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Comments on Electronic Transport in Transition Metal Oxides

Abstract: Several aspects of electronic transport in nonmagnetic and magnetic transition metal oxides are reviewed. These include high- and low-temperature measurements of conductivity, the Hall effect and the Seebeck effect, and their analysis in terms of the electronic energy structure. Particular emphasis is put on the temperature dependence of the Hall mobility, which gives essential information concerning the correct description of the energy states and the scattering of the charge carriers. The second half of the paper discusses the relation between the transport properties and the magnetic ordering. The properties of $LaCoO_3$ together with an interpretation suggested by Goodenough are presented to illustrate this point.

Introduction

Among the different families of semiconducting compounds the group of transition metal oxides occupies a very special position. Its members cover an extremely wide range of different properties; attempts to discover any systematic trends in the physical and chemical characteristics of closely related materials have met only with very limited success. In discussing the transport properties, one has to pay attention to many different aspects of these compounds, such as

1) the physical chemistry of the materials (crystal perfection, nonstoichiometry, order-disorder, etc.),
2) the description of the electronic energy states (localized or band model), and
3) the relation between the transport properties and the magnetic ordering.

In recent years a number of survey articles on transition metal oxides have appeared in the literature. These reviews give a good picture of the evolution in ideas concerning this family of compounds.

The Buhl Conference[1] of 1963 presented a dozen papers covering a wide variety of topics including electronic and mass transport, structural (dis)order, magnetic exchange and the question of "localized-or-band" electron states. At that time the "hopping" picture[1] was still considered to be the most acceptable model for electrical conduction in materials like NiO. Since then, several workers[2–7] have been able to measure the Hall effect in a number of transition metal oxides, and consequently the band picture has gained considerable support. The present situation has been described in ample detail by Adler.[8,9]

Goodenough[10,11] has discussed the transition metal oxides several times, emphasizing the magnetic exchange and chemical bond aspects. A comprehensive review of the polaron problem by Appel[12] stresses the *possible* interpretation of the electrical and optical behavior of several transition metal oxides in terms of the small-polaron picture. Covering somewhat the same area, the theoretical aspects of electrons strongly coupled to optical phonons have been surveyed at some length by Klinger.[13] The basic question in all these discussions is, What are the criteria for calling a mobility "low"? Many semiconductors might have mobilities of the order of 0.1 to 1 cm^2/V-sec at high temperature or at room temperature, but further down (100, 10 or 1°K) the mobility climbs to values of 10^2, 10^3, or even 10^4 cm^2/V-sec. The magnitude and temperature dependence of the Hall mobility are the major keys to an understanding of charge transport in transition metal oxides. On the one hand these quantities can decide the question of the most suitable description of the electronic energy states, and on the other they provide information about the dominant scattering mechanisms in different temperature ranges.

With the realization of the importance of the Hall mobility in mind, we review in this paper some aspects of electron (or hole) conduction in the transition metal oxides. First we make some remarks concerning transport measurements at high and at low temperatures and the interpretation of such experiments. This is followed by a brief discussion of the question "band- or hopping-conduction." Finally we address ourselves to the major

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topic of this conference: the relation between the magnetism and the (semi) conductivity of the oxide. The ternary compound $LaCoO_3$ has been chosen to illustrate the latter aspect.

High-temperature behavior

Analysis of the properties of transition metal oxides at high temperatures is encumbered by the fact that the composition is not constant. Like many other oxides (and sulfides, selenides, etc.) these compounds decompose. This is due, of course, to the rather rapid ionic diffusion or ionic conductivity at temperatures above 500 to 1200°C (depending on the compound). Although the electronic diffusivity (mobility) in the majority of oxides is considerably larger than that of the ions, it is nevertheless necessary to realize that one deals with "mixed conduction." Investigation of the electronic transport in oxides at high temperatures requires, therefore, more measurements than at room temperature. First of all, the conductivity has to be measured as a function of both temperature and oxygen pressure, and preferably with respect to ac as well as dc conduction. Furthermore, experiments should be performed on single crystals (if possible), or at least on ceramic samples with large density (within a few percent of bulk density), and on a number of specimens with different grain size. In this way one hopes to be able to avoid grain boundary and surface effects. If the objective is to obtain the three major electronic parameters (number of charge carriers n, effective mass m^* and mobility μ), it is necessary to measure three transport properties, e.g., conductivity σ, Hall coefficient R_H and Seebeck coefficient S.[14] Each of these quantities has to be determined over a considerable range of pressure P (at constant temperature) and of temperature T (at constant pressure). It appears that the gas pressure dependencies of the quantities σ, R_H and S have characteristic shapes: The conductivity plotted against log P has a minimum,[14,15] while both R_H and S show S-shaped curves with a minimum at the n-type (low pressure) side and a maximum in the p-type (high pressure) range.[14] The determination of the parameters n, m^* and μ from these curves is considerably simplified if one makes use of the extremal and reversal points.

