co_{0.5}O_4$.[28]

Electrical Transport Properties

Despite the nearly similar magnetic properties the electrical transport properties are qualitatively different as shown in Figs. 11 and 12. In all the cases studied by us so far, oxides which are metallic in the three-dimensional perovskite structure are insulating in the two-dimensional structure. In the tight-binding approximation, the band width is given by $2zb$, where b is the transfer integral. b determines the magnetic ordering temperature for a given spin value along with the correlation energy U for superexchange interactions. Thus the bandwidths should be marginally

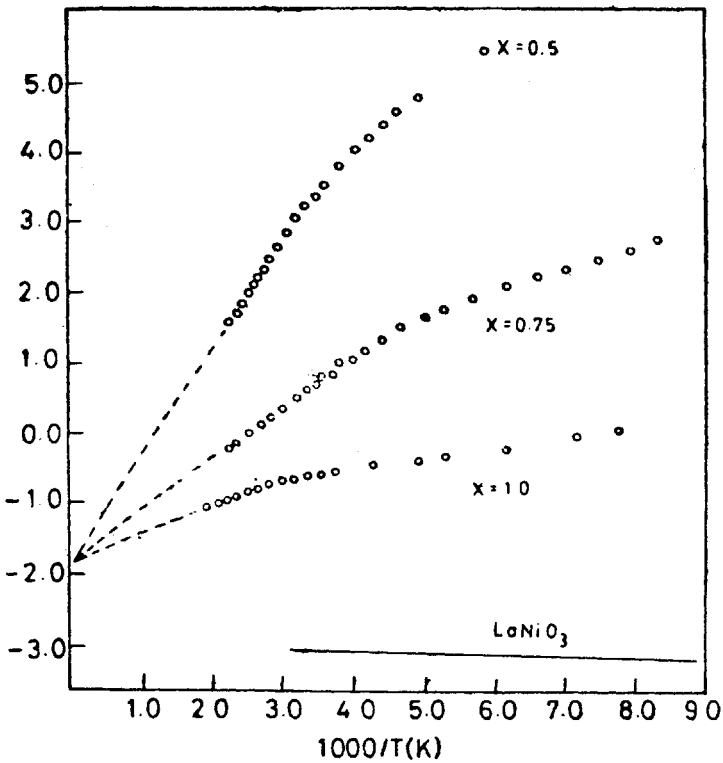

FIG 11 log ρ *vs* $1/T$ plot of $LaSrAl_{1-x}Ni_xO_4$ and $LaNiO_3$.[4,28]

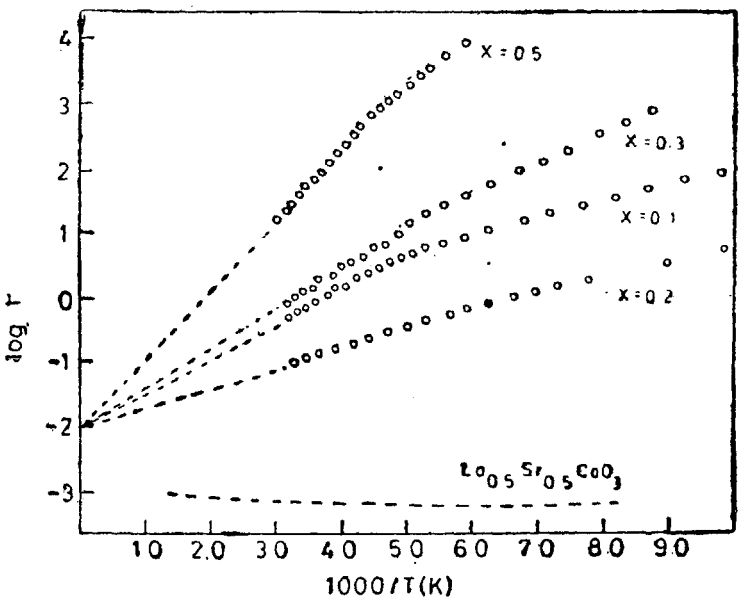

FIG 12 log ρ *vs* $1/T$ plots of $La_{1-x}Sr_{1+x}CoO_4$ and $La_{0.5}Sr_{0.5}CoO_3$.[28]

smaller in the two-dimensional systems and marked changes in conductivity are not anticipated.

