JOURNAL OF SOLID STATE CHEMISTRY **90**, 168–172 (1991)

LETTERS TO THE EDITOR

Simple and Perovskite Oxides of Transition-Metals: Why Some Are Metallic, While Most Are Insulating

JERRY B. TORRANCE AND PHILIPPE LACORRO*
IBM Research Division, Almaden Research Center, 650 Harry Road,
San Jose, California 95120-6099

AND CHINNARONG ASAVAROENGCHAI AND ROBERT M. METZGER
Department of Chemistry, University of Alabama, Tuscaloosa,
Alabama 35487

Communicated by J. M. Honig, October 1, 1990

Some 76 simple and perovskite transition-metal oxides are classified as "metals," "insulators," and those exhibiting metal–insulator transitions. Using the framework of Zaanen, Sawatzky, and Allen and a simple ionic model to estimate the two relevant energies (Δ_0 and U_0'), we can find boundaries which separate the insulating oxides from two types of metals: low Δ_0 metals and low U_0' metals. In addition, compounds with metal–insulator transitions are found to be on (or near) these boundaries. It is concluded that the large *differences* in conductivity behavior of oxides are largely due to differences in the ionization potentials of the transition metal cations. © 1991 Academic Press, Inc.

The discovery (*1–3*) of superconductivity at high temperatures has generated considerable effort at understanding the physical properties of bismuth and copper oxides. It is important to recognize that these oxides are members of the broad class of perovskite and simple transition metal oxides that usually do not exhibit metallic conductivity and even less often exhibit superconductivity. As part of an overall understanding of high temperature superconductivity, it is important to understand the fundamental electronic energies that determine why some oxides are metallic, whereas the majority have low conductivity. It is these fundamental energies for the undoped oxide systems that provide the basis for understanding the hole-doped systems and lie behind the assumptions of the various theories for high-temperature superconductivity.

The conductivity of a large number of simple and perovskite oxide compounds has been compiled in several review articles (*4–9*). In Table I we list (*10*) 76 such systems involving transition metals (including rare earths) in formally divalent (II), trivalent (III), and tetravalent (IV) oxidation states. Here the conductivity behavior of these ox-

---

[*] Permanent address: Laboratoire des Fluorures, Faculté des Sciences, Université du Maine, F-72017 Le Mans, France.

0022-4596/91 $3.00

0022-4596/91 $3.00
Copyright © 1991 by Academic Press, Inc.
All rights of reproduction in any form reserved.

TABLE I

BINARY OXIDES M_yO_z AND PEROVSKITE (OR PEROVSKITE-LIKE) OXIDES $A_xM_yO_z$ (ORDERED BY ATOMIC NUMBER, THEN BY FORMAL VALENCE): CONDUCTIVITY (M = METALLIC, I = INSULATING), OXYGEN–METAL ATOM MADELUNG SITE POTENTIAL DIFFERENCES ΔV_M (VOLTS), AND PARAMETERS U_0' (eV) AND Δ_0' (eV)

