Electrons in Oxides: A Summary*

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Oxides are traditionally associated with materials like clay, cement, and sand, and with products like brick, glass, and dinnerware. The chemical compounds involved are alumina, silica, magnesia, etc. They are characterized by chemical stability, good mechanical strength, high temperature resistance, and low cost. Discussion of these materials usually is in terms of macroscopic and atomic structure with emphasis on ionic bonding and defects like dislocations, grain boundaries, voids, etc. These aspects are listed on the left hand side of Fig. 1.

At this conference, we have focused our attention on the more atomic and electronic characteristics of oxides, presented in Fig. 1 on the right. These properties are best discussed in the language of solid state physics. Among the oxides one finds energy gaps all the way from 0 to 10 eV. Hence, this group of compounds comprises both the best insulators as well as good metallic conductors. Many oxides—especially the binaries and ternaries containing transition metal ions—undergo phase transitions, often accompanied by discontinuities in their physical properties. All varieties of magnetic and dielectric behavior are represented.

Oxide compounds lend themselves particularly well to substitution of one or more ions, thus producing mixed crystals with different magnetic, electric or optical properties. With this tool in hand, it is possible to create materials with just the right physical characteristics for a particular application. This does not imply that the properties of all oxides are clearly understood. Even the phenomena observed in some of the simple binary oxides of the first transition series have created extremely difficult problems in interpretation. It is clear, however, that research on oxides presents the physicist and the chemist with a fascinating challenge in scientific exploration and engineering development.

This conference has tried to give an overview of the multitude of electronic and lattice properties that have been observed in oxides and the great variety of applications that have resulted from this research. A first glance at the program would seem to indicate that the different topics discussed at this meeting have little relation to each other. We hope, however, to have erased this impression and to have shown that there is a rather close connection between the different physical aspects of oxides. Partly following the program and partly deviating from it, I have tried to divide the subject matter in 4 major topics: 1. optics, 2. magnetics, 3. electronic conduction, and 4. surfaces and interfaces (see Fig. 1). It should
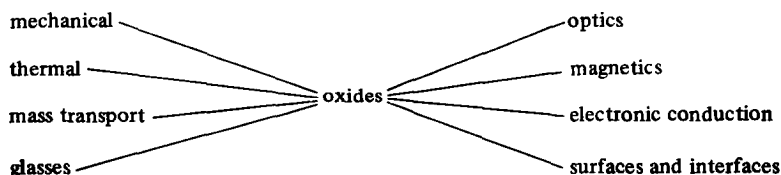

FIG. 1

* Invited paper.

TABLE I

OXIDES IN OPTICS

Physical aspect	Material	Application
$n = $ *refractive index*		
$NLO: P_i^{NL} = E_o d_{ijk} E_j E_k$	Ba_2NaNbO_{15}	SHG (doubling)
$d_{ijk} = $ nonlinear tensor	$LiIO_3$	Parametric oscillation
$EO: n = n_o + rE_o + p\sigma + \ldots$	$LiNbO_3$	Q-switch
$r = $ electrooptic coefficient	KTN (K-tantalate-niobate)	Modulator
$p = $ stress optic coefficient	$PbMoO_4$[a]	Beam deflector
$n, n - \Delta n$	Borosilicate glass	Optical fibers
ferroelectric domains	PLZT (Pb-La zirconate-titanate)	Memories, displays
Crystal field of ions in oxide host		
Energy spectrum	Ruby	Laser (red)
	YAG:Nd	Laser (ir)
Lifetime	$YVO_4:Eu$[a]	Color TV
	Halophosphate:Sb, Mn[a]	Fluorescent lamps
Energy transfer	$(La_{0.5}Na_{0.5})WO_4:Yb, Er$[a]	Counters, converters
Electron transfer	$SrTiO_3:Ni, Mo$	Photochromic (displays)

[a] Not discussed at this conference.

be stressed that this discussion of oxide materials is, of course, far from complete.

Table I lists a number of optical applications and indicates the preferred oxide material(s) in each case. From the physics point of view, the key words are *refractive index* and *crystal field*. The first one is a continuum parameter which is the basis of the electrooptical (EO) (low frequencies) and nonlinear optical (NLO) (optical frequencies) effects in polarizable crystals. The optical phenomena in the second group of Table I are the result of optical excitation and emission between energy levels of impurity ions embedded in an (oxide) crystal. These energy levels are determined by the atomic structure and the crystal field produced by the ligands surrounding the ion in question.

