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The Relation between Conductivity, Optical Absorption, and Ionicity in Oxides and Organic Compounds

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With a simple ionic model to quantify the ionicity in oxides and organic compounds, a common pattern of behavior is found for their conductivity and optical absorption. As the ionicity of these compounds decreases, the energy of optical absorption decreases, but they remain insulating, ionic compounds—until a critical ionicity, below which the optical gap vanishes, the ionic state becomes unstable, and interesting properties appear. In both classes of materials, just below this critical ionicity they are mixed valence and have metallic conductivity. Organic compounds with lower ionicity form neutral solids, while the corresponding oxides do not form stable compounds. In addition, there are some compounds of both types near the critical ionicity in which a phase transformation can be induced: neutral-ionic transitions in organics, and metal-insulator transitions in oxides. © 1992 Academic Press, Inc.

Introduction

During the last several decades, two classes of materials have attracted considerable attention because of their conductivity and electronic properties, i.e., oxides (*1–4*) and organic compounds (*5, 6*), with many important contributions to the former originating from Professor Hagenmuller's laboratory (*1*). Work on these two material classes continues with the renewed interest generated by the discovery in both systems (*7–10*) of superconductivity at relatively high temperatures. In comparing these apparently very different classes of materials, we have found some features in their conductivity and optical properties that are common to both; namely, the energy of optical absorption for a wide range of compounds of both types can be described by a simple ionic model. In addition, this simple model also accounts for why some compounds have metallic conductivity, while the majority are insulating. This model can furthermore be used to make predictions for new compounds and offers a clear physical interpretation: strongly ionic compounds are insulators; in a series of compounds with decreasing ionicity, they remain ionic and insulating until a certain critical value of the ionicity, beyond which they become mixed valence and have metallic conductivity.

According to the simple ionic model, the structure of these materials is viewed as composed of point charges and we neglect the electronic overlap between the anions and cations. The ionicity is determined by the competition between two contributions

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to the total energy: (i) the electrostatic (or Coulomb) interaction between the point charges, which favors an ionic state; and (ii) the atomic energy required to ionize the species, which is a net cost in energy and hence favors the neutral state. The ionicity can be related to a difference between these two energies. For the optical absorption, we are interested in the energy, Δ_0, required to excite an electron from the anion to the cation, which is given by

$$\Delta_0 = \left(e\Delta V_M - \frac{e^2}{a}\right) - (I - A), \qquad (1)$$

where $e\Delta V_M$ is the difference in the electrostatic energies between the cation and anion sites. In the case of organic compounds, I is the ionization potential of the neutral donor and A is the electron affinity of the neutral acceptor. In oxides with metal cations M^{v+}, I is the ionization potential of $M^{(v-1)+}$ and A is the electron affinity of O^-. The energy Δ_0 is thus the difference between an electrostatic and an atomic energy and we shall use it as a quantitative measure of the ionicity. This definition (Eq. (1)) emphasizes that the ionicity is not a black and white quantity; rather, the ionicity is a continuous variable. There are compounds with large values of Δ_0 in which the energy to excite the electrons is very high. In these compounds, the electrons are strongly bound to the anions and they are strongly ionic. In other compounds, Δ_0 is lower, the electrons are less strongly bound, and these are less ionic. When Δ_0 becomes as small as thermal energies, a compound cannot remain an ionic insulator.

The approach taken in this paper is to consider a large variety of both organic compounds and oxides with a wide range of ionicities. In each of these two series of compounds, we will examine what variations in the conductivity and optical absorption are induced by this variation in the ionicity. First with organic compounds and then with oxides, we will compare the experimental energies due to excitation of electrons from anions to cations with those calculated by the model, i.e., Eq. (1). Then we will study the conductivity of these series of compounds and will find that the onset of metallic conductivity appears when Δ_0 becomes small and the compounds "lose their ionicity."