Compound	Conductivity	ΔV_M(V)	U_0'(eV)	Δ_0'(eV)
TiO	M	48.2	9.0	20.0
Ti_2O_3	M/I	58.3	10.8	15.9
$LaTiO_3$	M/I	58.2[a]	12.2	15.8
TiO_2	I	70.6[b]	51.1	12.3
$SrTiO_3$	I	69.4	52.3	11.1
Sr_2TiO_4	I	70.4	52.2	12.0
VO	M	49.6	9.7	19.8
V_2O_3	M/I	57.7	12.5	13.6
$LaVO_3$	I	58.6[a]	13.7	14.4
$LaSrVO_4$	I	59.4[c]	13.7	14.9
VO_2	M/I	71.8[b]	13.5	9.9
$SrVO_3$	M	70.7	14.8	8.7
Sr_2VO_4	I	70.7[c]	14.8	8.7
Cr_2O_3	I	60.3	13.0	14.3
$LaCrO_3$	I	59.3[a]	14.4	13.3
$LaSrCrO_4$	I	60.5[d]	14.4	14.3
CrO_2	M	72.6	15.3	8.2
$SrCrO_3$	M	71.0[d]	16.4	6.7
MnO	I	45.4	13.4	15.6
β-Mn_2O_3	I	60.2	12.9	11.6
$LaMnO_3$	I	59.9	13.8	11.2
$(La,Sr)MnO_4$	I	59.3[d]	13.8	10.5
β-MnO_2	M	73.3	16.2	6.8
$SrMnO_3$	I	68.1[d]	17.6	2.0
Sr_2MnO_4	I	71.6[c]	17.4	5.1
FeO	I	46.7	9.7	16.1
α-Fe_2O_3	I	59.6	19.3	13.9
$LaFeO_3$	I	58.4[a]	20.5	12.9[a]
$LaSrFeO_4$	I	59.2[c]	20.4	13.4
$SrFeO_3$	M	70.1	16.5	0.1
CoO	I	47.2	11.7	15.7
La_2CoO_4	I	50.4[c]	12.7	18.2
$LaCoO_3$	I	60.9	14.1	12.2
$LaSrCoO_4$	I	60.5[c]	14.0	11.7
$SrCoO_3$	M	70.2	24.5	3.7
NiO	I	48.3	12.1	15.3
La_2NiO_4	I	49.6[c]	13.3	16.2
$LaNiO_3$	M/I	61.0	16.0	10.7
$LaSrNiO_4$	M	60.0[c]	16.0	9.6
CuO	I	48.0	11.6	12.6
La_2CuO_4	I	49.2[c]	12.8	13.7
$LaCuO_3$	M	60.5	14.6	8.6
$LaSrCuO_4$	M	60.4[c]	14.6	8.2
NbO	M	41.1	5.9	12.3
NbO_2	I	67.8[d]	7.1	14.7
β-MoO_2	M	69.2[b]	10.1	7.8
$SrMoO_3$	M	68.2	11.2	6.9
Sr_2MoO_4	M	69.2[d]	11.1	7.8
$LaRuO_3$	M	58.1[d]	12.7	14.8
RuO_2	M	70.4	12.4	5.4
$SrRuO_3$	M	69.1[d]	13.3	4.2
Sr_2RuO_4	M	70.1[d]	13.3	5.1
Rh_2O_3	I	58.7[b]	12.5	12.8
$LaRhO_3$	I	58.4[d]	13.8	12.5
RhO_2	M	70.6	12.6	2.0
SnO	I	39.0	12.0	10.1
SnO_2	I	67.9	27.0	12.4
$SrSnO_3$	I	67.2[d]	28.0	11.6
Sr_2SnO_4	I	68.4[c]	28.0	12.8
LaO	M	39.1	4.2	14.8
La_2O_3	I	49.0	27.0	16.0
CeO	M	39.6	5.4	15.3
Ce_2O_3	I	49.5[b]	12.8	15.5
CeO_2	I	61.9	24.3	11.3
$SrCeO_3$	I	63.2[d]	24.8	12.0
PrO	M	40.0	7.0	16.1
Pr_2O_3	I	50.0[b]	13.6	14.5
PrO_2	I	62.5	14.7	9.6
$SrPrO_3$	I	63.4[d]	15.1	10.0
NdO	M	40.3	7.3	16.1
Nd_2O_3	I	50.6[b]	14.5	14.6
EuO	I	39.1	9.7	14.6
Eu_2O_3	I	51.0	13.3	12.1
YbO	I	41.3	8.7	15.5
Yb_2O_3	I	52.8	14.6	13.7
$LaYbO_3$	I	54.3	15.4	14.9

[a] Averaged between crystallographically inequivalent sites.
[b] Ref. (*12*).
[c] In-plane *M* and O only.
[d] Estimated (from known calculations) or for approximate crystal structure.

ides has been crudely and arbitrarily divided into "metals" and "insulators" on the basis of the magnitude of their conductivity, $\sigma(300\ \mathrm{K})$, at room temperature: "metals" are defined as having $\sigma(300\ \mathrm{K}) > 1$ S/cm, while "insulators" have $\sigma(300\ \mathrm{K}) < 1$ S/cm. A few oxides have metal–insulator transitions and are so labeled in Table I.