Seebeck coefficients do not show any changes in sign in changing dimensions. But there are some differences as far as temperature dependences are concerned. This is best illustrated in the system $La_{1-x}Sr_xCoO_3$.[51] This system is considered to be an itinerant electron ferromagnet. A Zener double-exchange model was rejected on the ground that no anomalies was observed in the Seebeck effect at the magnetic ordering temperature. In the two-dimensional $La_{1-x}Sr_{1+x}CoO_4$ system clear anomalies was seen in the Seebeck effect (Fig. 13) at the magnetic ordering temperature. This is most marked for the $x = 0.5$ sample. These results are consistent with a Zener double-exchange mechanism involving Co^{III} and Co^{IV} ions.

Another interesting difference is in the high-temperature intercept of the log ρ *vs* $1/T$ plots. In three-dimensional systems considerations based on the mobility-edge model and minimum metallic conductivity shows that the intercept in such concentrated systems should approach a value of 10^{-3} ohm cm. In most three-dimensional systems this is actually observed.[6,52] The log ρ *vs* $1/T$ plots of some of the solid solutions $LaSrFe_{1-x}Ni_xO_4$ (Fig. 14), $La_{1-x}Sr_{1+x}CoO_4$, $LaAl_{1-x}Ni_xO_4$

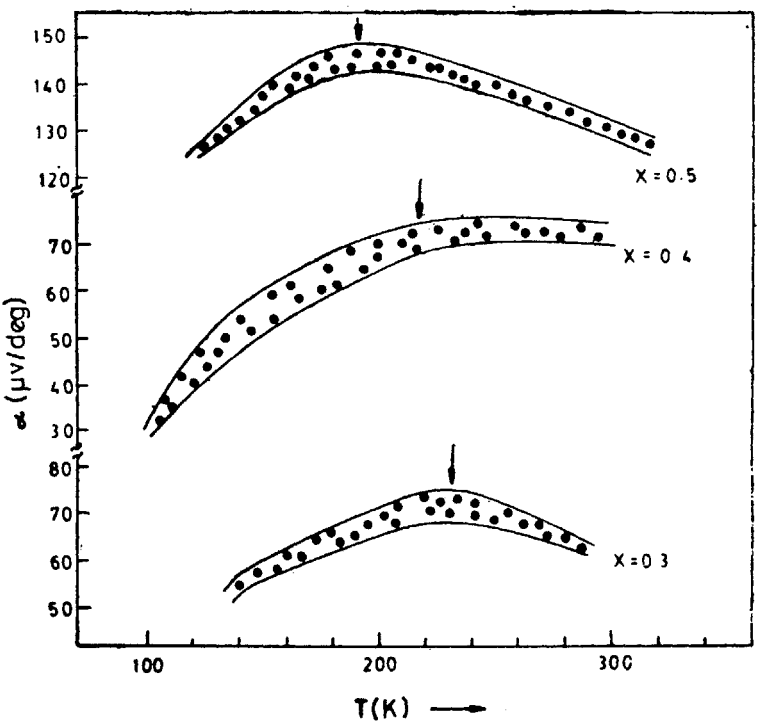

FIG 13 Variation of Seebeck coefficient with temperature for $La_{1-x}Sr_{1+x}CoO_4$. Arrows indicate magnetic ordering temperature.[28]

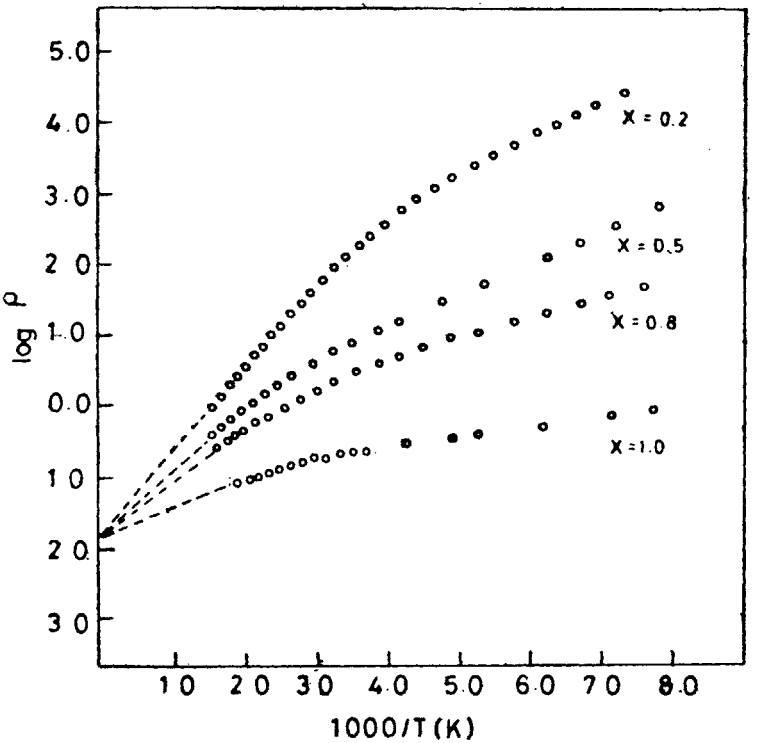

FIG. 14 log ρ *vs* $1/T$ plot of $LaSrFe_{1-x}Ni_xO_4$[17]