The intrinsic energy gap may be deduced from the shift of the conductivity minimum σ_{min} (ln σ vs ln P) as a function of temperature.[14]

$$d \ln \sigma_{min}/d\,(1/T) = E_g/2k.$$

The above analysis is independent of the nature of the defect. Some information concerning the *type of defect* and its degree of ionization can be obtained from the slope of ln σ vs ln P.

Two of the most important results of transport measurements are the magnitude of the Hall mobility and its dependence on temperature. Many investigators of high-temperature conductivity have added to the confusion by reporting mobilities deduced either from insufficient data or from results obtained on poor quality crystals. A few years ago it was shown that reliable measurements of Hall coefficients could be made on such oxides as NiO, CoO and Fe_2O_3, even at temperatures above 1000°C.[7] The resulting Hall mobilities are small (10^{-2} to 10^{-1} cm^2/V-sec) and show a slight decrease with rising temperature.

Low-temperature experiments

Measurements at temperatures below room temperature are desirable in order to obtain information about the scattering mechanisms and the density of intrinsic and extrinsic electron states. In most semiconducting oxides both the resistivity and the Hall effect increase rapidly with decreasing temperature. In fact, in most cases this rise is so steep that the material virtually becomes an insulator at temperatures of the order of 100°K. At these temperatures oxides like Cu_2O,[16] CoO[7] and $BaTiO_3$[17] reach resistivity values of 10^5 to 10^{10} ohm-cm in spite of heavy doping or considerable non-stoichiometry. Often the activation energies for samples of the same material range from a few hundredths of an electron volt to 0.5 or 1.0 eV.[18] This is due to a varying amount of compensation; most oxides contain large numbers of donors and acceptors, some of them shallow and others quite deep.

Only a few oxides are metals or degenerate semiconductors and consequently show a nearly independent Hall coefficient all the way down to liquid helium temperatures. Such behavior has been observed, for example, in CrO_2 (metal)[19] and in $SrTiO_3$[20] and $KTaO_3$.[21] In the latter two cases the donor activation energies are extremely small (10^{-6} to 10^{-7} eV) as a result of the very high dielectric constants. (The conductivity and Hall effect of TiO_2 can be followed down to 4°K; however, the electron gas is nondegenerate due to a somewhat higher effective mass.)[22]

The fact that some oxides show a (very sudden) transition from semiconductor to metallic behavior has been discussed by several authors[23] in these proceedings. We will come back later to the rather puzzling behavior of some magnetic and ferroelectric oxides.

Charge carrier mobility

As mentioned earlier, the temperature behavior of the Hall mobility can serve as a clue to an appropriate model for the electronic energy states of a given solid. The basic features of the low carrier mobility in polar semiconductors have been most clearly described by Holstein.[24] If the mean free path of the electron (or hole) is of the same order as the cell dimension, the carrier will not experience the translational symmetry of the lattice. Hence the Bloch

function and energy-band concepts are not valid for describing the electronic states in this case. At low temperature the charge carrier will tunnel from site to site, which is equivalent to a band description. At higher temperatures [$T > \frac{1}{2}\theta$ (the Debye temperature)], the only possibiltiy of transport is activated "hopping" (diffusion mechanism). Consequently, Holstein predicts for this case (small polarons) a mobility which decreases at temperatures below $\frac{1}{2}\theta$ and increases exponentially with rising temperature at $T > \frac{1}{2}\theta$.

Experimental observation of such a temperature dependence would be extremely interesting for testing the small-polaron ideas. However, it is questionable if a mobility minimum has ever been observed in any transition metal oxide (or in any other polar semiconductor). Consequently it appears that the hopping mechanism is *not* the proper description for conduction in these materials. Of course, polaron effects do play a role. However, the electron-phonon coupling constant[25] α is usually of the order of 1 to 6 (intermediate coupling range) and hence we are dealing with moderately "dressed" electrons.

