

# Semiempirical Correlation between Optical Band Gap Values of Oxides and the Difference of Electronegativity of the Elements. Its Importance for a Quantitative Use of Photocurrent Spectroscopy in Corrosion Studies

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A semiempirical correlation between the optical band gap of binary oxides and the difference of electronegativity between the oxygen and metallic elements (Pauling's extraionic energy) is proposed. In the frame of the proposed correlation an estimate of the repulsive term in the total lattice energy of ionic oxides is obtained in very good agreement with the existing data. An extension of the correlation to the ternary oxides and hydroxides is proposed by using the concept of average cationic or anionic group electronegativity. The usefulness of the proposed correlation for the in situ characterization of passive films on metals and alloys by photocurrent spectroscopy is illustrated by reporting some preliminary experimental results on Sn and AlTi alloy.

## Introduction

The use of photocurrent spectroscopy (PCS) for the physicochemical characterization of passive films is very attractive owing to some advantages with respect to other in situ optical techniques. In fact, (a) it is less demanding in terms of surface finishing, thus allowing monitoring of surface changes in long-lasting corrosion processes and/or in heavily attacked metal surfaces, and (b) it does not need high light intensity, thus minimizing the risk of modifications of very thin passive films.

Apart from intrinsic limits, due to the fact that only photoactive (semiconducting or insulating) corrosion layers can be scrutinized, PCS suffers limitations in providing direct information on the composition and structure of passive films. It is our opinion that the use of PCS in a more quantitative fashion requires the extension of interpretative models for the photoelectrochemical behavior of crystalline bulk materials to the case of very thin and often strongly disordered or amorphous materials. In previous papers<sup>1</sup> we have shown that some new features in the photoelectrochemical behavior of passive films are attributable to the amorphous nature and/or to the extreme thinness of the passive films covering the metallic substrates.

In this paper we propose a general correlation between the optical band gap of oxide films on passive metals and the average single-bond energy in oxides calculated on the basis of Pauling's electronegativity scale.<sup>2</sup> On such a basis a possible quantitative correlation between optical band gap and composition of passive films grown on metals and alloys will be delineated, which allows us to use in a more quantitative way the PCS technique.

## A Correlation between Optical Band Gap of Binary Oxides and the Difference of Electronegativity of the Elements

To predict the physical properties of inorganic compounds, like the width of the forbidden gap in semiconductors, without applying theoretical models based on very complex quantum mechanical calculations, different authors have proposed semiempirical models and correlations for calculating or predicting energy effects and energy gaps in inorganic solids. Despite their

evident simplicity and widely discussed limitations,<sup>3</sup> Pauling's equations for the calculation of single-bond energies and heats of formation of inorganic compounds, based on the concept of electronegativity of the elements, are still a touchstone for more sophisticated and recent theories.<sup>3–5</sup>

A short review of previous works on the argument is reported in ref 7c. Starting points of our considerations are the results reported in two papers.

In the first one Manca<sup>6</sup> correlates the optical gap energies of different semiconducting compounds having diamond or zincblende structure to the single-bond energy,  $E_s$ , through the relationship

$$E_g = a(E_s - b)$$

where  $a$  and  $b$  are constants characteristic of the series of investigated compounds. The single-bond energy was assumed by the author as given by Pauling's equation:

$$D_{A-B} = (D_{A-A}D_{B-B})^{1/2} + (X_A - X_B)^2 \quad [\text{eV}] \quad (1)$$

where the first term on the right represents the nonpolar contribution and the second one the polar contribution to the bond energy of an A–B compound.  $X_A$  and  $X_B$  are the electronegativity values of the elements A and B in Pauling's scale, while  $D_{A-A}$  and  $D_{B-B}$  represent, according to Pauling,<sup>2</sup> the bond energy of molecules A–A and B–B in the gas phase. Really the use of the arithmetic mean between  $D_{A-A}$  and  $D_{B-B}$  in eq 1 should be more correct (see Chapter 3 and eqs 3–12 of ref 2).

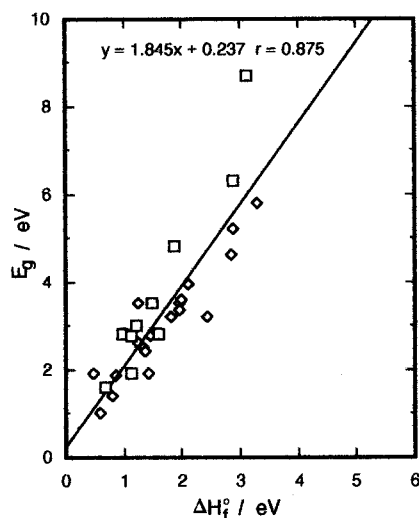
The second paper we like to mention is that of Vijh,<sup>7a</sup> who in an attempt to rationalize Manca's results and the empirical correlation between band gap and enthalpy of formation of a number of inorganic compounds reported by Ruppel et al.,<sup>8</sup> derived for uni-univalent ionic compounds (e.g. alkali halides) the following theoretical relationship between the energy gap,  $E_g$ , and the bond energy,  $E_s$ :

$$E_g = 2(E_s - R) \quad (2a)$$

This last parameter was assumed coincident with the heat of atomization per mole, in the case of alkali halides, or with the heat of atomization per equivalent in the case of polyatomic