(Fig. 17) as a function of x all show an extrapolated high-temperature intercept of $\simeq 10^{-2}$ ohm cm.[28] This discrepancy is difficult to understand. This value is close to the upper limit of small-polaron conduction.[53] Anisotropic bonding in lower dimensions increases polaronic effects.

Among other explanations that may be put forward are the following:

(*i*) there may be metallic conduction in the basal plane and activated conduction along the *c* axis. The conductivity in powdered samples may be dominated by the higher-resistivity component. Single crystal studies should resolve this problem. Anisotropy in electrical conduction of La_2NiO_4 and $La_{2-x}Sr_xNiO_{4+d}$ ($x \sim 0.04$) has been observed.[15,27] In the latter samples, preliminary studies showed that the anisotropy decreases as the conductivity was increased by increasing *d*. In none of these samples, however, did the resistivity in the basal plane decrease below 10^{-2} ohm cm, the limit found from high-temperature extrapolation studies.

(*ii*) The effects may be due to additional disorder that is introduced; for example, the Sr^{2+} ions in $LaSrNiO_4$ as well as the random distribution of the La^{3+} and Sr^{2+} ions. This effect may not be important in the $La_{0.5}Sr_{1.5}BO_4$ systems. It is interesting to note that $BaPbO_3$ is metallic while Ba_2PbO_4 is an insulator.

Comparisons with metallic $SrBO_3$ compounds and the corresponding Sr_2BO_4 compounds should be useful.

(*iii*) We may adopt the suggestion made among others by Mott and Davies[56] that polaronic effects decrease the bandwith without affecting the transfer integral mainly responsible for magnetic interactions. The increase in the metal-oxygen stretching frequency observed in the K_2NiF_4 structures suggests that polaronic effects are stronger. Since compounds such as $LaNiO_3$ and $La_{0.5}Sr_{0.5}CoO_3$ have conductivities close to the minimum metallic conductivity, decrease in bandwidth may easiiy render these systems insulating. In this context, it may be remarked that since almost all oxides undergoing a temperature-induced metal-insulator transition have a low-dimensional character in the insulating phase, and in the metallic phase have conductivity close to σ_{min}, such transition may be controlled by changes in the dimensionality of electrical conduction and is dominated by polaronic effects.

In order to explore the effects of dimensionality further, we have studied the changes in the electrical transport properties of perovskites in the homologous series $(LaO)_n(LaNiO_3)_n$. In these systems the number of perovskite-like layers is n. These studies[23] showed clearly a gradual increase in the conductivity as n was increased. Although the results show a striking dependence on n the choise of the system is unfortunate as there is a change in the number of Ni^{3+} ions. The increase in conductivity with n, however, cannot simply be attributed to the Ni^{3+} content as $LaSrNiO_4$ has a high resistivity. These results seem to imply that σ_{min} increases as the three-dimensional character of the system increases which is consistent with an earlier observations on the value of the high-temperature intercept for the oxides with the K_2NiF_4 structure. Another important feature that emerged from these studies is that the magnetic susceptibility per gram atom of Ni is nearly independent of n although there is large changes in resistivity. $LaSrNiO_4$ and $LaNiO_3$ also show similar magnetic susceptibility behaviour despite large differences in resistivity.

Percolation Effects

It has been demonstrated in studies[54] with fluorides such as $K_2Mg_{1-x}Mn_xF_4$ that Neel temperature drops abruptly to zero when the value of x decreases below the site-percolation threshold value of ~ 0.60. implying that nearest neighbour interactions determine the ordering temperature. In the $LaSrAl_{1-x}Fe_xO_4$ system, the $x = 0.75$ composition showed evidence for long-range order while the $x = 0.5$ sample did not show such evidence down to 12K (Fig. 15). In the three-dimensional system $LaAl_{1-x}Fe_xO_3$ the $x = 0.5$ composition showed both Mössbauer and magnetic susceptibility evidence for the existence of long-range antiferromagnetic order. In the $LaSrAl_{1-x}Ni_xO_4$ system the magnetic susceptibility per g atom of Ni decreases sharply on going from $x_- = 0.5$ to 0.75. It seems therefore that these effects could also be attributed to percolation. The log χ *vs* log T plots in these systems (Fig. 16) was fairly linear over large temperature ranges. The slopes