Conduction by large polarons in a conventional energy band has been abundantly demonstrated[26] in $SrTiO_3$. The band structure calculated by Kahn and Leyendecker[27] has been confirmed by a considerable amount of experimental evidence.[28] Due to the high dielectric constant of $SrTiO_3$,[29] electrons are not bound to shallow donors, but move in a conduction band over a very wide temperature range (10^{-2} to 10^{3}°K). Hence, the number of charge carriers is independent of temperature and the crystal lends itself well to a study of the scattering mechanism. Measurements of the Hall mobility in La- or Nb-doped samples between 300 and 1000°K showed an exponential decrease with increasing temperature.[26] Around 1000°K the slope corresponded to an activation energy of 0.10 to 0.12 eV, while at 600°K an energy of $\approx$ 0.06 eV was observed. These values agree rather well with the energies of the highest LO_1 (longitudinal optical) phonon (0.099 eV) and the second highest LO_2 phonon (0.058 eV) in $SrTiO_3$.[30] Hence it seems that the dominant scattering mechanism above room temperature is optical mode scattering. The electron-phonon coupling constant α was calculated by Eagles[31] and found to be 2.6 for the LO_1 mode and 0.7 for the LO_2 mode. Low and Pines[32] have derived an expression for the intermediate coupling range. Quantitative agreement between the data of Ref. 26 and their predictions is another confirmation of the optical-mode collision process in $SrTiO_3$.

A recent study[33] of electron scattering in a number of (pseudo) ferroelectric semiconductors ($SrTiO_3$, $BaTiO_3$ and $KTaO_3$) has pointed out the remarkable similarity between the pressure dependence of the mobility and the reciprocal (static) dielectric constant of these materials. On this basis these workers have suggested that the electron scattering is caused by the polarization fluctuations associated with the soft TO (transverse optical) mode. The fact[34] that the mobility of electrons in $BaTiO_3$ in the range 300 to 450°K does not show any discontinuity at the Curie point casts some doubt on this allegation. Considering that neither the magnitude nor the temperature dependence of such an electron-phonon interaction has been worked out in any detail, we see it remains difficult to assess the validity and relevance of the proposed scattering mechanism.

Conduction in magnetic semiconductors

So far we have paid attention mainly to the non-magnetic transition metal oxides. However, many members of this group are either ferromagnets or antiferromagnets, and it is a prime topic of current study to explore the possible relation between semiconductivity and spin ordering. We use the word "possible" because the nature or even the existence of this relation is not at all clear. A survey of the transition metal oxides[8] shows a rather confusing picture. Most ferromagnets (CrO_2 and a few others) are metals. Insulators are very seldom ferromagnetic; EuO[35] (not a transition metal oxide) and one or two other compounds are the exceptions. Many of the antiferromagnetic oxides are insulators or semiconductors; some of them undergo a transition to the metallic state, often, but not always, at the Néel point. The occurrence or absence of this transition is one of the more puzzling aspects of the transition metal oxides. This is clearly illustrated by contrasting the well known behavior of the following two groups. NiO, CoO, and FeO are definitely antiferromagnetic solids; however, the (doped) semiconductors show only a slight change in the slope of the conductivity at the Néel point, but no discontinuity.[5] On the other hand, in VO_2, V_2O_3, and Ti_2O_3 one observes transitions in conductivity of 1 to 6 orders of magnitude.[36] Nevertheless, VO_2 exhibits no long-range magnetic order[9] and the antiferromagnetism of V_2O_3 and Ti_2O_3 is reported by some [37,38] and denied by others.[39,40]

In crystals like VO_2, the metal-semiconductor transition is explained[41] by the generation of an energy gap at the Fermi level. Above T_t two (or more) 3d bands overlap and are half-filled (metal). Below T_t a pairing of the vanadium ions takes place; hence the size of the Brillouin zone is halved and the energy band is split in two with a small gap in between. One assumes that the lower band is entirely filled and the higher one empty, producing a semiconductor. For a solid like VO_2, that does not show any magnetic ordering, the reason for the ion pairing is not clear. In contrast, one would expect that a similar band doubling takes place in antiferromagnetic materials (e.g., NiO) where the pair formation is obvious. It is possible that in this case the Fermi level lies close to the bottom of a nearly empty conduction band (or near the