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**Figure 1.** Optical band gap values,  $E_g$ , vs standard heat of formation per equivalent of binary oxides: (□) sp-metal oxides; (◇) d-metal oxides.

compounds. According to Vijn,  $R$  is an energy parameter that includes repulsive and London components of the lattice energy.<sup>7a,c</sup>

By using further simplifying assumptions, Vijn suggested the following relationship between the standard heat of formation  $\Delta H_f^o$  and the band gap of inorganic compounds:

$$E_g = -2\Delta H_f^o \quad (2b)$$

This relation was employed to correlate the heat of formation per equivalent of several oxides with their optical band gap values.<sup>7b</sup> The approximate nature of eq 2b is evident after a close inspection of the data reported in Figure 1, where the optical band gap value of 29 oxides (including both oxidation states for Fe, Sn, and Cu oxides) is reported as a function of their standard heat of formation per equivalent. Data of Figure 1 are also listed in Table 1, where the electronegativities of metal elements are also reported. By fitting the experimental points, it comes out an interpolating line with a slope around 2 (1.845 in Figure 1), according to eq 2b, and a relatively low correlation coefficient ( $r = 0.875$ ). It is noteworthy that in Figure 1 the best fitting line separates sp- from d-metal oxides, with the noticeable exceptions of  $\text{In}_2\text{O}_3$  and  $\text{PbO}_{\text{tetr}}$  (lying below) for sp-metal oxides and  $\text{HgO}$  and  $\text{NiO}$  (lying above) for d-metal oxides. By interpolating separately sp- and d-metal oxides higher correlation coefficients were obtained for both sp- ( $r = 0.96$ ) and d-metal ( $r = 0.93$ ) oxides. In this case an higher slope (2.67) was obtained for sp-metal oxides with respect to the value (1.47) obtained for d-metal oxides.

As for the optical band gap values, we have to mention that most of the reported data come from photoelectrochemical studies, while for oxides with  $E_g^{\text{opt}} \geq 5.5$  eV data were obtained from different sources. This fact as well as the experimental difficulties in getting reliable values of  $E_g^{\text{opt}}$  for large band gap materials, arising from the strong influence of impurities and excitonic structures on the optical properties of such oxides, suggested that we should ground our considerations on lower band gap systems and use only a limited number of large band gap oxides for which more reliable measurements or theoretical estimates of  $E_g$  are reported in the literature ( $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Y}_2\text{O}_3$ ).

For  $\text{Al}_2\text{O}_3$  and  $E_g^{\text{opt}}$  value of 6.3 eV has been chosen, in agreement with both the calculated band structure and the optical band gap value of barrier-type anodic oxide films<sup>9a,b</sup> inferred

**TABLE 1: Band Gap Value,  $E_g$ , Heat of Formation Per Equivalent,  $\Delta H_f^o$ , and Electronegativity of the Metallic Element,  $X_M$ , of Binary Oxides**

oxide	$E_g$ (eV)	ref	$\Delta H_f^o$ (eV)	$X_M^c$
MgO	8.70	12	3.116	1.20
$\text{Al}_2\text{O}_3$	6.30	9	2.897	1.50
$\text{Ga}_2\text{O}_3$	4.80	13	1.870	1.60
SnO	4.22 <sup>a</sup>		1.480	1.70 <sup>d</sup>
$\text{SnO}_2$	3.50	15	1.500	1.80 <sup>d</sup>
$\text{Sb}_2\text{O}_3$	3.00	16	1.224	1.90
$\text{In}_2\text{O}_3$	2.80	22	1.600	1.70
$\text{Bi}_2\text{O}_3$	2.80	17	0.986	1.90
$\text{PbO}_{\text{ort}}$	2.75	23	1.140	1.80
$\text{PbO}_{\text{tetr}}$	1.904	23	1.140	1.87 <sup>e</sup>
$\text{Ti}_2\text{O}_3$	1.60	18	0.674	2.04 <sup>e</sup>
$\text{Y}_2\text{O}_3$	5.80	10	3.290	1.20
$\text{HfO}_2$	5.20	19	2.880	1.30
$\text{ZrO}_2$	4.60	1, 20a	2.850	1.40
$\text{Ta}_2\text{O}_5$	3.95	20d	2.120	1.50
MnO	3.60	21	1.990	1.50
$\text{Cr}_2\text{O}_3$	3.50	20c	1.950	1.60
NiO	3.50	14	1.247	1.80
$\text{Nb}_2\text{O}_5$	3.35	1	1.970	1.60
$\text{TiO}_2$	3.20	1	2.450	1.60
ZnO	3.20	6	1.820	1.60
$\text{WO}_3$	2.75	1	1.456	1.70
CoO	2.60	21	1.236	1.80
CdO	2.50	39	1.344	1.70
FeO	2.40	21	1.370	1.80
$\text{Fe}_2\text{O}_3$	1.90	21	1.420	1.90
HgO	1.90	24	0.470	1.90
$\text{Cu}_2\text{O}$	1.86	20b	0.867	1.90
CuO	1.40	21	0.80	2.00
PdO	1.00	21	0.58	2.20

<sup>a</sup> Present study, experimental value (see text). <sup>b</sup> Reference 25.

