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Study of Optical Properties of Transition Metal Oxides on the Basis of Energy Band and Energy State Analysis

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INTRODUCTION

By Optical Properties is meant a material's response to exposure to electromagnetic radiation and, in particular, to visible light. In this article we will discuss the optical properties of Transition Metal Oxides on the basis of band structure. The energy band structure of 3d transition metal oxides are very helpful to determine their magnetic, electrical and optical properties. On the theory of energy band analysis of the scandium, titanium and vanadium oxides it is found that nonbonding 3d orbitals of neighboring cations overlaps each other and forms a 3d conduction band. 3d orbitals does not overlap with the oxides of other 3d metals. Due to this fact the 3d electrons remains in isolated energy states. In addition to this, transport of electrons takes place through the process of electron exchange between cation neighbors and also involves an activation energy. Conduction in these oxides includes transport of high mobility holes in the 2p band of the oxygen lattice and of low-mobility holes and electrons in the 3d levels of the cation lattice[1].

The transition metal oxides combines with other elements and this combination results in the synthesis of new compounds of different properties. These compounds ranges from chemical bonding from ionic (Oxides) through covalent (Sulphides, Arsenides) to metallic (Carbides, Nitrides). This range in the valence character provides a vast variety of energy band structures and transport processes. This in turn provides great field for theoretical and experimental investigations.The energy band structure of the solid is its most fundamental aspect. The main focus of this paper is to provide tentative energy band scheme for the 3d oxides. Due to the lack of reliable experimental data about single-crystal material, the proposed energy band can be regarded as tentative only. But at the same time it provides useful input for the experiment in future.

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THEORY

Zinc Oxide is made of ions having closed-shell electronics configuration.The energy band in Zinc Oxide arisess to a first approximation from the filled 2p levels of the O^- and the empty 4s levels of Zn^{++}. These are broadened when ions are brought together to form the solid. The filled 2p band is separated from the empty 4s band by a forbidden energy gap. This is the region why the Zinc Oxide is a semiconductor. In similar way 2p band and 4s band are expected to arise in 3d oxides.

In 3d metal oxides calculation for energy bands has been done by using the cellular and the tight binding methods [2]. Generally it is found that 4s band overlaps the 3d band. In addition to this, 3d band can hold 10 electrons per atom while 4s band can hold only two electrons per atom which leads into the difference of bandwidth.If the band is narrow it means there is low mobility of charge carriers in the band. Transport in a 4s or 2p band is evidenced by the relatively high mobility of low-mass carriers in a wide band. Result of soft X-ray emission indicates the 2p band in oxides to be 10 to 20 ev wide [3].

ATOMIC ORBITALS AND CRYSTAL FIELD.

In a transition metal oxide if the wave function of 3d oxide do not overlap to form an energy band but remains concentrated near the cations, in that case the cations are isolated. It experiences the electrostatic forces only due to surrounding oxygens. Such situations prevailed in the hydrated salts of transition metal oxides. In NiO, which is a face centered cubic structure, the negative oxygen are also arranged in a regular octahedron pattern about the Ni^{++}. Actually, the optical absorption spectrum for NiO is very similar to that for the hydrated salt. In the context of all these factors it can be considered that the same theories might be applied to the 3d oxides.This theory have been used in the recent years to explain the optical properties of complex salt of 3d ions. In converse it implies that, if a given oxide spectrum can be explained in this way, the 3d wave function in that oxide are concentrated near the cation and do not overlap to form a band.

Three theories can be used to describe the optical properties of the transition metal oxides.

1. Molecular Orbital [4]
2. Valence Model [5]
3. Crystal Field.

The main advantage of crystal field theory is that it gives the information in a very simple manner about the excited states of the cations. It explains the absorption spectra and gives insight into the electric and magnetic properties of the oxides. The crystal field theory assumes a purely ionic model and considers the effect of octahedrally coordinated negative anions on the 3d electrons of central cation. Regarding the splitting of energy levels, there is one rule exists according to which centre of gravity in energy are not altered by perturbation. That is given by

$$3E_e + 2E_\gamma = 0 \text{ ----------(1)}$$

If we fix the energy scale as zero at ground state of the free ion and assume 10Dq as the energy difference between two levels which a single 3d electron can occupy when subjected to a cubic field gives, from (1).

$$Ee = -4Dq \text{ ----------(2)}$$

$$E\gamma = +6Dq \text{ ----------(3)}$$

In Fig.1 the relative locations of excited states above the ground state determined for ions with electron configurations d^1 to d^9 subjected to cubic field are shown. In each diagram ground states are shown in left. Diagram (c)and (d) shows the first free ion excited states and (b) shows two excited levels for free ions. The right part of the diagram shows the ground states and excited states for the ions in solid. In these diagrams, the first excited state of the ion corresponds to the excitation of electrons from d_e to d_γ levels. These transitions of energy levels became allowed as a result of lattice vibration [6] and hemihedral distortion[7].