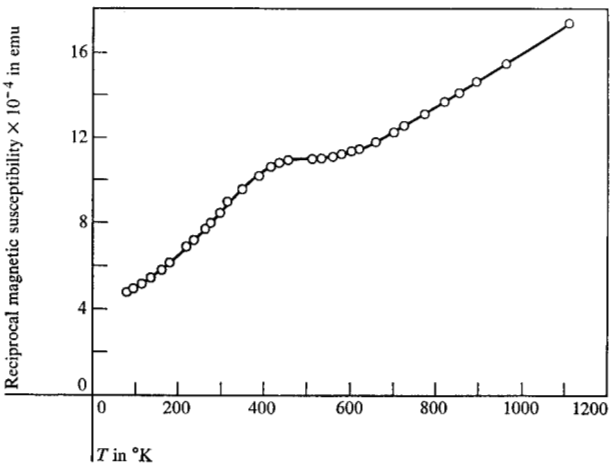


Figure 1 Reciprocal magnetic susceptibility vs temperature for $LaCoO_3$ (after Heikes et al., Ref. 42).

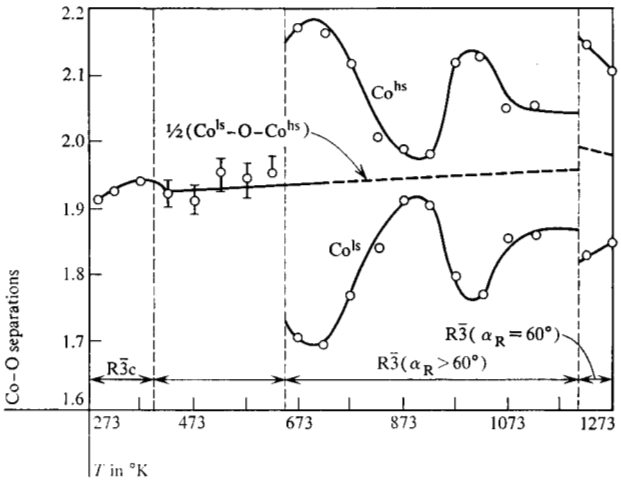


Figure 2 Cobalt-oxygen separations in $LaCoO_3$ as a function of temperature (after Raccah and Goodenough, Ref. 43).

top of a nearly filled valence band). Hence a doubling of the energy bands will cause no important change in the distribution of electrons and the conductivity will hardly be affected.

Magnetism and conduction in $LaCoO_3$

A number of experimental and theoretical studies of this "perovskite" crystal performed during the last five years are of considerable importance for the understanding of transition metal-oxygen compounds. Let us first look at the data.

The *magnetic susceptibility*[11,42] (Fig. 1) shows two regions with different slopes separated by a transition range of about 250°K (400 to 650°K). The magnetic moment in the high temperature range corresponds to $\sqrt{15.7}\ \mu_B$, and below 400°K to $\sqrt{9.4}\ \mu_B$.

X-ray measurements[43] (Fig. 2) indicate that the crystal is rhombohedral throughout the entire temperature range. However, the local symmetry changes three times: at 400°K, 650°K and 1210°K.

Measurements of the electrical *resistivity* and *Seebeck coefficient* by Heikes et al.[42] (Figs. 3 and 4) are in good agreement with those made by Acket.[44] The latter also determined the *Hall coefficient* (Fig. 3). The temperature dependence of the Hall coefficient parallels that of the resistivity; this behavior favors an exponentially increasing carrier concentration.

An intercomparison of these data leads to an interesting, qualitative picture of the magnetic and electrical behavior of this compound. Most of this picture is similar to the one drawn by Goodenough.[11] However, his assumption of "hopping"-type conduction (at least up to room temperature) is difficult to accept in the light of Acket's Hall measurements.