<sup>c</sup> Reference 2. <sup>d</sup> Reference 36. <sup>e</sup> Reference 37.

experimentally, while in the case of  $\text{Y}_2\text{O}_3$  the onset energy of excitonic optical absorption has been chosen as the optical band gap value, in agreement with the theoretical calculations.<sup>10,11</sup> For MgO we assumed the optical band gap value reported by Hale<sup>12</sup> (8.7 eV) although lower values (7.5–7.8 eV) have been suggested by others.<sup>11</sup> As for  $\text{Fe}_2\text{O}_3$  and  $\text{Cu}_2\text{O}$  oxides, different optical band gap values were detected with values around 2.1–2.2 eV for both oxides in bulk crystalline forms, while lower values (around 1.90 eV) are reported in both cases for thin anodic films.<sup>20b,26</sup> We mention that a value of 1.90 eV has been quoted also for the optical band gap of  $\text{Fe}_2\text{O}_3$  in a recent review on transitional metals oxides.<sup>21</sup>

Apart from such small uncertainties in the  $E_g$  values, which do not affect sensibly the proposed correlation, there are some specific weak points in the correlation proposed by Vijn that we like to stress in order to suggest a possible solution: (1) in several cases (Cu, Fe, Sn) the optical band gap values of semiconducting oxides at different oxidation states are appreciably different, while the heats of formation per equivalent are nearly coincident; (2) there are several experimental findings that lend support to the hypothesis that lower optical band gap values are measured for hydrated oxide films and/or hydroxides.<sup>20a,c,27–33</sup> If we take into account that usually higher heat of formation per equivalent is obtained for oxyhydroxides and hydroxides with respect to the corresponding anhydrous oxides, it is clear that such a finding is unexplainable in the frame of Vijn's correlation, which was however suggested only for anhydrous oxides.<sup>7b</sup>

To rationalize the results reported in Figure 1 as well as to try to overcome the above mentioned limits of Vijn's correlation, we rewrite eq 2a for the general case of a polyatomic oxide molecule,  $\text{MO}_y$ , taking into account Pauling's equation for the average bond energy  $D_{A-B}$ :<sup>2</sup>

$$E_g = 2\left\{E_1(X_M - X_O)^2 + \frac{1}{2y}[(D_{M-M} + yD_{O-O}) - R]\right\} \quad (3a)$$

where, according to Phillips,<sup>3</sup>  $E_1$  is the extraionic energy unit orbitally dependent, assumed "to vary with hybridization configuration, i.e., with different atomic coordinations in different crystal structures". For ionic compounds, e.g. alkaline halides, a value of  $E_1 = 1$  eV per atom pair is assumed in the electronvolt scale, while a different value is expected for hybridized bonds involving d-orbitals.  $X_M$  and  $X_O$  are the electronegativities of metal and oxygen in Pauling's scale. The stoichiometric coefficient  $y$  is obtained from the oxide formula  $MO_y$ ;  $D_{M-M}$  and  $D_{O-O}$  are the bond energy of diatomic molecules in the gas phase. Generally the repulsive term  $R$  is given by

$$R = U_{\text{lattice}} - U_{\text{bond}}$$

In the ionic limit  $U_{\text{bond}}$  coincides with the Madelung energy,  $U_M$ , and the previous relationship reduces to eq 2a, while in the covalent or metallic limit a quantum mechanical calculation of the bonding energy is required.<sup>4</sup> Equation 3a can be written as

$$E_g = 2[E_1(X_M - X_O)^2 + \Xi] \quad [\text{eV}] \quad (3b)$$

and it allows the correlation of the optical band gap of the oxide with the square of the difference of the electronegativities between metal and oxygen (the "extraionic energy" of Pauling<sup>2</sup>), as long as the term

$$\Xi = \frac{1}{2y}[(D_{M-M} + yD_{O-O}) - R] \quad (3c)$$

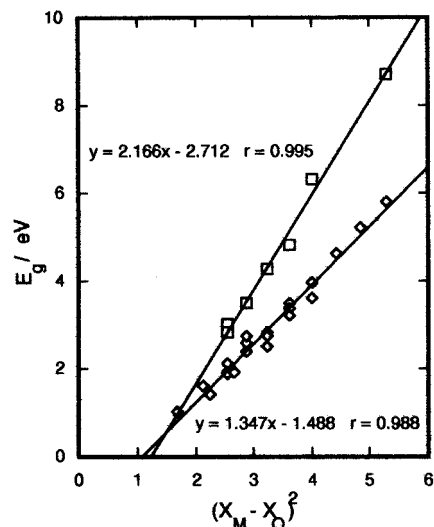
is constant (not necessarily equal to zero, as explicitly assumed by Vijh in deriving eq 2b). Moreover, eq 3b allows us to rationalize the different slopes emerging in Figure 1 for sp- and d-metal oxides once we recall that as a first approximation the heat of formation of ionic compounds, following Pauling's suggestion, can be expressed as<sup>2-4</sup>

$$\Delta H_f^\circ = -N_R E_1 (X_A - X_B)^2 \quad [\text{eV/mol AB}]$$

where  $X_A$  and  $X_B$  are the Pauling electronegativities of the elements A, B and  $N_R$  is the number of resonating bonds per atom pair. Equation 2b follows from eq 3b if we assume  $\Delta H_f^\circ_{\text{eq}} = \Delta H_f^\circ/N_R$  and  $\Xi = 0$ .