Although at first the two groups of effects seem to be unrelated, they are, in fact, closely tied together. The refractive index is determined by the electronic energy band structure. These energy bands can be calculated in the case of relatively narrow ($3d$ bands) by a tight binding method using the crystal field splitting as the first approximation (1). DiDominico and Wemple (2) have shown for the case of perovskite crystals how the EO

and NLO effects can be derived from the energy band shifts produced by the electric field induced polarization.

Table II refers to a group of effects and applications in oxide materials that were not discussed at this conference. For the sake of completeness, I have listed a number of magnetic oxides and their uses in transformers, storage devices, etc. (3).

The next category (Table III) has considerable overlap with Table II. Many oxides listed in Table III show magnetic transitions. However, the emphasis in the discussion of these oxides was on the nature of the conduction process. Electronic transport in transition-metal oxides brings two closely related problems to the fore: 1. What is the proper way to describe the electrons in such crystals? and 2. What causes the transition from semiconductor to metal in some of these oxides? The debate about these questions has been raging for the last ten to fifteen years and has been continuing at this conference. During the 1960's several theories or explanations were proposed. Mott was first in pointing out the importance of electron correlation (4). As the lattice constant decreases, the material will change discontinuously from an insulator

TABLE II

MAGNETIC OXIDES[a]

Physical aspect	Material	Application
χ = magnetic susceptibility	$BaFe_{12}O_{19}$	Permanent magnets
M_s = saturation magnetization	$(Ni_{1-x}Zn_x)Fe_2O_4$	Transformer cores, antennas
H_c = coercive force	$(Mg_{0.5}Mn_{0.5})Fe_2O_4$	Computer memories
B_r = remanence	γ-Fe_2O_3	Magnetic tapes
T_c, T_N = Curie–Néel temperature	Rare earth orthoferrite	Magnetic bubbles (storage)
J = exchange integral	EuO	Curie writing (storage)
	YIG (yttrium iron garnet)	Magneto-optical modulator

[a] Not discussed at this conference.

to a metal (Mott transition). This model has one major difficulty; it requires that the critical lattice parameter falls within the small range of lattice contraction. It is, of course, true that the one-electron model neglects the electron interaction completely and that electron correlation must be considered. Other workers (5) have suggested that the insulator–metal transition is due to a lattice distortion either driven by a lowering of the total ground state energy or by a lattice instability (e.g., a ferroelectric transition). Another suggestion is that of the excitonic insulator (6), a phase that can occur at low temperatures when the energy gap of a semimetal is decreased to zero (e.g., under pressure). Finally one should mention the early proposal made by Slater (7), which should apply to all antiferromagnetic materials. Below the Néel point the antiferromagnetic array of spins will double the cell size and reduce the Brillouin zone to half its original size. Hence, an energy gap will develop and the material will transform from a high temperature metal to a low temperature semiconductor. Unfortunately, this theory has a major weakness: several antiferromagnetic

TABLE III

ELECTRONIC CONDUCTION IN OXIDES

Physical aspect	Material[b]	Application
Energy spectrum	SnO_2, $(ZnO)^a$	Transparent electrodes
Bands or levels	TiO_2, CoO (292 K)	Oxygen sensors
Collective or localized	NiO(:Li) (523 K)	
Itinerant or hopping	$Fe_{1-x}O$ (198 K)	Thermistors
	$(LaSr)CrO_3$ (285 K)	High temperature electrodes
	YIG (yttrium iron garnet)	
Semiconductor–metal transition	V_2O_3 (150 K)	
	Ti_2O_3 (450–650 K)	
	Ti_4O_7 (130 K)	
	$(Cr_xV_{1-x})_2O_3$	
	$(V_xTi_{1-x})_2O_3$	
	$Cd_2Os_2O_7$ (225 K)	
Superconductivity	$Rb_{0.2}WO_3$ (4.35 K)^c	

[a] Not discussed at this conference.
[b] Figures in parentheses indicate the transition temperatures or range.
[c] Superconducting transition temperature.

solids remain semiconductors above the Néel point. Goodenough (8) has related the degree of d-electron localization to the relative size of the (direct or indirect) orbital overlap energies and the crystal field splitting. The application of this idea to a large number of compounds of the perovskite family has been very successful.

