

A Simple Approach to the Ionic-covalent Bond Based on the Electronegativity and Acid Strength of Cations. Part Two: Application to the Description of the Electronic Properties of Oxides

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(Received May 1, 1997)

ABSTRACT. The acid strength of cations, determined with ICP (Ionic Covalent Parameter): $ICP = \log(P) - 1.38\chi + 2.07$ where P is the polarizing power and χ its electronegativity expresses the competition between the covalent and ionic forces. This concept, together with electronegativity, is used to describe the properties of oxides with various electronic properties (insulators, metals, degenerate semiconductors, superconductors).

INTRODUCTION

A useful model should aim toward two types of goals: to explain the experimental findings and serve as a guide for the discovery of new materials. In the lines that follow, we will attempt to show that the combination of electronegativity and acid strength can be applied to these two goals. The examples selected uniquely refer to oxides. In effect, given the oxidizing environment of Earth's atmosphere, these are the most widespread inorganic materials and consequently the most widely used (ceramics, glasses, materials for optics, ferro- and ferrimagnetic, ferroelectric materials, superconductors, etc.).

Investigators have attempted to rationalize knowledge of oxides to classify and predict their properties. For example, we cite the fundamental work by Goodenough in this domain.¹ In the case of transition element oxides, he defines an electron transfer energy between neighbouring cations, " b ". When b is less than a critical value, b_c , the oxide is insulating, as the electrons are localized. Beyond this critical value, we pass from a system of localized electrons to another characterized by collective electrons.

More recently, Torrance *et al.*² also proposed another classification of insulating or metal oxides based on the Zaanen-Sawatzky-Allen model (ZSA model)³ which takes into consideration three para-

meters Δ , U , and W , where Δ is the energy separating the occupied p orbital of the O^{2-} ion from the first unoccupied orbital of the cation, U the energy separating the last occupied orbital of the cation from the first unoccupied and W the gap.

The two preceding models utilize physical parameters whose values are sometimes difficult to estimate. It seemed interesting to investigate whether simple chemical parameters such as the electronegativity and/or acid strength, whose values were defined numerically in preceding studies, could lead to the same result.

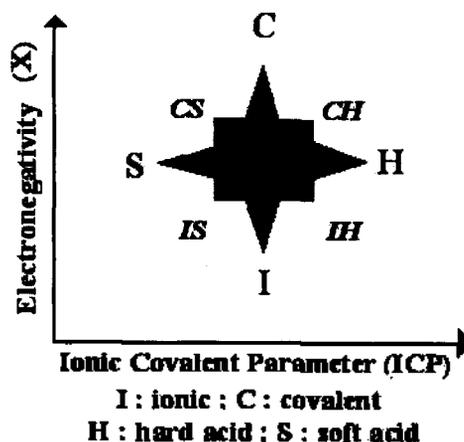


Fig. 1. "Chemical compass" pointing to cations giving rise to covalent (C), ionic (I), soft (S), or hard (H) bonds.

The present study essentially concerns binary oxides. We will attempt to describe their transport properties by working in a two-dimensional electronegativity acid strength space. This space will be explored with a "chemical compass" indicating the "cardinal points:" covalent or ionic, soft or hard (Fig. 1).

INSULATORS AND SEMICONDUCTORS

The great majority of binary stoichiometric oxides are insulators. They occupy almost all of the space limited by oxides with hard (P_2O_5) or soft (WO_3) covalent cations and oxides with hard (Li_2O) or soft (Cs_2O) ionic cations (Fig. 2).

Of course, intrinsically insulating oxides can acquire high conductivity by doping or due to non-stoichiometry. The oxides formed from *s* and *p* elements can be described by the charge transfer model (Fig. 3a). The oxides of semiconducting transition elements often correspond to the Mott-Hubbard model (Fig. 3b).

It is interesting to compare parameter ICP to a basic property such as the forbidden band width. ICP takes into account forces of ionic origin (polarizing power) and forces of covalent origin (electronegativity). This duality also appears in the ZSA model for charge-transfer nonconductors (Fig. 3).³ This model, interpreted in light of ICP, implies that the charge transfer energy, *D*, is more or less dependent on the polarizing power, while the band wide *W* is correlated with the electrone-

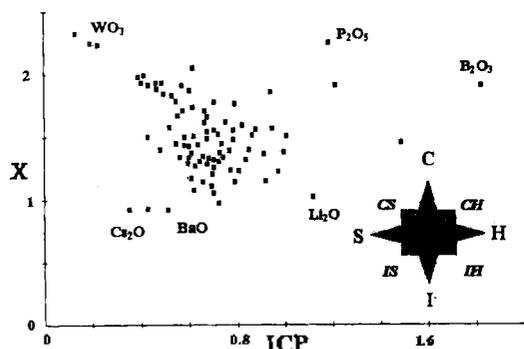


Fig. 2. Variation of electronegativity as a function of the acid strength of the cations giving rise to the oxides.