To test the validity of eq 3b as well as the constancy of the term  $\Xi$ , we plotted in Figure 2 the band gap values of oxides as a function of  $(X_A - X_B)^2$ . With respect to Figure 1 the new plot presents (a) two separated interpolating lines with slopes of about 2.16 and 1.34 eV for sp-metal and d-metal oxides, respectively, apart from a few exceptions (see below), and (b) an improved fitting of the data, as evidenced by the higher correlation coefficients of both interpolating lines.

Moreover, both interpolating straight lines intersect the electronegativity axis nearly at the same value. From the fitting of the data according to eq 3b we derive  $E_1 = 1.08$  and  $\Xi = -1.36$  for sp-metal oxides, while for d-metal oxides  $E_1 = 0.67$  and  $\Xi = -0.75$ . The average value of  $-1.05 (\pm 0.3)$  will be assumed in the following as a common  $\Xi$  value in eq 3b for calculating the repulsive energy term  $R$ . The  $E_1$  value derived from Figure 2 for sp-metal oxides coincides with an analogous term in Manca's equation pertaining to the  $A^{IV}A^{IV}$  semiconductors and is very close to the  $E_1$  value (1 eV) expected for alkaline halides (see above). This observation rules out any hypothesis



**Figure 2.** Optical band gap values,  $E_g$ , vs the square of difference of Pauling's electronegativity of binary oxides: ( $\square$ ) sp-metal oxides; ( $\diamond$ ) d-metal oxides.

relating the slopes of the straight lines in Figure 2 with the ionic or covalent nature of the compounds.

Interestingly, from both interpolating lines it follows that metallic oxides ( $E_g \approx 0$ ) are expected for metals having Pauling's electronegativity values around 2.40, in agreement with the common experience that noble metal oxides at higher oxidation states ( $\text{RuO}_2$  and  $\text{IrO}_2$ , characteristically) usually exhibit metallic conductivity.

We have to mention that NiO in this correlation fits neatly the sp-metal oxides interpolating line. The definition of transition metal oxides employed here is the widest one, including elements of the Sc and Zn columns.<sup>21,34</sup> However, even using this wide definition still three non-transition-metal oxides ( $\text{PbO}$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Tl}_2\text{O}_3$ ) are better interpolated as d-metal oxides. This result in an intriguing d-/sp-metal oxide dividing line along the diagonal Zn, In, Pb/Ga, Sn, Bi with some sp-metals (In, Tl, Pb) of higher atomic number showing a d-like behavior in terms of average bond strength. On the other hand similar (or larger) difficulties arise if the interpolating lines of Figure 2 would be specified on the basis of purely ionic/covalent bonding character of the different oxides.<sup>35a,b</sup>

As for the electronegativity values, we have to mention that for all calculations the Pauling's scale of electronegativity, integrated with the Gordy-Thomas values,<sup>36</sup> has been used with the exception of Tl(III) oxide, for which the value given by Allred<sup>37</sup> has been preferred. It is noteworthy that if we calculate the electronegativities of the elements according to the best fitting straight lines of Figure 2, the values derived differ from Pauling's values for a quantity of about 0.05, which is more or less the uncertainty in the given values of electronegativity.<sup>2</sup>

A final check of eq 3b was performed by substituting the average value derived experimentally for  $\Xi$  in eq 3c and rearranging it as

$$R = (D_{M-M} + yD_{O-O}) - 2y\Xi \quad (4)$$

As previously reported, for ionic compounds the repulsive term  $R$  is given by the difference between the lattice energy and the Madelung energy,  $U_M$ . This last quantity can be calculated once the Madelung constant of the oxides and the metal-oxygen minimum distance are known. In the case of compounds with total or partial covalent bonding the calculations are more complex.<sup>4</sup>

**TABLE 2: Calculation of the Madelung Energy,  $U_M$ , and Repulsive Contribution,  $R^a$** 

oxide	$r_{M-O}^b$	Madelung constant <sup>c</sup>	$U_M$ (kJ/mol)	$R$ (kJ/mol)
MgO	2.105	1.747	4610	709.12
CaO	2.405	1.747	4030	746.71
SrO	2.580	1.747	3760	710.10
TiO <sub>2</sub>	1.950	2.408	13710	1542.30
MnO	2.222	1.747	4360	726.50
FeO	2.145	1.747	4518	775.60
CoO	2.133	1.747	4545	867.10
NiO	2.084	1.747	4650	903.00
SnO <sub>2</sub>	2.010	2.408	13300	1588.00

<sup>a</sup> See eq 4. <sup>b</sup> Oxygen–metal ion minimum distance (Å) from ref 38.<sup>c</sup> Reference 39.**TABLE 3: Lattice Energies of Binary Oxides from  $U_{lat}^{cal} = U_M - R$ , and from Literature,  $U_{lat}$** 

oxide	$U_{lat}^{cal}$ (kJ/mol)	$U_{lat}^a$ (kJ/mol)	$U_{lat}^{cal}/U_{lat}$
MgO	3901	3795	1.028
CaO	3283	3414	0.962
SrO	3050	3217	0.950
TiO <sub>2</sub>	12168	12150	1.001
MnO	3633	3724	0.975
FeO	3742	3795	0.986
CoO	3678	3837	0.958
NiO	3747	3908	0.959
SnO <sub>2</sub>	11712	11810	0.992

<sup>a</sup> Reference 39.