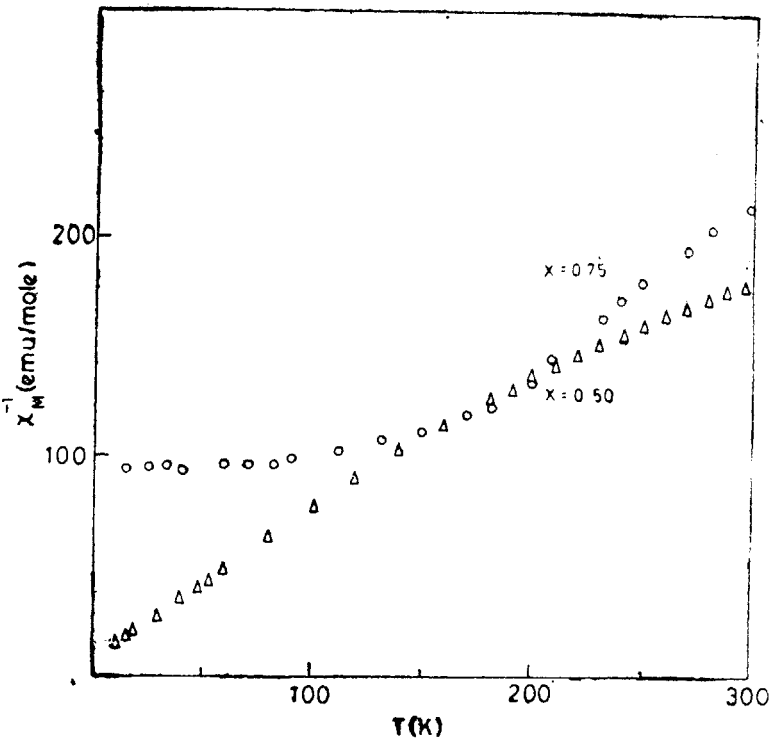

FIG 15 log χ_M *vs* log T plots of some samples.

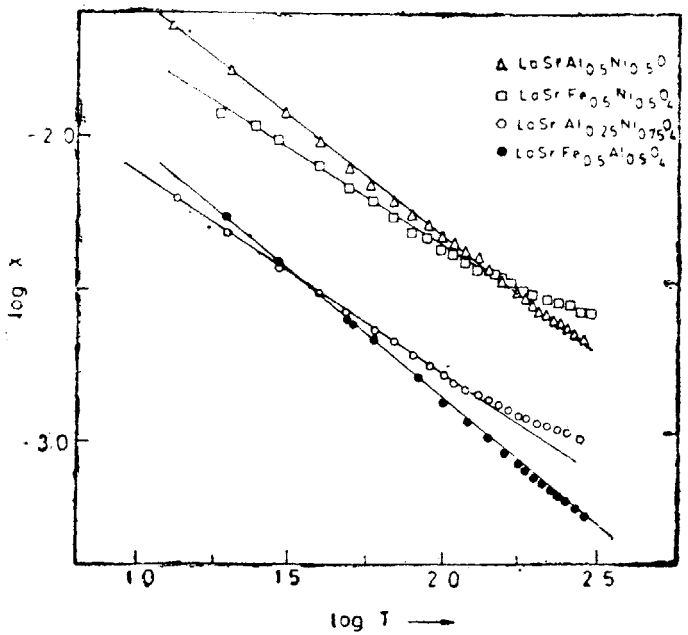

FIG 16 χ_M^{-1} *vs* T plot of $LaSrAl_{1-x}Fe_xO_4$ $x = 0.75$ and 0.5.[27]

were less than 1 implying that the susceptibility obeyed the relation $\chi = C/T^{\beta}$, where β is less than 1. This kind of behaviour is seen in amorphous antiferromagnets.[55] The behaviour in the oxides may then be attributed to the presence of isolated clusters of different sizes within which the spins are antiferromagnetically coupled. These clusters behave like superparamagnetic particles of different spins. The magnitude of the exchange energy between these clusters would therefore be different. The hierarchy of exchange strengths may give rise to the $T^{-\beta}$ dependence observed at low temperatures for the susceptibility. At the lowest temperatures three-dimentional effects may dominate although this has not been seen in our studies.