Optical Absorption in Organic Charge-Transfer Compounds

Organic donor molecules (D) and acceptor molecules (A) often form solids which contain stacks of alternating donors and acceptors that may be neutral ($\cdots D^0A^0 D^0A^0\cdots$) or ionic ($\cdots D^+A^-D^+A^-\cdots$). In the case of ionic stacks, the energy $h\nu_{CT}(I) = \Delta_0$ to transfer charge from the anion (A^-) to the cation (D^+) is given (*11*) by Eq. (1). In the case of neutral stacks, an electron may be excited from D^0 to the neighboring A^0 with an energy given (*11*) by

$$h\nu_{CT}(N) = (I - A) - e^2/a, \qquad (2)$$

which involves the ionization potential (I) of the donor and the election affinity (A) of the acceptor, as well as the Coulomb attraction between the charges created at a separation a. (This absorption gives these solids a much stronger color than the donors and acceptors separately.) As a function of the ionicity, Δ_0, the energy of the optical absorption (Eqs. (1) and (2)) has the behavior shown by the solid lines in Fig. 1. Starting with compounds with high ionicity, which have ionic stacks (right of Fig. 1), the energy of absorption in the ionic phase decreases as the ionicity decreases until a critical ionicity (where $2(I - A) = e\Delta V_M$), beyond which the compounds are neutral and the energy $h\nu_{CT}$ increases with decreasing ionicity. Thus, Eqs. (1) and (2) predict a V-shaped curve for $h\nu_{CT}$, with a transition between ionic and neutral states occurring where $h\nu_{CT}$ is a minimum.

In order to compare these predictions of

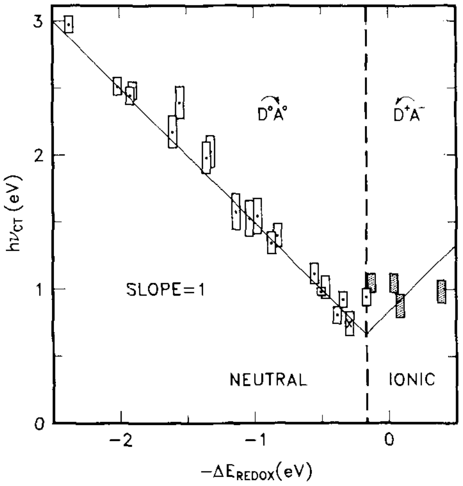

FIG. 1. The energy of the observed charge transfer band vs. the ionicity in a variety of neutral and ionic organic solids, compared with the predictions (straight lines) of a simple ionic model (after Ref. (*14*)).

the ionic model with experimental data of $h\nu_{CT}$, we need a measure of the ionicity, Δ_0 (Eq. (1)). There are only a few calculations of ΔV_M and measurements of I and A for a few molecules, but we need consistent values for a wide range of compounds. Fortunately, the calculated values (*12*) of ΔV_M for several different organic compounds vary by only a few 0.1 eV and thus we shall assume that this energy is a constant. Fortunately also, it has been shown (*13*) that $(I - A)$ is reasonably accurately equal to a constant plus ΔE_{REDOX}, where ΔE_{REDOX} is the difference in electrochemical oxidation potential for the donor and the reduction potential for the acceptor, measured in solution, and where the constant includes various solvent effects. Thus, we have from Eq. (1)

$$\Delta_0 = \Delta_c - \Delta E_{REDOX}, \qquad (3)$$

where Δ_c is a correction term which includes the solvent effects (*13*) (~ -3.9 eV), the average value (*12*) of $(e\Delta V_M - e^2/a) \sim 5.4$ eV, and other (constant) corrections. The basic assumption is not that Δ_c and other neglected effects are small, but rather that they are approximately constant compared with the large variation in ΔE_{REDOX} over the series of organic compounds under consideration.