We calculated the lattice energies ( $U_{lat}^{cal} = U_M - R$ ) of several sp- and d-metal oxides for which the ionic character is unquestioned, as well as for some disputed ones. The  $U_{lat}^{cal}$  values obtained in this way were then compared to the lattice energies reported in the literature and obtained by different routes.<sup>39</sup> The results of these calculations are reported in Tables 2 and 3 together with the Madelung constants, the oxygen–metal ion minimum distance ( $r_{M-O}$ ), and the lattice energies  $U_{lat}$  taken from the literature.<sup>38,39</sup> It is evident from the data in Table 3 that for unquestioned<sup>30</sup> truly ionic compounds (MgO, CaO, SrO) there is good agreement between  $U_{lat}$  and  $U_{lat}^{cal}$ , allowing us to conclude that the values of the repulsive term calculated according to eq 4 are reliable. Analogous conclusions can be reached by looking at the data of NiO, FeO, MnO, CoO, TiO<sub>2</sub>, and SnO<sub>2</sub>. For these oxides the results suggest that the ionic model is able to describe quantitatively the lattice interactions. From the data in Table 3 it comes out that the lattice energies calculated according to our suggestion are as good as those obtained by using the usual formula for the lattice energy including the repulsive ( $1 - 1/n$ ) term.<sup>40</sup> We like to mention that the ratios  $U_{lat}^{cal}/U_{lat}$  for all these oxides give a mean value of 0.979, with a standard deviation of 0.024.

Our quantitative analysis was limited to these oxides because for them there is no uncertainty in the choice of the Madelung constant, whose value could affect in a meaningful way the  $U_{lat}^{cal}/U_{lat}$  value. Nevertheless, this limited number of oxides is sufficient to show that the calculation of the repulsive energy term by means of eq 4 is able to account for the repulsive interaction in sp- and d-metals oxides.

We have to mention that larger discrepancies ( $\geq 10\%$ ) between the  $U_{lat}^{cal}$  and  $U_{lat}$  values were observed in the case of ZnO, CdO, Ag<sub>2</sub>O, and Cu<sub>2</sub>O if we assume such oxides as truly ionic. This finding is in agreement with the disputed “ionic” character of these oxides already reported in the literature.<sup>35,40</sup>

Before concluding this section we have to mention that the different optical band gap values measured for oxides with the same metal in different oxidation states (which have nearly equal heats of formation per equivalent; see Fe, Cu, Sn in Table 1)

are now correctly explained in the frame of the proposed correlation, taking into account the differences in the electronegativity of the metallic cation in the two oxidation states.

### A Generalized Correlation $E_g^{opt}$ vs $(\Delta X)^2$ Including Ternary Oxides and Hydroxides

In this section we present an attempt to generalize the previous results to more complex systems like ternary oxides, oxyhydroxides, and hydroxides. Although the number of ternary oxides taken into account appears rather limited, in our opinion, it is still possible to explain an empirical correlation between the optical band gap values and the cationic group average electronegativity,  $\bar{X}_c$ , of different ternary oxide. With this aim, usually we can define the  $\bar{X}_c$  parameter as the geometric mean:

$$\bar{X}_{c,g} = [(X_A)^a (X_B)^b]^{1/(a+b)} \quad (5a)$$

or as the arithmetic mean

$$\bar{X}_{c,a} = \frac{aX_A + bX_B}{a + b} \quad (5b)$$

of the electronegativity values,  $X_A$  and  $X_B$ , of the two metallic cations in the oxide. Here  $a$  and  $b$  represent the stoichiometric coefficients of cations in the ternary oxide  $A_aB_bO_o$ . As expected, for not too large differences in the  $X$  values,  $\bar{X}_{c,a}$  and  $\bar{X}_{c,g}$  differ very little (less than 0.05 in the systems reported in Table 4) so that no further analysis was performed on this aspect.

On the basis of the results reported in the previous section and by taking into account that MgAl<sub>2</sub>O<sub>4</sub> contains only sp-metal cations, a preliminary test was performed by checking if the value of the band gap for this ternary oxide is in agreement with that foreseen by the proposed correlation for sp-metal oxides. A value of 7.5 eV is reported in the literature, with optical excitons onset energy values ranging between 6 and 8 eV, and a band gap of 6.5 eV was estimated theoretically,<sup>9b,11</sup> compared to a calculated value of  $E_g^{opt} = 6.80$  eV. By taking into account the experimental difficulties and uncertainties in the determination of optical band gap values for such a large band gap material, the agreement between the two values seems to us quite acceptable. Further checks on analogous systems (ternary oxides with only sp-metal cations) are however necessary before reaching a final conclusion on the possible extension of the correlation proposed to ternary systems.