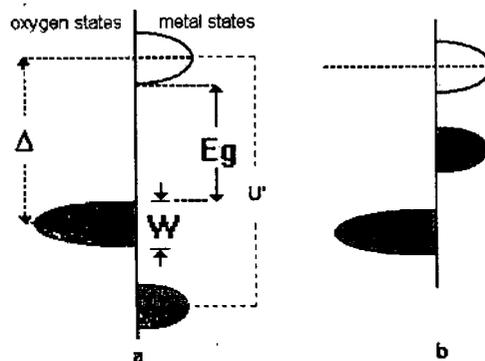


Fig. 3. Schematic representation of the energies of different levels of anions and cations in charge-transfer insulators.

gativity. The forbidden band width is equal to:

$$E_g \gg \Delta - W \approx f(P) \cdot f(\chi)$$

a formulation similar to that of ICP. As a consequence, this parameter should account for the forbidden band width of solids. As an illustration, Table 1 shows the variation of the optical "gap" of a certain number of oxides. Note globally that it increases regularly with the ICP. The electronegativity cannot explain such an evolution.

Table 1. Forbidden Band Width of Some Oxides, ICP, and Electronegativity of the Corresponding Cations

Oxide	E_g (eV)	X	ICP
SiO ₂	10	1.91	1.21
Al ₂ O ₃	8.3	1.51	1.00
MgO	7.3	1.22	0.97
Sc ₂ O ₃	5.4	1.37	0.92
Ga ₂ O ₃	4.4	1.52	0.87
Sb ₂ O ₃	3.4	1.402	0.85
SnO ₂	3.8	1.71	0.83
Y ₂ O ₃	5.6	1.32	0.82
GeO ₂	5.4	1.763	0.8
CaO	6.8	1.15	0.79
ZrO ₂	5	1.48	0.78
In ₂ O ₃	2.8	1.45	0.74
Bi ₂ O ₃	2.6	1.298	0.73
SrO	5.3	1.11	0.70
PbO	24.5	1.615	0.67
BaO	4.8	1.08	0.62
PbO	2	1.171	0.61
HgO	2.2	1.31	0.60

Table 2. Acid Strength and Electronegativity of Cations of Metal Oxides

Oxide	Eg (eV)	X	ICP
ReO ₃	0.133	2.34	2.2566
PtO ₂	0.383	1.95	2.00726
IrO ₂	0.397	1.94	1.99346
OsO ₂	0.408	1.93	1.98237
MnO ₂	0.570	1.92	1.81982
RhO ₂	0.466	1.92	1.92384
ReO ₂	0.435	1.91	1.95477
RuO ₂	0.468	1.90	1.92169
CrO ₂	0.596	1.88	1.79376
WO ₂	0.496	1.84	1.89402
MoO ₂	0.522	1.83	1.86848
TaO ₂	0.546	1.78	1.84377
VO ₂	0.700	1.77	1.69043
NbO ₂	0.618	1.73	1.77201
V ₂ O ₃	0.785	1.56	1.60473
Ti ₂ O ₃	0.994	1.38	1.39639
NbO	0.729	1.36	1.66071
NdO	0.603	1.34	1.78708
VO	0.736	1.33	1.6539
PrO	0.621	1.27	1.76881
TiO	0.921	1.15	1.46862

METAL OXIDES

Some stoichiometric binary oxides have metallic conductivity. They are located in a restricted domain of space X —ICP. Table 2 shows that they are localized in the vicinity of the line for the equation $X \gg -ICP + 2.4$ if suboxides (VO, TiO, ...) are not taken into account.

This linearity nevertheless conceals two types of behavior.^{1,2} Oxides whose cation is a weak acid

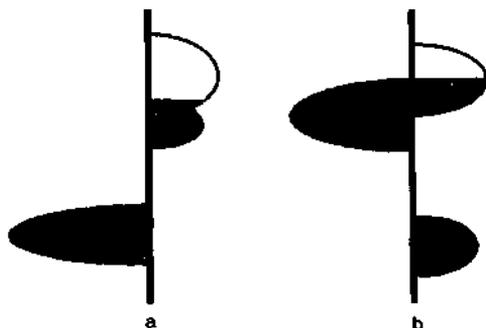


Fig. 4. Schematic representation of the energies of different levels of anions and cations for metals (a) and semimetals (b).

with high electronegativity (trioxides and dioxides of elements 4d and 5d) are semimetals, with formation of a partially filled conduction band due to overlapping of the p orbital of the oxygen and the d orbital of the cation (Fig. 4b). On the contrary, in the case of cations with low electronegativity and high ICP, we would have metals whose conductivity was due to the formation of a metal-metal band (Ti₂O₃, V₂O₃, ...) (Fig. 4a).