The observed (*14*) energy, $h\nu_{CT}$, of the charge-transfer absorption is plotted in Fig. 1 vs. ΔE_{REDOX} for 24 organic compounds. It is seen that there is a critical value of the ionicity (corresponding to $-\Delta E_{REDOX} = -0.2$ eV) which separates the ionic compounds (filled rectangles) from the neutral compounds, which have lower ionicity. In the neutral phase, the absorption energy decreases with Δ_0 with a slope of 1, in agreement with the simple ionic model. In the ionic phase, there is not a wide enough range of compounds to confirm the fit to the theory (but it appears not to fit as well as in the neutral phase). The fit in Fig. 1 corresponds to a value of $\Delta_c = 0.8$ eV from Eq. (3). Comparing this value with estimates of the solvent effects (-3.9 eV) and $(e\Delta V_M - e^2/a) \sim 5.4$ eV suggests that there are corrections due to other effects of only $\sim$0.7 eV. Considering the simplicity of the model, the agreement evident in Fig. 1 is remarkable.

One feature evident in Fig 1 is that there are compounds (like TTF-chloranil marked with an x) which are neutral, but which lie very near the neutral–ionic boundary. Recalling that the ionicity is a balance between two terms, can we shift the balance and push these compounds over the boundary into the ionic state? The electrostatic term, ΔV_M, in Eq. (1) can be increased either by applying pressure or decreasing the temperature (thermal contraction). In the case of TTF-chloranil, such a neutral–ionic phase transition has been induced by applying pressure (*14*) ($\sim$10 kbar) and by decreasing the temperature (*15*) ($T < 85$ K). Some of the other compounds in Fig. 1 can also be transformed (*14*) into the ionic state, requiring higher pressure when they are farther from the neutral–ionic boundary. Very recently, a second compound has been found (*16*) to undergo a neutral–ionic phase transition at low temperature.

Optical Absorption in Closed-Shell Oxides

In oxides we can expect to see a charge-transfer optical absorption corresponding to exciting an electron from O^{2-} to the metal cation. The energy of this excitation is given by Δ_0, Eq. (1). From the point of view of electronic bands, this transition corresponds to exciting an electron from the oxygen $2p$-valence band up to the metal conduction band. The energy of the lowest excitation at the gap is given by $(\Delta_0 - W)$, where the ionic model estimate (Δ_0) is reduced by the average bandwidth (W), an effect not included in the simple model. We shall focus our attention on the closed-shell oxides, in order to avoid complications of other types of excitation (e.g., d-to-d, metal-to-metal, etc.).

Concerning estimations for the values for Δ_0 in oxides, we can readily carry out the Madelung sum and calculate the electrostatic term in Eq. (1) $(e\Delta V_M - e^2/a)$, within the ionic model. For the atomic term, we shall use the ionization potentials (*17*) from cations in the gas phase and an estimate (*18*) of $A = -7.7$ eV. In this way, we use the ionic model to calculate Δ_0 for a series of 17 closed-shell oxides and compare (*19*) them with experimental measurements (*20*) of the optical absorption energy in Fig. 2. It is seen that for most of these oxides the optical gap decreases with decreasing ionicity, with a slope of 1 and extrapolating to zero near $\Delta_0 = 10$ eV. The fact that this extrapolation is larger than estimates of the bandwidth $(W \sim 5$ eV) suggests that there are large energies (~5 eV) which are not included in the super-simple ionic model (as we should expect). The deviations of the data from the theoretical prediction (the straight line in Fig. 2) suggest that there are variations of order 1 eV in the energies not included. In general, however, Fig. 2 shows a remarkably good agreement with the simple ionic model.

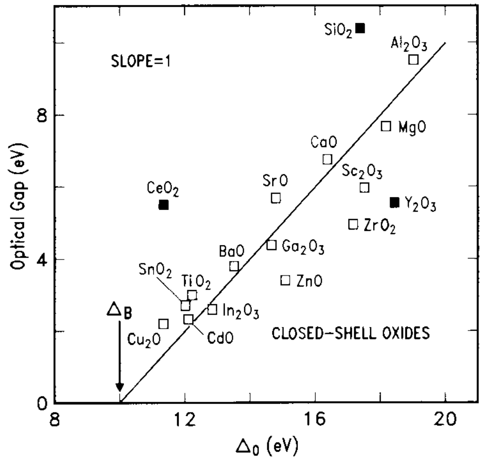

FIG. 2. The observed energy gap vs. the ionicity (Δ_0) calculated from the simple ionic model for a series of closed-shell oxides (after Ref. (*19*)).