A good agreement between experimental and calculated  $E_g^{opt}$  values was also observed for ternary oxides consisting of d-metal cations only (FeTiO<sub>3</sub>, MnTiO<sub>3</sub>, Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, La<sub>2</sub>TiO<sub>7</sub>), by using the correlation found in the previous section for d-metal oxides with  $X_M \equiv \bar{X}_{c,a}$ . As for the ternary oxides involving both sp- and d-metal cations, a different behavior was observed as a function of the difference of electronegativity of the two cations. In fact, with the exception of LiNbO<sub>3</sub>, the ternary oxides consisting of s- and d-metal cations displaying a large difference of electronegativity ( $\geq 0.5$ ) present experimental  $E_g^{opt}$  values practically coincident with the value of the corresponding binary d-metal oxide. This finding would suggest that in these compounds a negligible interaction between the d-orbital and s-orbital of the cationic components is occurring after formation of the ternary phase.

In the case of ternary s- and d-metal oxides with a small difference in the electronegativity values of cations ( $\Delta X_c \leq 0.4$ ) a good agreement between experimental and calculated  $E_g^{opt}$  values was, once again, observed by using the previous correlation for d-metal oxides with  $X_M \equiv \bar{X}_{c,a}$ . In this frame a borderline case is the behavior of MgTiO<sub>3</sub> ( $\Delta X_c = 0.4$ ), for

which the agreement is within only 20%. These findings strongly support the idea that the changes in the  $E_g^{\text{opt}}$  value are mainly due to the shift in energy of the conduction band formed by sp- and d-orbitals of the cations.

By analogy with the procedure followed for ternary oxides an attempt was also made to rationalize the experimental findings pertaining to the behavior of hydroxides and oxyhydroxides. In this case, in the presence of a variable number of OH groups in the molecular unit, we may define the average electronegativity of the anionic groups in a generic oxyhydroxide, having the formula  $\text{MO}_{(y-m)}\text{OH}_{2m}$ , by means of the geometric or arithmetic mean between those of oxygen and hydroxyl groups, as

$$\bar{X}_{\text{an,g}} = [(X_{\text{OH}})^{2m}(X_{\text{O}})^{y-m}]^{1/(y+m)}$$

or as

$$\bar{X}_{\text{an,a}} = \frac{2mX_{\text{OH}} + (y-m)X_{\text{O}}}{y+m}$$

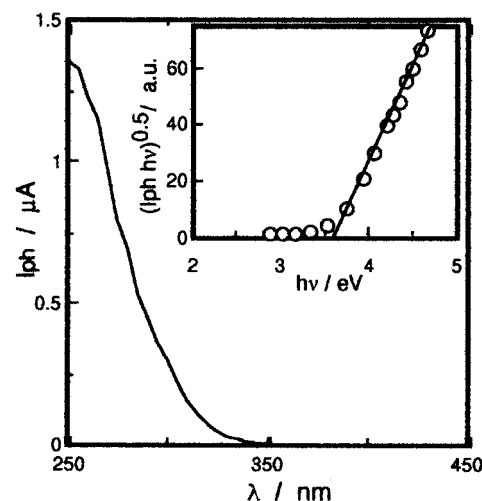
For the same oxyhydroxide numerical values of  $\bar{X}_{\text{an,g}}$  and  $\bar{X}_{\text{an,a}}$  differ less than 0.1, which is a non-negligible amount. A still more complex average group electronegativity could be defined according to another author,<sup>42</sup> but this does not change the essential aspects of our reasoning, while the final choice of the best mean to use for fitting data will be postponed after the collection of a sufficiently large number of experimental data. Regardless of the final choice, it comes out from a previous definition of  $\bar{X}_{\text{an}}$  that with increasing the number of OH groups the average anionic electronegativity decreases from the value of oxygen (3.5) to that of the hydroxyl group (2.71 or 2.80, according to the geometric or arithmetic means between those of O and H, respectively).

In agreement with the previous findings on binary and ternary oxides, we will assume that also for oxyhydroxides and hydroxides the correlation holds between the optical band gap values of these compounds and the square of the difference of electronegativity between the metallic cation and the average anionic electronegativity defined previously. Such an assumption should help to rationalize the aforementioned discrepancy in the Vijn's correlation (see eq 2b), when extended to hydroxides, which assigns to the hydroxides  $E_g^{\text{opt}}$  values higher than those of the anhydrous counterparts (at variance with the experimental results) in the presence of an increase of heat of formation per equivalent of the hydroxides (see, for example, Al, Cr, Sn, Zr). There are in the electrochemical literature few, but experimentally well-reproducible, investigated systems that seem to support our assumption.<sup>1,9a,20,27-33</sup> In the next section we present some more experimental evidence in favor of our hypothesis.

### Toward a More Quantitative Use of Photocurrent Spectroscopy in Corrosion Studies

On the basis of the previous correlation we are now able to stress new quantitative aspects in the use of PCS for the characterization of passive films on metals and alloys. With this aim we need to recall previous experimental findings as well as to present some new experimental results, which will be discussed in more details in forthcoming papers.