In the $LaSrNi_{1-x}Fe_xO_4$ system (Fig. 17) it is observed that the magnetic ordering temperature decreases much faster than in the $LaSrAl_{1-x}Fe_xO_4$ system as

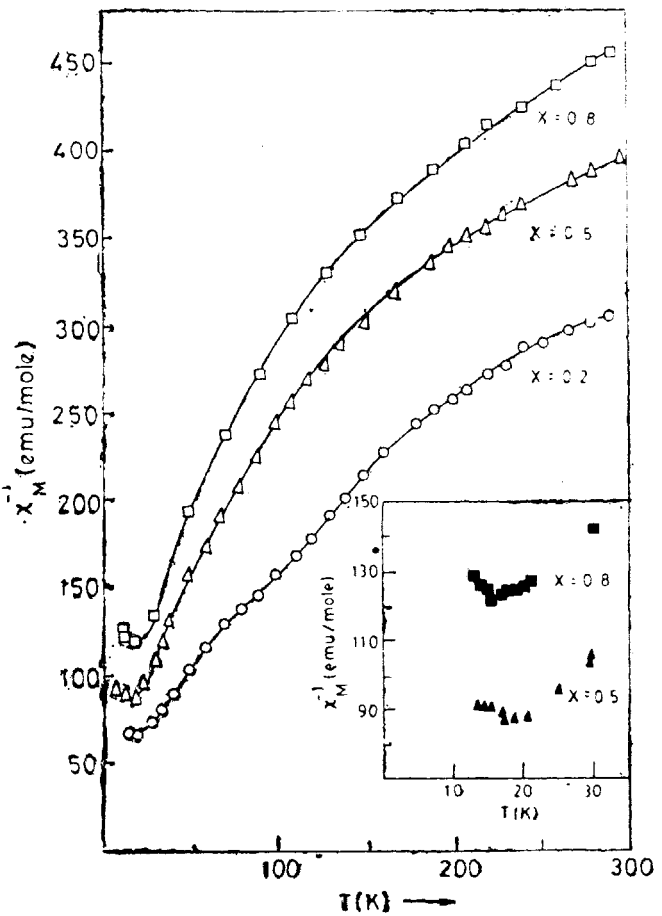

FIG 17 χ_M^{-1} *vs* T plot of $LaSrFe_{1-x}Ni_xO_4$ samples.[28]

seen by a comparison of Figs. 24 and 23 of Ref 28. Apparently, even when x is above the percolation threshold, the Ni ions involve the Fe ions on the periphery of the Fe clusters interactions which oppose the magnetic ordering. Frustration may occur for example if the Ni–Fe interactions are ferromagnetic and the Ni–O–Ni interactions antiferromagnetic. This effectively decreases the concentration of Fe ions in the core of the clusters which are not involved in frustrated interactions. At the lowest temperatures the decrease in the susceptibility (Fig. 17) must be attributed to antiferromagnetic ordering of these clusters. This should be dominated by the strength of the Ni–O–Ni interactions. Similar behaviour is observed in the $LaNi_{1-x}Fe_xO_3$ systems.

Since in these transition metal oxides the magnetic as well as the electrical properties are dominated by the d-electrons, one may expect percolation effects appearing in electrical transport properties as well. We have failed to observe such effects in electrical resistivity studies. However, the sign of the Seebeck coefficient at room temperature shows some correlation. Thus in the $LaM_{1-x}Ni_xO_3$ system (M = Cr, Fe, Co, Mn) the sign of the Seebeck coefficient changes sign from positive to negative when x becomes greater than ~ 0.3 which is the site percolation threshold for a cubic system. In $LaSrAl_{1-x}Ni_xO_4$ and $LaSrFe_{1-x}Ni_xO_4$ such a change in the room-temperature Seebeck coefficient occurs when $x \sim 0.60$. It is interesting to note that in several $La_{1-x}Sr_xMO_3$ systems (M = Co, V, Mn) the metal-insulator transition is observed when $x = 0.28 \pm 0.02$ which is close to the site-percolation threshold value for three-dimensional systems.[6] We note that in these three-dimensional systems the $0.70 < x < 0.30$ compositions have connected paths of both trivalent and tetravalent ions. Such a situation is not possible in the two-dimensional systems. Whether this has a role to play in explaining some of the anomalous properties has yet to be examined.

Acknowledgement

The author would like to thank Professor C N R Rao for his encouragements. He would also like to thank the University Grants Commission for support of this research.

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