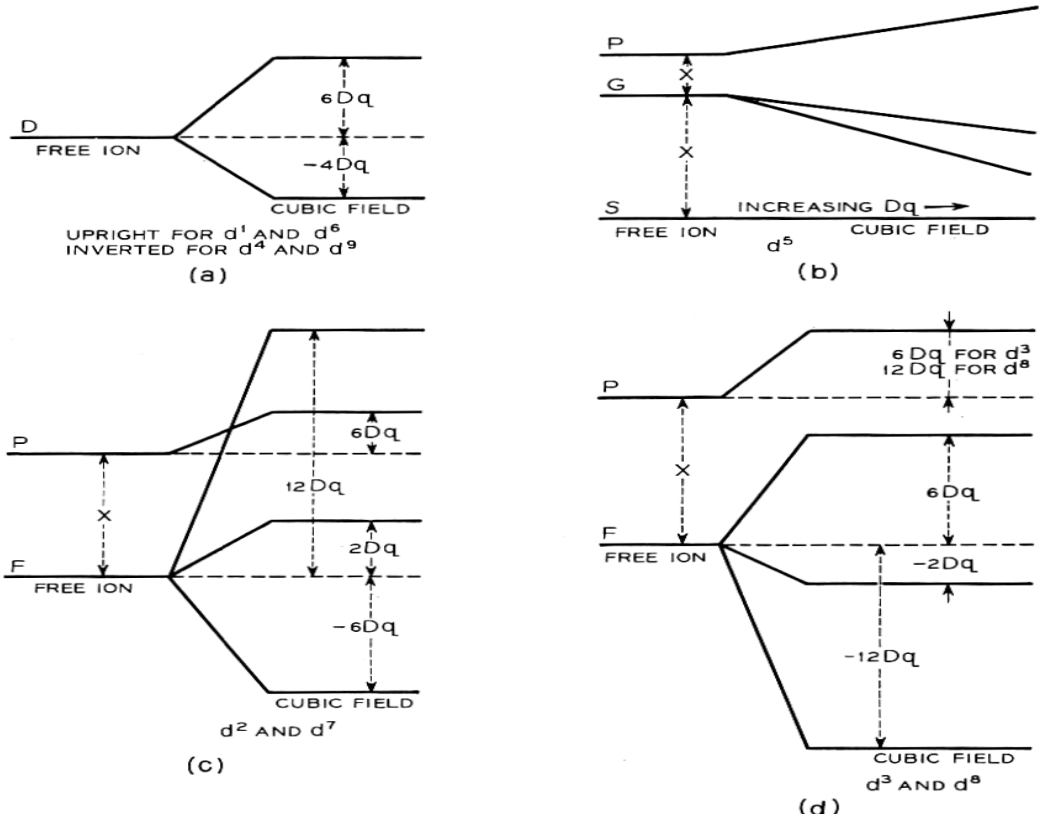

Fig.1: Location of some excited states above the ground state for ions with electron configurations d^1 to d^9.