DEGENERATE SEMICONDUCTORS

Some rare, intrinsically insulating oxides, acquire properties of the metallic type while remaining transparent in the visible when they are nonstoichiometric or doped.⁴ This concerns degenerate semiconductors; the ones most widely used as materials for transparent electrodes in display devices are In₂O₃ and SnO₂. We have shown in Fig. 5 the representative point of GeO₂, an insulating oxide which is an interesting dopant for In₂O₃. In effect, with an equal number of carriers, the electron mobility in IGO (indium germanium oxide) is twice that of ITO (indium tin oxide).^{5,6}

In fact, this undoped oxides are insulators. Some of them have a forbidden band width of the order of 3 eV and are thus transparent in the visible. They can acquire metallic conduction either by reduction or by appropriate doping.⁷ In practice, the most widely used materials are In₂O₃ doped with tin (ITO, indium tin oxide) or SnO₂ doped with antimony.

Fig. 6 shows the simplified band structure of this type of materials. The valence band originates in oxygen levels 2p, while the conduction band is

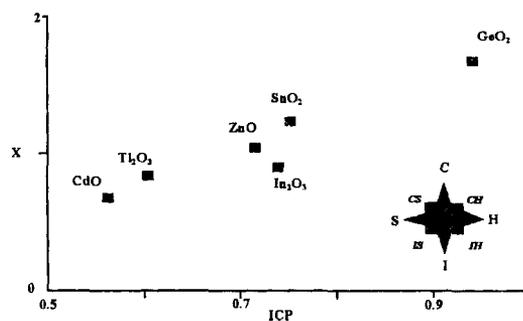


Fig. 5. Degenerate semiconductors in space X -ICP.

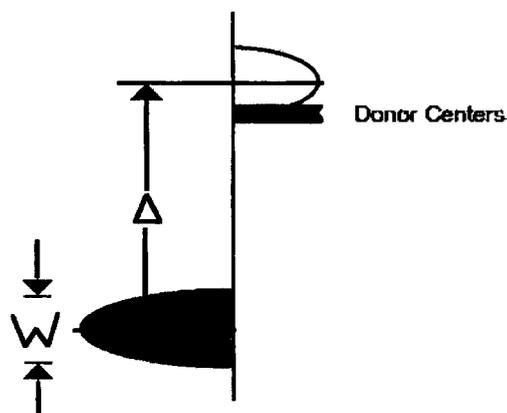


Fig. 6. Schematic representation of the energies of different levels of anions and cations for a degenerate semiconductor.

constructed from the empty ns orbitals ($n=4, 5$, or 6) of the cation. The donor centers are contributed by the doping ion. In the case of cationic dopants such as tin for indium oxide or antimony for tin oxide, this band corresponds to the dopant cation associated with an electron. In the case of the oxides cited above, this would concern $(\text{Sn}^{4+}+e)$ and $(\text{Sb}^{5+}+e)$. These levels should be located near the conduction band to cause metallic conductivity while preserving the transparency in the visible.

The metal-oxygen bonds involved in these materials are of the ionic-covalent type. It is believed that the band width W is correlated with the covalency of the metal-oxygen bond, while the energy difference Δ is determined by the Coulomb forces involved. For the donor centers to be ideally positioned in the forbidden band, it is desirable that the compromise between energies W and Δ be of the same order of magnitude for the host oxide and the ionized dopant.

We calculated the acid strength of the pseudoions $(\text{M}^{n+}+e)$, assuming that the electronegativity on one hand and the ionic radius of these ions on the other hand were intermediate between those of $\text{M}^{(n+1)+}$ and $\text{M}^{(n-1)+}$, where n is the degree of oxidation of the cation of the host oxide. For example, in the case of ITO, n is equal to 3; we calculated the electronegativity of the pseudoion $(\text{Sn}^{4+}+e)$ as the arithmetic mean of the electronegativity of

Sn^{4+} and Sn^{2+} ; in addition, the polarizing power was calculated by assigning the value of 3 to the oxidation number of the pseudoion, and its ionic radius was also the arithmetic mean of the ionic radii of Sn^{4+} and Sn^{2+} . The following table reports the difference in absolute value, D , between the acid strength of cations of the host oxides and the doping ions.