A simple, and yet powerful, framework which includes correlation effects has been introduced and developed by Zaanen, Sawatzky, and Allen (ZSA) (*11*). According to this picture, oxides (as well as halides, sulfides, etc.) can be described in terms of

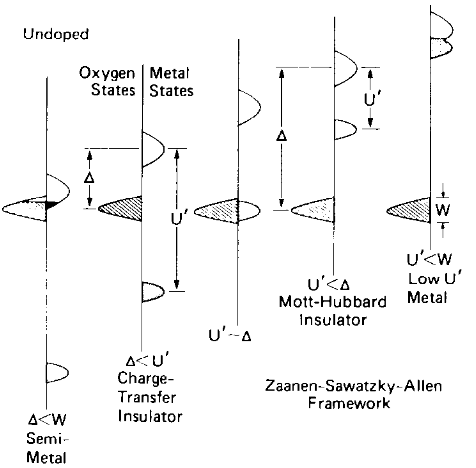

FIG. 1. A schematic diagram of the energy levels of the ZSA framework, specifying the definitions of Δ, U'_0, and W.

the relative energies of three electronic energy levels near the Fermi level, shown in Fig. 1. The fully occupied oxygen $2p$ states are shown as the shaded band on the left side of the vertical energy axis. On the right side of the vertical energy axis and shown unshaded is the lowest unoccupied metal orbital (corresponding to the metal conduction band) which lies at an energy Δ above the former. Δ is seen to increase in going toward the right in Fig. 1. This unoccupied metal orbital lies at an energy U' above the highest occupied (shaded) $3d$- or $4d$-metal states, as shown in Fig. 1. (The prime on U' signifies that this energy (defined in Fig. 1) is not always the Hubbard U.) For simplicity, we assume that the width, W, of these three bands is the same.

For the case of $W < \Delta, U'$, the compounds are insulating, and ZSA *(11)* distinguish two different types of insulators:

(1) Charge transfer insulators when $W < \Delta < U'$ (left of Fig. 1). In this case, the gap $\sim(\Delta - W)$ is dominated by the value of Δ; and

(2) Mott–Hubbard insulators, when $W < U' < \Delta$ (right of Fig. 1). Here the gap $\sim(U' - W)$ is dominated by U'.

A metal results when either of these two gaps approaches zero. Hence, there exist two types of correlated electron metals:

(1) "Low-Δ metals", when $\Delta < W$ (far left of Fig. 1), in which the lowest-lying metal conduction band overlaps the occupied oxygen $2p$-valence states; and

(2) "Low-U' metals", when $U' < W$ (far right of Fig. 1), in which case the two metal orbitals merge to form a partially filled band.

The goal of this paper is to obtain values of U' and Δ for each of the 76 compounds in Table I and examine these within the ZSA framework. While experimental values for a few of these compounds are available, a comparison among all oxide systems is more appropriately carried out with a self-consistent set of approximate values, obtained in the same manner for each. Such a set may be obtained, if we approximate these oxides as ionic solids containing transition metal cations M^{v+} and oxygen anions O^{2-}, with a negligible wave function overlap. The values of U' and Δ obtained in this approximation are called U'_0 and Δ_0, where the zero subscript serves as a reminder that they are theoretically calculated values for the simple ionic model. The energy U'_0 corresponds to the excitation of an electron from one transition metal cation to its neighbor (at a distance $d_{M\text{-}M}$), and is specified in terms of the ionization potential I_{v+l} of M^{v+} and its electron affinity $A = -I_v$:

$$U'_0 = I_{v+1}(M) - I_v(M) - e^2/d_{M\text{-}M}. \quad (1)$$

Correspondingly, the energy Δ to excite an electron from O^{2-} to a neighboring transition metal (at a distance $d_{M\text{-}O}$) involves the ionization potential $I(O^{2-})$ of O^{2-} (the negative of the electron affinity $(A(O^-))$ and the electron affinity $A = -I_v$ of M^{v+}. In addition, there exists a term ΔV_M, the difference in electrostatic Madelung site potentials, that the electron experiences when it changes sites:

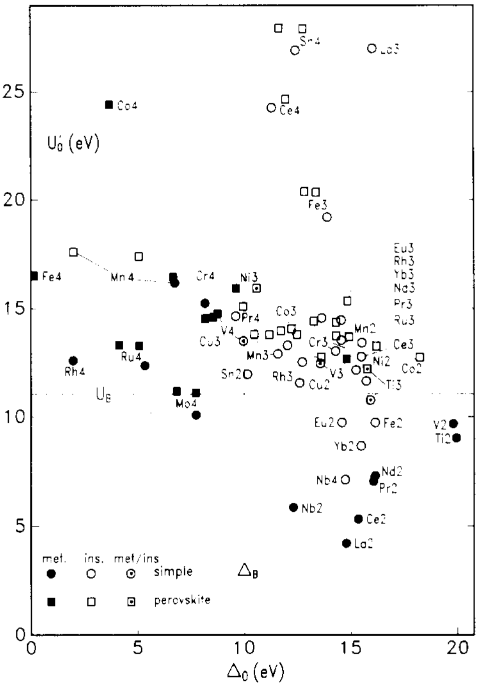

FIG. 2. A plot of the calculated values of U_0' and Δ_0 for the 76 oxides in Table I. The lines attempt to separate the "insulators" (open symbols) from the "metals" (solid symbols) according to the ZSA framework.

$$\Delta_0 = \Delta V_M - I_v(M) - A(\mathrm{O}^-) - e^2/d_{M\text{-}\mathrm{O}}. \quad (2)$$

In this very simple ionic model, the values for U_0' and Δ_0 depend only on the electrostatic interactions between ions and the gas-phase ionization potentials. In Table I, we show values of ΔV_M, calculated earlier *(12)* or here *(13)*, together with the values of U_0' and Δ_0 calculated from Eqs. (1) and (2), using the experimental *(14)* gas-phase values for I_v, while a value *(15)* of 7.70 eV was used for $A(\mathrm{O}^-)$. In Fig. 2, we plot U_0' versus Δ_0 for each of the simple and perovskite oxides. In this letter, we present the major features of these data and discuss the details elsewhere *(10)*. It is clearly seen in Fig. 2 that the "metallic" oxides tend to have low values of either Δ_0 or U_0'. In fact, one can separate most of the "insulators" from the "metals" by drawing a vertical boundary line and a horizontal one, such that the metals have either $\Delta_0 \lesssim \Delta_B = 10$ eV or $U_0' \lesssim U_B' = 11$ eV. Thus, there are eight metals in Fig. 2 which we can classify as low-U' metals and 16 metals which are classified as low-Δ metals. Within this framework, oxides with metal–insulator transitions should fall on (or near) the boundaries in Fig. 2. Such is the case for each of the five examples in Table I (shown in Fig. 2 as symbols with a dot in the center).

We should recall the approximations made in the ionic model calculations of Δ_0 and U_0'. We have neglected the effects of the electronic overlap between ions (covalency, crystal field splittings, screening, electronic polarizability) and the motion of the ions (lattice relaxation, ionic polarizability). Our basic assumption is *not* that these effects are small, rather, that they are similar for all the oxides in Table I, so that the *differences* in Δ and U' are caused by the large differences in I_V and ΔV_M via Eqs. (1) and (2). The main consequence of these neglected effects is to reduce (or screen) the actual values of Δ and U' well below the ionic values of Δ_0 and U_0' in Table I. For example, for an electron or a hole in $\mathrm{La_2CuO_4}$, the decrease in energy due to screening is calculated *(16)* to be ~5–6 eV. For an excitation of a *neighboring* electron and hole (as for U_0' and Δ_0), the decrease should be considerably less than twice this value. This screening will decrease the metal–insulator boundaries at $\Delta_B \sim 10$ eV and $U_B' \sim 11$ eV to values comparable with estimates *(17)* of the electronic bandwidth $W \sim 6$ eV. Thus, the magnitudes of Δ_B and U_B' in Fig. 2 are not unreasonable.