Figure 3 shows the photocurrent spectrum and the determination of the optical band gap, obtained by extrapolation of the  $(I_{\text{ph}}hv)^{0.5}$  vs  $h\nu$  plot in the hypothesis of indirect (or nondirect for amorphous material) optical transitions, for a passive film grown on a AlTi alloy (Al/48Ti/1V atom %). The  $E_g^{\text{opt}}$  value,



**Figure 3.** Photocurrent spectrum and determination of optical band gap (see inset) of a passive film on AlTi anodized in 0.1 M ammonium tartrate up to  $U_f = 8$  V (MSE). The spectrum was obtained at  $U_E = 3$  V (MSE) in the anodizing solution.

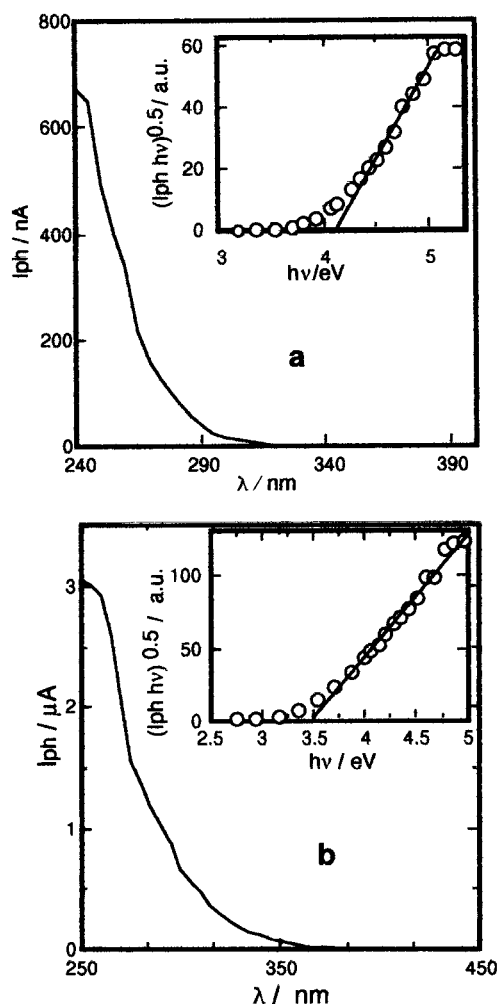
**TABLE 4: Calculated Band Gap Values<sup>a</sup> of Ternary Oxides,  $E_g^{\text{calc}}$ , Compared to the Literature Ones,  $E_g^{\text{exp}}$**

oxide	$\Delta X_c^b$	$\bar{X}_c^c$	$E_g^{\text{calc}}$ (eV)	$E_g^{\text{exp}}$ (eV)	ref
MgAl <sub>2</sub> O <sub>4</sub>	0.3	1.40	6.80	7.50	9, 12b
MgTiO <sub>3</sub>	0.4	1.40	4.40	3.70	21
Al <sub>2</sub> TiO <sub>5</sub>	0.1	1.53	3.68	3.60	d
FeTiO <sub>3</sub>	0.2	1.70	2.84	2.85	41
MnTiO <sub>3</sub>	0.1	1.55	3.60	3.10	41
Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	0.7	1.64	3.14	3.00	21
La <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	0.4	1.40	4.41	4.00	21
SrZrO <sub>3</sub>	0.4	1.20	5.60	5.40	21
BaTiO <sub>3</sub>	0.7	1.25	5.28	3.20	41
SrTiO <sub>3</sub>	0.6	1.30	5.00	3.15	41
LiNbO <sub>3</sub>	0.6	1.30	5.00	3.80	21
KNbO <sub>3</sub>	0.8	1.20	5.60	3.30	21
LiTaO <sub>3</sub>	0.5	1.25	5.28	3.80	21
NaTaO <sub>3</sub>	0.6	1.20	5.60	3.80	21

<sup>a</sup> Calculated according to eqs 3b and 5b (see text). <sup>b</sup> Difference in the electronegativity values of metallic elements of ternary oxides from ref 2. <sup>c</sup> From eq 5b. <sup>d</sup> Present study, experimental value (see Figure 3).

obtained in a large range of film thickness and electrolyte composition, is equal to  $3.60 \pm 0.05$  eV. Such a value of optical band gap is in very good agreement with that estimated for a ternary oxide of composition Al<sub>2</sub>TiO<sub>5</sub> and in agreement with the reported correlation  $E_g^{\text{opt}}$  vs  $(\bar{X}_{c,a} - X_{\text{O}})^2$  for ternary d-metal oxides (see Table 4). This preliminary result, which seems to support our main hypothesis, is important because it allows us to put forward a rationale for many previous interpretations trying to correlate the composition of passive films grown on metallic alloys (noticeably, on stainless steels) with the measured optical band gap values. We are aware of the fact that in many cases it will be not so easy to get information on the composition of very thin passive films just by measuring the optical band gap; however it should be kept in mind that such a task is not an easy one also for more sophisticated techniques, which often demand a removal of the electrode from the solution.