Conductivity of Organic Compounds

The vast majority of organic donor-acceptor compounds are insulating, with $\sigma(300\ K) < 10^{-5}\ ohm^{-1}\ cm^{-1}$. There are a few with 1 : 1 stoichiometry $(D:A)$, however, that have $\sigma(300\ K) > 10\ ohm^{-1}\ cm^{-1}$ and show metallic temperature dependence (above a metal–insulator transition at lower temperature). In order to explore the possible role of ionicity, we use the same measure of ionicity as earlier for the optical absorption, e.g., Eq. (3). In this discussion, however, we will include structures in which there are separate, segregated donor stacks and separate acceptor stacks (*21*), in addition to the alternating stacks discussed earlier. In Fig. 3, we plot (*22*) the magnitude of $\sigma(300\ K)$ as a function of the ionicity, i.e., $-\Delta E_{REDOX}$. As in Fig. 1, we see that compounds with high ionicity (right of Fig. 3) are ionic while compounds with low ion-

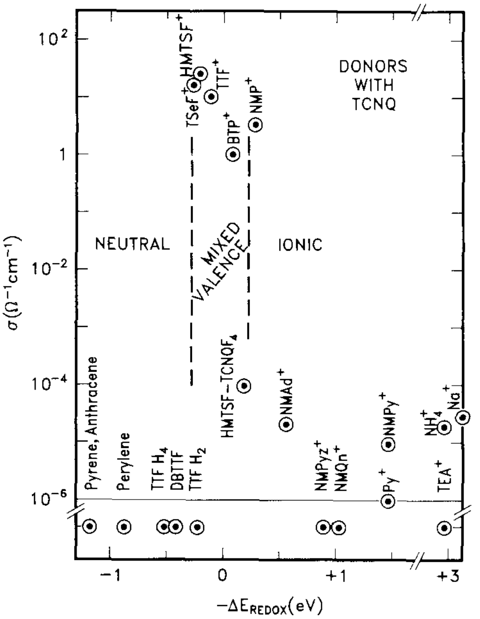

FIG. 3. The observed electrical conductivity at 300 K for a series of organic compounds vs. the ionicity, showing that the metallic conductors lie in between the ionic and neutral compounds (after Ref. (*22*)).

icity are neutral. Both of these groups are insulating, with the ionic compounds having a higher conductivity than the neutral ones, as expected. The compounds with metallic conductivity are found to cluster together with intermediate values of the ionicity. This observation is readily understood (*22*) by realizing that compounds intermediate between fully ionic and neutral could have mixed valence (partially filled bands) and hence be metallic. This mixed valence state is due to an incomplete transfer of charge from donor to acceptor. (Compounds with a $D:A$ stoichiometry other than 1 : 1 have mixed valence more trivially.)

Previously, it was observed that high conductivity appeared to occur only in compounds having TCNQ as the acceptor. Using the above ideas (*22*) and using the common (but hitherto unsuccessful) acceptors chloranil, bromanil, fluoranil, and DDQ, a series of new compounds were synthesized and found (*23*) to be the first highly conducting organic compounds not employing TCNQ.

Conductivity in Oxides

The conductivity behavior for the known oxides (*1–4*) is summarized (*19, 24*) in Table I. This table illustrates the breadth of oxide compounds, including first row and second row transition metals (third row not included) as well as some rare earths, in divalent, trivalent, and tetravalent oxidation states. They form binary as well as perovskite-like ternary oxides, for a total of 76 compounds. It is also clear from the table that there is no clear pattern to the conductivity behavior, with metals, insulators, and compounds showing metal–insulator transitions seemingly randomly distributed over Table I. In order to see whether the ionicity can bring some order or sense to this behavior, we obtain values of Δ_0 (Eq. (1)) as before (using Madelung calculations and gas phase ionization potentials). In Fig. 4 we show the 76 compounds of Table I and their values of Δ_0. Also shown are their values of another parameter (the disproportionation energy U') which is included in the more complete analysis of Refs. (*19*) and (*24*). For the purpose of this paper, however, we neglect the vertical axis and concentrate on the horizontal variations, which indicate the dependence on the ionicity Δ_0. It is clearly seen that a vertical line can be drawn in Fig. 4 at $\Delta_0 = 10$ eV which separates most of the insulating compounds (open symbols) from most of the metals (closed symbols). (Here we ignore the metals in the lower right of Fig. 4, which are metallic for a different reason. These are discussed in the more complete analysis of Refs. (*19*) and (*24*)). A comparison with Fig. 2 reveals that the optical gap of the closed-shell oxides extrapolates to zero at the same value of $\Delta_0 = 10$ eV. This is not a coincidence and has a clear