In general, it seems that all the suggested theories have a common defect: they are able to explain the behavior of a few materials, but often fail when applied to very similar compounds even of the same homologous series. The lack of understanding of the relation between large changes in magnetic behavior and in electrical conductivity at the Néel point of antiferromagnets is discouraging.

It should be realized that the transition-metal oxides are very sensitive to slight changes of the lattice constants and to small symmetry distortions, which are often accompanied by enormous variations in physical properties. This has the advantage that these materials can be studied with the aid of modest pressures, reasonable electric or magnetic fields, or by the introduction of small amounts of foreign ions. However, the drawback is that extremely perfect crystals are required if one wants to measure and understand the properties of the pure material.

Surface phenomena are in many respects an extrapolation of the bulk properties dis-cussed above. The question is, how are the energy states, the charge distributions and the binding energies modified by the presence of the surface? And how can one exploit these physical and chemical surface properties for technological applications? Table IV lists a number of oxides that are being used in semiconductor devices and in catalytic pro-cesses.

The semiconductor devices considered here are basically variable capacitors. They usually consist of Si covered with a SiO_2 film (~1000 Å) on which a metal is evaporated. The charge (produced, for instance, by light) is stored at the Si–SiO_2 interface. Surface states and impurities (Na, H) in the oxide film will affect the efficiency and response time of these devices. Hence, it is important to determine the concentration, activation energies and lifetimes of these defects.

The phenomena of the second group in Table IV are chemisorption and catalytic reactions. The role of oxides in catalysis is well known (9); for instance, V_2O_5 has been used in oxidation processes and $CoO \cdot MoO_3$ for desulfurization. More recently, it has been shown that ABO_3 oxides of the perovskite group (slightly distorted cubic structure) hold promise for the oxidation of CO and reduction of NO (10) and for use as electrodes in low temperature fuel cells (11). The oxides lend themselves particularly well for funda-mental studies of the chemisorption process.

TABLE IV

OXIDE SURFACES

Physical aspect	Material	Application
Space charge barrier	Si–SiO_2	M.O.S. capacitor
Surface states		F.E.T. (transistor)
		C.C.D.
Surface acoustical waves	ZnO	Delay lines
Chemisorption	(LaSr)MnO_3	Automobile catalyst
Catalysis	Zeolites (Ge)	Hydrogenation
	$CoO.MoO_3^a$	Desulferization
	$V_2O_5^a$	Oxidation
	NiO:Li^a	Fuel cell batteries
(Surface states)	$SrTiO_3$	

^{a} Not discussed at this conference.

Transition-metal oxides, especially, are efficient catalysts, pointing to the particular role of d electrons in chemisorption and surface reactions. The question is whether the band picture or the crystal field model provides the best description for the binding of the ad-atom on the surface. From the experimental point of view a host of methods is available to study the electronic requirements of an oxide catalyst and to probe its surface with or without adsorbed species. The n- or p-type character of semiconducting oxides has been correlated with the preference for chemisorption of simple gas molecules. In a few cases, the effect of cation substitution on the chemisorption and catalytic activity of certain oxides has been explored. At this meeting a number of surface studies have been reported: ir measurements on silica, alumina, titania, and zeolites, as well as EPR experiments of radicals on ZnO and MoO_3. Several other spectroscopic techniques are promising tools for the study of oxide surfaces. Low energy electron diffraction (LEED) has been used recently to investigate the structure of a (0001) face of α-Al_2O_3 with excess Al or excess O on the surface (12). Kim and Winograd (13) have applied X-ray photoelectron spectroscopy (XPS or ESCA) to study the oxides produced on a Ni surface when exposed to an $O_2{}^+$ ion beam.

It is quite conceivable that the exploration of oxide surfaces will become a major focal point of materials research in the next few years.

Several factors contribute to this possibility:

1. The increasing interest of physicists and chemists in the structure and properties of oxides;
2. The greatly expanded arsenal of experimental and theoretical tools now available for the study of oxide surfaces;

and 3. the technological need for a better understanding of surface phenomena and for the development of new (oxide) catalysts.

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