A glance at Fig. 1 indicates that the compound follows two different Curie-Weiss laws in different temperature ranges. This reminds us of the fact that Co can exist in two different spin states depending on the strength of the crystal field. These spin states have different magnetic moments (see above). This fact has been recognized by both Goodenough and Heikes; however, the former speaks of the diamagnetic state $s = 0$ and the paramagnetic state $s = 2$, while Heikes considers the low-temperature low-field state as the one having a spin $s = 1$. It is unfortunate that no susceptibility measurements have been performed at liquid helium temperature. The curvature of $1/\chi$ around 100°K might indicate that this quantity would reach zero slope at very low temperature.

The different spin and valence states of Co^{3+} are shown in Fig. 5(a–e). It is well known that the (octahedral) crystal-field splitting Δ_{cf} and the exchange energy Δ_{ex} of Co^{3+} are of the same order of magnitude ($\approx$1 eV).

The energy difference between the high-spin and the low-spin states is only 0.05 to 0.1 eV. Because both Δ_{cf} and Δ_{ex} depend on the inter-atomic distances, it is obvious that both of these quantities will vary with temperature. Consequently ($\Delta_{cf} - \Delta_{ex}$) will strongly depend on temperature.

The main aspects of the interpretation of the data as presented by Goodenough (and somewhat similarly by Heikes et al.) are as follows. At absolute zero the ions are all in the low-spin state (Co^{ls}). Between 0°K and 400°K high-spin states (Co^{hs}) are created by excitation across an energy gap of the order of 0.05 to 0.1 eV.

As a result of this process the upper level (e_g) of the spin-up states will become populated by electrons while holes are being created in the t_{2g} levels of the spin-down states. This situation is somewhat analogous to the pro-

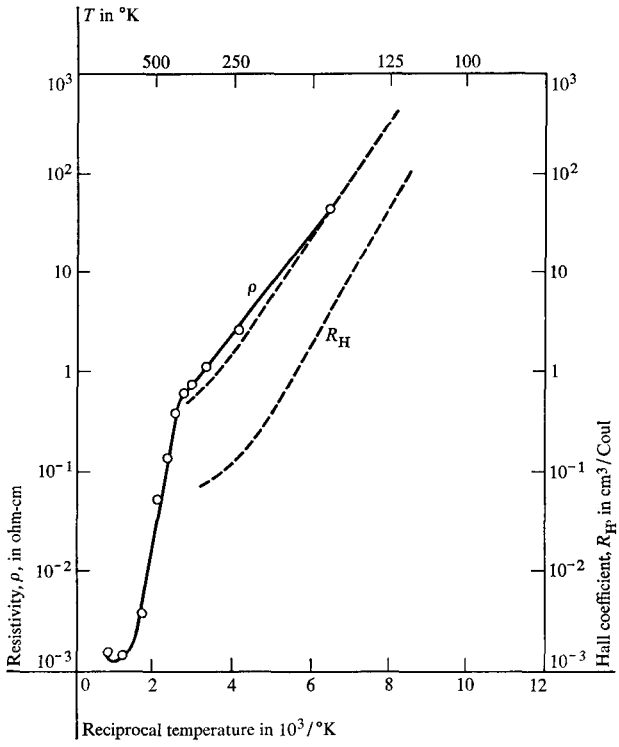


Figure 3 Electrical resistivity vs. $1/T$ for $LaCoO_3$ (after Heikes et al., Ref. 41), (solid line). Electrical resistivity and Hall coefficient vs. $1/T$ for $LaCoO_3$:0.2% Sr (after Acket, Ref. 43), (dashed lines).