There are a few insulating oxides that lie deep in the metallic regions of Fig. 2, such as $\mathrm{SrMnO_3}$, $\mathrm{Sr_2MnO_4}$, and $\mathrm{NbO_2}$ (which has a strong pairing of metal cations). There are several more minor exceptions nearer the boundary, many of which can *(10)* be related to the assumption that the bandwidths W and hence the boundaries U_B' and Δ_B are the same for all three types of orbitals in Fig. 1 and for all oxides. Among the oxides in Table I there are significant differences in W between the rare earth and the first series transition metal oxides, for example, as well as differences due to distortions and to different dimensionalities. Taking these factors into consideration (*10*), there still remains an uncertainty of ~1–2 eV in the location of the boundaries in Fig. 2, which is an estimate of the relative errors in the agreement between the data and our ionic model of the ZSA framework. Considering the simplicity of the ionic model and the number of factors neglected, the combination of an ionic model and the ZSA framework forms a remarkably good starting point for an understanding of the electronic structure of both simple and perovskite oxides of transition metals. In this way, a simple picture is able to account for the *differences* in conductivity for a wide range of oxides and to attribute these differences primarily to differences in the ionization potentials of the transition-metal cations. It is hoped that such a broad perspective of oxides will complement the common approach of examining each particular compound in detail.

References

1. A. W. SLEIGHT, J. L. GILLSON, AND P. E. BIERSTEDT, *Solid State Commun.* **17,** 27 (1975).

2. J. G. BEDNORZ AND K. A. MÜLLER, *Z. Phys. B* **64,** 189 (1986).

3. R. J. CAVA, B. BATLOGG, J. J. KRAJEWSKI, R. FARROW, AND L. W. RUPP, *Nature (London)* **332,** 814 (1988).

4. J. B. GOODENOUGH AND J. M. LONGO, "Landolt-Börnstein Tabellen," Vol. 111/4a, Springer-Verlag, Berlin (1970); S. NOMURA, "Landolt-Börnstein Tabellen," Vol. 111/12a, Springer-Verlag, Berlin (1978); J. B. GOODENOUGH, *Progr. Solid State Chem.* **5,** 149 (1971).

5. D. ADLER, *Radiat. Eff.* **4,** 123 (1970).

6. C. N. R. RAO AND G. V. SUBBARAO, *Phys. Status Solidi A* **1,** 597 (1970); C. N. R. Rao, *Annu. Rev. Phys. Chem.* **40,** 291 (1989).

7. M. POUCHARD *et al., Mater. Res. Symp. Proc.* **156,** 13 (1989).

8. G. V. SAMSONOV (Ed.), "The Oxide Handbook," IFI/Plenum, New York (1982).

9. A. W. SLEIGHT, "Proceedings of the Welch Conference on Valency," p. 123 (1989).

10. For a more complete account of this work, see J. B. TORRANCE, P. LACORRE, C. ASAVAROENGCHAI, and R. M. METZGER, submitted for publication.

11. J. ZAANEN, G. A. SAWATZKY, AND J. W. ALLEN, *Phys. Rev. Lett.* **55,** 418 (1985).

12. J. Q. BROUGHTON AND P. S. BAGUS, *J. Electron Spectrosc. Relat. Phenom.* **20,** 261 (1980).

13. R. M. METZGER, *J. Chem. Phys.* **57,** 1870 (1972); *J. Chem. Phys.* **64,** 2069 (1976); J. B. TORRANCE and R. M. METZGER, *Phys. Rev. Lett.* **63,** 1515 (1989).

14. "CRC Handbook of Physics and Chemistry," CRC Press, Boca Raton, FL (1981); W. C. MARTIN, L. HAGAN, J. READER, and J. SUGAR, *J. Phys. Chem. Ref. Data* **3,** 771 (1974).

15. M. O'KEEFFE, *J. Solid State Chem.* **85,** 108 (1990).

16. M. S. ISLAM, M. LESLIE, S. M. TOMLINSON, AND C. R. A. CATLOW, *J. Phys. C Solid State Phys.* **21,** L109 (1988).

17. See, for example, W. E. PICKETT, *Rev. Mod. Phys.* **61,** 433 (1989).