TABLE I

CONDUCTIVITY OF UNDOPED TRANSITION METAL OXIDES

	Divalent		Trivalent			Tetrvalent		
	MO	La_2MO_4	M_2O_3	$LaMO_3$	$LaSrMO_4$	MO_2	$SrMO_3$	Sr_2MO_4
Ti	met.		met/ins	met/ins		ins.	ins.	ins.
V	met.		met/ins	ins.	ins.	met/ins	met.	ins.
Cr			ins.	ins.	ins.	met.	met.	
Mn	ins.		ins.	ins.	ins.	met.	ins.	ins.
Fe	ins.		ins.	ins.	ins.		met.	
Co	ins.	ins.		ins.	ins.		met.	
Ni	ins.	ins.		met/ins	met.			
Cu	ins.	ins.		met.	met.			
Nb	met.					ins.		
Mo						met.	met.	met.
Ru				met.		met.	met.	met.
Rh			ins.	ins.		met.		
Sn	ins.					ins.	ins.	ins.
La	met.		ins.					
Ce	met.		ins.			ins.	ins.	
Pr	met.		ins.			ins.	ins.	
Nd	met.		ins.					
Eu	ins.		ins.					
Yb	ins.		ins.	ins.				

interpretation: oxides with large ionicity are ionic and insulating with large optical gaps. Compounds with decreasing ionicity have gaps which correspondingly decrease, but they remain insulating—until a certain critical ionicity corresponding to $\Delta_0 = 10$ eV. Compounds with $\Delta_0 \leq 10$ eV, have no optical gap and for this reason display metallic conductivity.

Note also that there are two compounds near the critical ionicity marked by a symbol with a dot in the center, namely VO_2 and $LaNiO_3$. Both VO_2 and the system $LnNiO_3$ show *(25)* an insulator–metal transition, corresponding to a thermally induced transition from above to below the critical ionicity.

Conclusion

The conclusion of this paper can be seen in Fig. 5. In this study of the ionicity of oxides and organic compounds, a common pattern of behavior is found. In strongly ionic compounds, the energy required to excite an electron from anion to cation is high and the compounds are insulating. For a series of compounds with decreasing ionicity, the energy of this excitation decreases, but they remain stable, insulating ionic compounds—until a critical ionicity, below which the ionic state becomes unstable and interesting properties appear. In both organic compounds and oxides just below the critical ionicity, the loss of ionicity manifests itself as a state of mixed valence: in the organic case, $D^{+}A^{-}$ becomes $D^{(1-\delta)+}A^{(1-\delta)-}$; while in oxides $Ln^{3+}Ni^{3+}(O_3)^{6-}$, for example, becomes $Ln^{3+}Ni^{(3-\delta)+}(O_3)^{(6-\delta)-}$. This mixed valence state *(26)* is evidenced by the appearance of metallic conductivity in both systems. In addition, there are some ionic compounds that lie so close to this critical ionicity that they can be induced to lose their ionicity at high temperatures, either to a neutral phase (ionic–neutral transition in organics) or to a mixed-valence metallic state (insula-