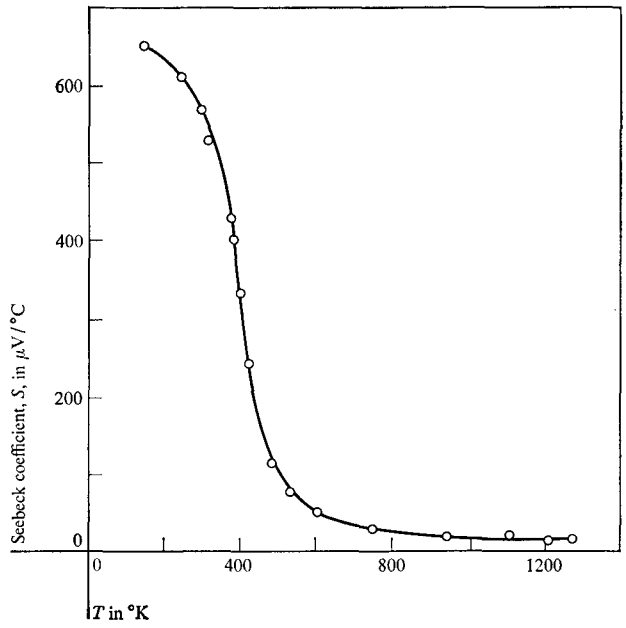
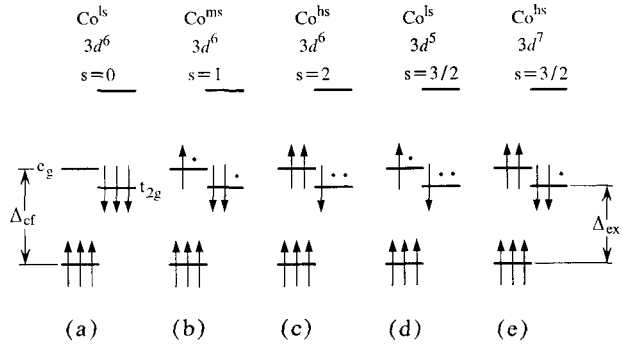


Figure 4 Seebeck coefficient as a function of temperature for $LaCoO_3$ (after Heikes et al., Ref. 42).

Figure 5 (a-e) Several spin-states of Co^{3+}, Co^{4+}, and Co^{2+} ions. Δ_{cf} is the crystal-field splitting and Δ_{ex} is the exchange splitting. [The dots refer to the unoccupied states (holes) in the e_g and t_{2g} levels.]



duction of electrons (in the conduction band) and of holes (in shallow donor states) when the temperature of an n-type semiconductor is raised from helium temperatures. In the present case the number of donors (high-spin Co ions) is not constant, but increases with temperature much like the formation of oxygen vacancies at high temperature. The electron excitation as discussed here will give rise to conductivity first primarily in the "conduction" levels. As the donor concentration increases, one expects the formation of a donor band which will widen and hence produce a decrease in the donor activation energy. In the temperature range 400 to 650°K, the numbers of Co^{ls} and Co^{hs} will reach equality, and an ordering of the two ions on alternate (111) planes will begin to take place: [— — — Co^{ls} — La — Co^{hs} — La — Co^{ls} — La —]. The rapid production of Co^{hs} ions will increase the susceptibility, while the ordering will decrease the energy difference ($\Delta_{cf} - \Delta_{ex}$) and thereafter give rise to a fast rise in conductivity.

The ordering process is completed at about 650°K, and above this temperature long-range order is established. Because the high-spin Co^{3+} ion has a larger radius than the low-spin Co^{3+} ion, conservation of elastic energy requires that the oxygen ions will move closer to Co^{ls} and somewhat further away from the Co^{hs}. X-ray data have confirmed such an asymmetry (Fig. 2). As a result of these displacements the covalency of both kinds of Co ions will not remain the same. The $(Co^{3+})^{hs}$ will tend to change its charge and become $(Co^{4+})^{ls}$, while the low spin Co^{3+} ion will transform into $(Co^{2+})^{hs}$. These processes involve charge transfer; because four different Co ions [Co^{2+}, Co^{4+}, $(Co^{3+})^{hs}$ and $(Co^{3+})^{ls}$] are now present in large numbers, a metallic type conduction is expected. Both the magnetic behavior and the conductivity results are in agreement with these predictions (Figs. 1, 3 and 4).

Goodenough in his analysis[11] considers the charge carriers (electrons and holes) localized on the Co ions. However, the Hall data of Acket[43] lead to a Hall mobility of the order of 0.1 cm^2/V-sec at room temperature, slowly

increasing with decreasing temperature; no thermally activated mobility is involved. It seems, therefore, that we have to modify the above picture of Co ions with sharp energy levels into one where these levels are broadened into narrow bands ($\Delta E \approx 3$ to 4×10^{-2} eV) in accordance with an effective mass $m^* = 30m_e$.[43]

In spite of the difficulties concerning the (non) localization of the charge carriers, the model sketched above has many attractive points. The idea, first mentioned by Goodenough,[10] of a subtle balance between ions in different spin- as well as charge-states, producing noncooperative transitions from the insulating to the metallic phase may well have wide applicability to a large number of cubic and rhombohedral oxides.

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