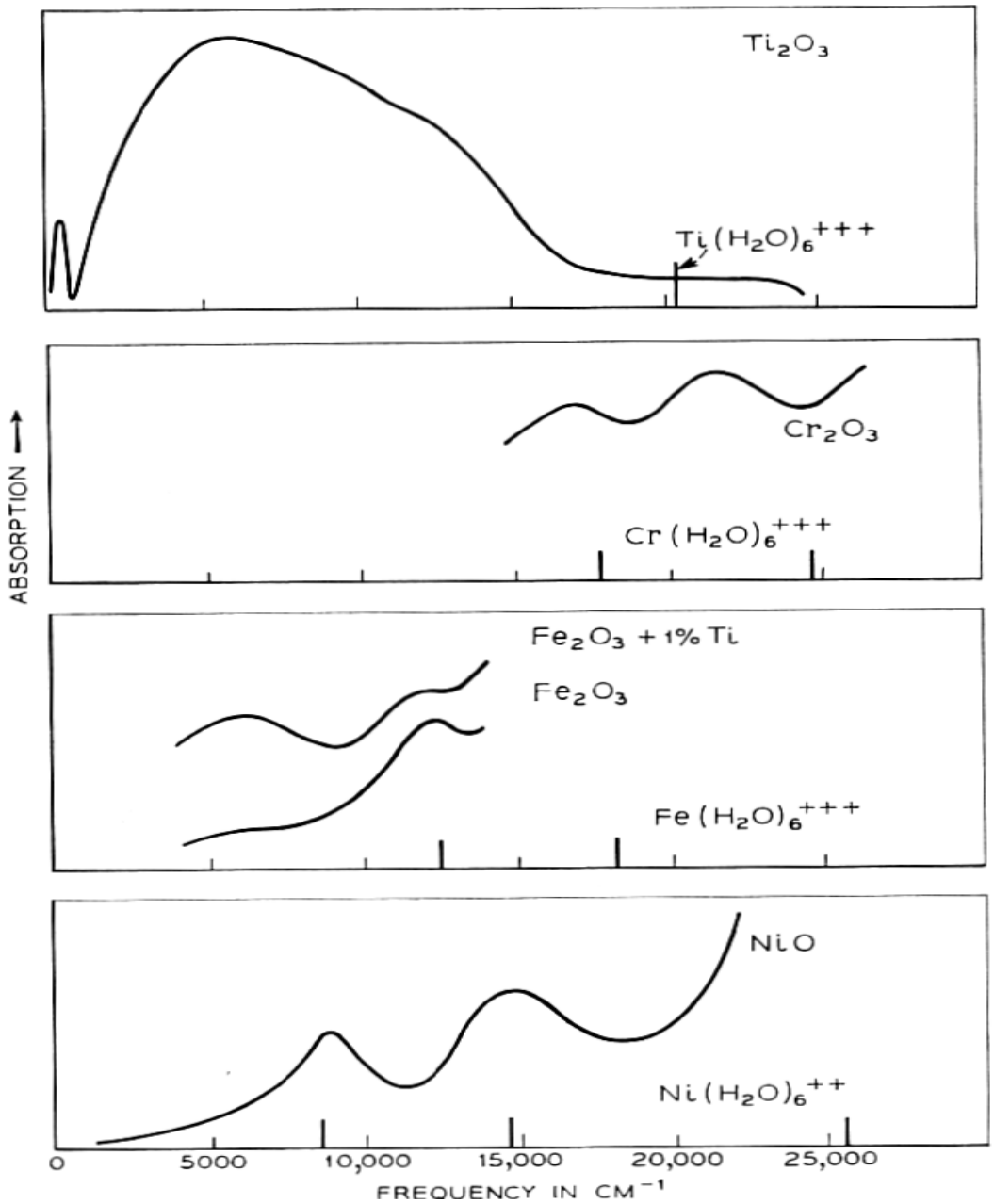

Fig: 2

The available absorption spectra for some of the oxides are shown in Fig.2. The close correspondence between maxima found in hydrated complex and oxide for Fe^{++} and Ni^{++} indicates that the cation is isolated in the oxide as it is in the hydrated salt. It also suggests that the 3d wave functions do not overlap in the oxides of metal Nickel and Iron. The spectra of Cr_2O_3 show a slight shift to frequencies lower than that of the hydrated salt which indicates slight overlap of the 3d wave functions. This shift becomes very large in the case of spectra of Ti_2O_3. This indicates that cation in this oxides are not isolated as in their hydrated salts, and may be due to overlap of 3d orbitals, with the formation of 3d bands. Another information can be obtained from the absorption spectrum of Fe_2O_3 containing titanium. This shows an additional absorption band appearing at 6100 cm^{-1} when one percent of titanium is added. The titanium is the donar in Fe_2O_3 and, in this concentration, it is nearly all ionized to give Ti^{++++} and Fe^{++} ions. In above discussion we have focused on the optical properties of Transition Metal Oxides on the basis of concept of band structure and subsequently the transportation of electrons.It is found that the study of optical properties of Transition Metal Oxides is always of great significant.

RESULT AND DISCUSSION.

Optical properties of transition metal oxides are always of great significance. It helps us to understand the behavior of transition metal oxides on different platform. Magnetic, electrical and optical properties of transition metal oxides can be determined by the study of their band structure. On the basis of this study we have found that transition metal oxides nonbonding 3d orbitals of neighboring ions overlaps each other and forms a 3d conduction band. This study also shows, how transportation of electrons takes place between different catiions neighbors. It can also be concluded that the conduction in these transition metal oxides includes the transport of high mobility holes in 2p band of oxygen lattice as well as the low mobility holes and electrons in the 3d levels of cation lattice. Study of optical properties of transition metal oxide facilitate us to combine the different transition metal oxides and to synthesis of new material of desired properties.

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