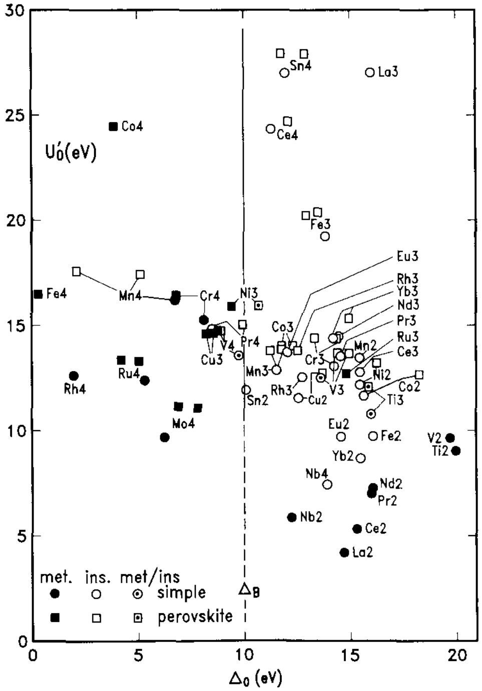

FIG. 4. The values of the parameters U_0' and Δ_0 for the 76 oxides in Table I, calculated using the simple ionic model. The symbols refer to the transition metal and its formal valence in the oxide. Note the vertical line at $\Delta_0 = 10$ eV which separates the metals (solid symbols) on the left from the insulators (open circles) (after Refs. (*19*, *24*)).

tor–metal transition in oxides). Organic compounds with even lower ionicity form neutral solids, while the corresponding oxides (which would have neutral oxygen) are unstable and do not form (*27*).

We conclude that a simple ionic model remarkably well describes the conductivity and the energy of optical absorption of both classes of compounds. This success demonstrates that this model is an excellent starting point for more sophisticated future studies that will add the (many) important interactions and effects not included in this oversimplified model. Nevertheless, this model will continue to be useful for the simple physical interpretation it provides for

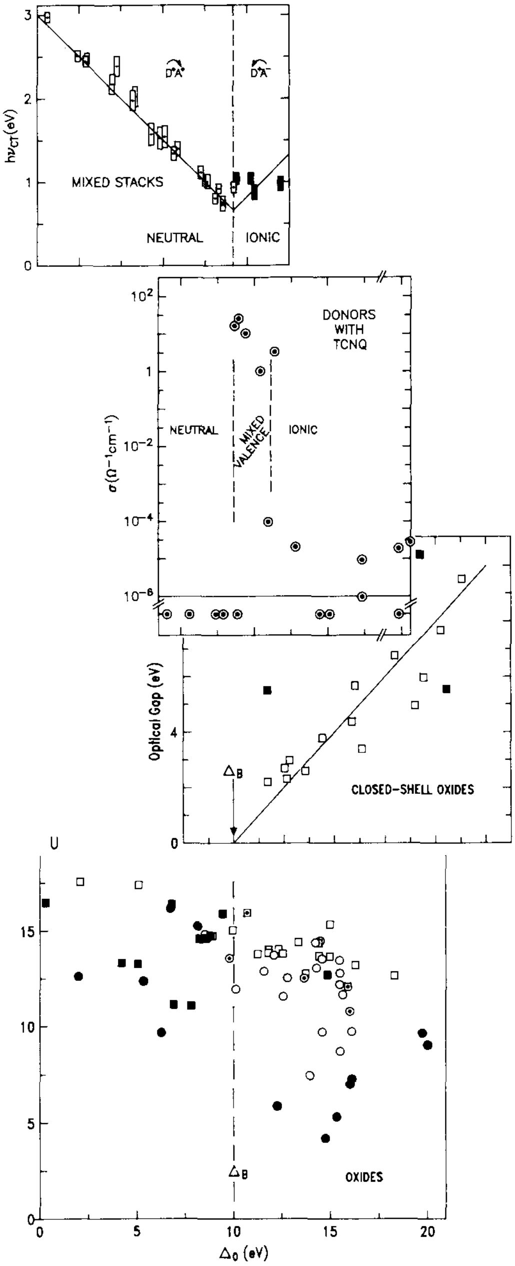

FIG. 5. Summary of the behavior of organic compounds and oxides as a function of ionicity, showing that where the compounds "lose their ionicity" is where they have interesting properties: small optical gaps, metallic conductivity, ionic–neutral transitions, and insulator–metal transitions.

understanding these materials and for predicting properties for new materials.

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