In_2O_3		SnO_2	
cation	$D= \text{ICP}_n^{3+} - \text{ICP} $	cation	$D= \text{ICP}_{\text{Sn}^{4+}} - \text{ICP} $
In^{3+}	0	Sn^{4+}	0
$\ll \text{Sn}^{4+}+e \gg$	0.059	$\ll \text{Sb}^{5+}+e \gg$	0.006
$\ll \text{Ge}^{4+}+e \gg$	0.096	$\ll \text{As}^{5+}+e \gg$	0.025
$\ll \text{Pb}^{4+}+e \gg$	0.099	$\ll \text{Bi}^{5+}+e \gg$	0.047
$\ll \text{Si}^{4+}+e \gg$	0.312	$\ll \text{P}^{5+}+e \gg$	0.114

In the case of In_2O_3 , note that D is very close to 0 in the case of doping with tin: ITO is effectively an efficient transparent electrode. Note also that D is relatively small for germanium: this result is in agreement with the results we recently obtained for IGO (indium germanium oxide).^{6,7} The case of lead also seems favorable. In fact, the $(\text{Pb}^{4+}+e)$ pseudoion is not stable: in this case, formation of PbO in the grain boundaries is observed.⁵

In the case of SnO_2 , we also note that D is very close to 0 for antimony and higher for arsenic, bismuth, or phosphorus. This is effectively what is observed experimentally: the electrical performances of $\text{SnO}_2:\text{Sb}$ are the best.⁸

It thus seems that the acid strength of cations is a pertinent parameter for predicting the electrical performances of degenerate semiconductors.

SUPERCONDUCTORS

Since the discovery of superconductors with a high critical temperature by Bednorz and Müller in 1986,⁹ an enormous research effort has been instituted to search for new materials whose critical temperature is compatible with practical use. These studies were conducted more or less randomly, as the physical models which could serve as a guide for such a goal could not be elaborated by either chemists or physicists. Could the acid strength lead to such a model?

Superconducting cuprates having the highest critical temperatures have the general formula of A_mM

$2R_{n-1}Cu_nO_x$ (A=Bi, Tl, Hg; M=Ba, Sr; R=Ca and rare earth metals; $m=1,2$; $n=1 \dots 5$ or more). They are based on alternation of units of the perovskite type and NaCl. These units are composed of layers of the (CuO_2) , (AO), (MO), and (R) type.¹⁰

We can assume that the critical temperature of these materials will be a function of the properties of the oxygen ions surrounding the (CuO_2) layers. Their donor character, that is, their basicity, should play an important role. It is difficult to gain access to this basicity. However, as we showed previously, the cation acidity can account for this basicity (Eq. 5). We can define a parameter $S(ICP)$ such that

$$S(ICP) = (mICP_{(A)} + 2ICP_{(M)} + (n-1)ICP_{(R)})/n$$

which will be representative of the base strength exercised on a copper atom.

This point of view was found to be justified. Fig. 7 shows that the critical temperature of mercury cuprates varies linearly with $S(ICP)$ according to the equation

$$T_c = -79.5S(ICP) + 223.$$

It is interesting to note that if this equation is linearly extrapolated for $S(ICP)=0$, the maximum critical temperature of this type of material would be 220-230 K. This textbook case would correspond to an infinite network of (CuO_2) layers. This result should be maximum critical temperature of this type of material would be 220-230 K. This textbook case would correspond to an infinite network of (CuO_2) layers. This result should be compared with the re-

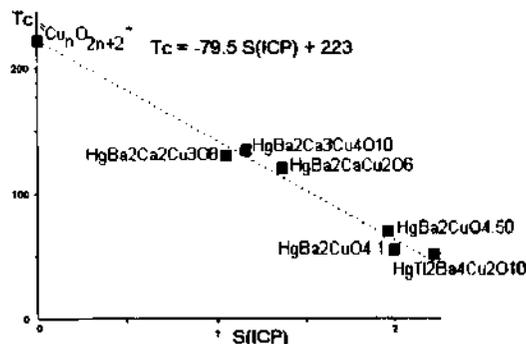


Fig. 7. Variation of the critical temperature as a function of $S(ICP)$ for some mercury-based superconductors.

cent results of Lagues *et al.* and Thorence *et al.* concerning critical temperatures of 250 K.^{11,12}

CONCLUSION

Old concepts such as the electronegativity (1932) and acid strength of cations (1960) allow defining a framework adapted to description of the ionic-covalent bond. The correlations observed between electronegativity, charge number, and ionic radius allow proposing a scale that covers all electronic and crystallographic situations encountered in practice for ionic-covalent solids. The ICP parameter, representative of the acid strength of cations, takes into account the competition between forces of the electrostatic type and forces of covalent origin within the bond, and χ and ICP provide a simple frame for interpreting the basic properties of solids and for elaborating models adapted to materials design.

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