The other example of quantitative use of PCS we present is related to the possibility of identifying metal oxides with different oxidation states of the cation and/or OH group content. Figure 4a,b shows some of the photocurrent spectra obtained on passive tin polarized in a large range of electrode potentials ( $-1$  to  $+1$  V/MSE) and solution compositions ( $-1.0 \leq \text{pH} \leq 14$ ). Although the details of the passivation process and film composition will be discussed in forthcoming papers, we



**Figure 4.** Photocurrent spectrum and determination of optical band gap (see insets) for passive films grown on Sn: (a) at 2 mV/s up to  $-0.9$  V (MSE) in  $0.01$  M  $HClO_4 + NaOH$  solution, pH = 3.5; (b) at  $100$  mV/s up to  $1.3$  V (MSE) in  $0.2$  M  $H_3PO_4$ . This last spectrum was recorded at  $U_E = 0.75$  V (MSE) in  $0.01$  N  $H_2SO_4$  after 90 min of aging.

anticipate some important experimental findings that make tin a possible model system for a quantitative use of PCS in passivity studies. According to previous works<sup>27,43</sup> and on the basis of a detailed study as a function of pH, nature of solution, electrode potential, and polarization time, it is possible to say that (a) in suitable solutions at electrode potentials very close to the equilibrium potential of the Sn/SnO couple a passivation film showing an indirect (nondirect if amorphous) optical band gap value of about  $4.25$  eV is formed (see Figure 4a); (b) at high anodic potentials and for lower pH values a passive film with insulator-like behavior and an optical band gap around  $3.50$  eV is formed (see Figure 4b); (c) for higher pH values (pH  $\geq 13$ ) and anodic potentials the formation of a low band gap corrosion film having  $E_g^{opt}$  values of  $2.30 \pm 0.05$  eV is observed;<sup>27</sup> (d) in solutions with intermediate pH values at not too low anodic potentials and/or after long polarization times optical band gap values ranging between the last two previous limits ( $2.25$ – $3.50$  eV) are measured.

The first two findings suggest that in acidic solutions passive films having composition near SnO and  $SnO_2$  are preferentially grown at low and high electrode potentials, respectively. We stress that the formation of SnO was inferred on the basis of the  $E_g^{opt}$  value calculated from the previous relationships ( $4.28$  eV), by taking into account the electronegativity of Sn(II) and the sp nature of tin metal. On the contrary, the value of  $3.5$  eV

was detected experimentally for the optical band gap of  $SnO_2$  crystalline oxide.<sup>15</sup>

The lowest band gap value and the pale-yellow color, typical of stannic hydroxide (or  $SnO_2 \cdot 2H_2O$ ), sometimes observed after longer polarization times of tin electrodes in strong alkaline solutions, agree with our hypothesis that the decrease from  $3.5$  to  $2.8$  (or  $2.71$ ) in the average electronegativity of the anionic groups in  $Sn(OH)_4$  is responsible for the decrease of the measured optical band gap value in such films with respect to  $SnO_2$ .

In the absence of a sufficient number of experimental data allowing us to verify the existence of a correlation for hydroxides and oxyhydroxides analogous to the previous ones, we suggested on a purely heuristic basis<sup>31</sup> the correlation of the optical band gap of a generic oxyhydroxide having the formula  $MO_{(y-m)}(OH)_{2m}$  with the hydration degree,  $m$ , of the corresponding hydrated oxide,  $MO_y \cdot mH_2O$ , through the following relationship:

$$E_g^{hyd} = E_g^{anh} / (1 + K_{ox} m) \quad (6)$$

where  $E_g^{hyd}$  and  $E_g^{anh}$  are the optical band gaps of the hydrated and anhydrous oxide forms, respectively, and  $K_{ox}$  is a constant parameter typical of the investigated system. The value of this parameter is determined once the band gap values of the anhydrous oxide and hydroxide phases are known for the system.

By assuming an optical band gap value of  $3.50$  eV for  $SnO_2$  and a value of  $2.30$  eV for  $Sn(OH)_4$  we get a value for  $K_{SnO_2} = 0.26$ , which allows the prediction of a value of optical band gap for  $SnO(OH)_2$  around  $2.75$  eV. It is worth noting that values of optical band gap ranging around this last value have been found in our experimental investigations and are also reported in the literature for passive films on tin anodized in quasi-neutral aqueous solutions or after removal of the external (more hydrated) layer grown in strongly alkaline solutions.<sup>27,43</sup> Further details on the photoelectrochemical behavior of tin will be published elsewhere.

We have to mention that a very good agreement has been found between the hydration degree estimated by means of eq 6 and the composition of chromium passive films detected by XPS and EXAFS techniques.<sup>20c,28,33,44</sup> Such successes, although very encouraging, deserve further verification with a large number of systems before reaching final conclusions on the validity of the proposed correlations.

## Conclusions

A semiempirical correlation between the optical band gap and the difference of electronegativity of the metallic element and oxygen in the traditional Pauling's scale has been proposed in order to correlate quantitatively the experimental data for a quite large number of binary oxides. Based on the same arguments, an extension to ternary oxides, oxyhydroxides, and hydroxides (as well as hydrated oxides) has also been suggested. The proposed correlation allows the rationalization of data on the optical band gap of metal oxides with different degrees of oxidation in a more satisfying way with respect to other correlations proposed previously. Preliminary checks seem to support this, within some restrictions, but our correlations need to be tested further. On the basis of these preliminary results, a more quantitative use of PCS in corrosion studies as an in situ technique for a better characterization of the anodic oxides film on metals and alloys is advocated by the present authors.

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