

CHAPTER - II

Theoretical

Background .

C H A P T E R - I I

THEORETICAL BACKGROUND

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2.1 Introduction :

The nature of the material (conducting or insulating) can be identified experimentally by measuring the transport properties. Theoretically the electronic bands of the material explain the conducting or insulating nature of the material. Thus the calculation of bands should be correct one. To get a good agreement between theory and experiment different theories, correlations and interactions between electrons are taken into account. These theories, correlations and interactions give different models. In this chapter a short survey of models is taken and the transport properties on the basis of these models are explained.

2.2 Theoretical Models [to explain electrical properties].

2.2.1 Itinerant Models :

According to the elementary band theory most of the transition metal oxides must be metallic but actually they are insulators. On the other hand the detailed band calculations show that many other materials which principally could be insulating are metallic due to inefficiency of coupling of spin orbit and crystalline field effect to split the bands and to introduce a real gap into the density of states. Thus the more sophisticated band calculations can be done on individual materials to yield to correct electrical properties.

To understand how these models explain the nature of material, consider an example of NiO. It has rocksalt structure and eight '3d' electrons per Ni^{++} ion. It is antiferromagnetic below 520°K and highly insulating.

Yamashita/1/, found that the '3d' band is very narrow and is located exactly in the middle of the oxygen 2p and if 'p-d' mixing is neglected. Thus there is no gap between the bands and NiO shows an excellent metallic nature. Though the '3d' band is raised entirely above '2p' band the metallic nature of NiO still remains. This is contradictory to the actual property of NiO.

By including 'p-d' mixing, Switendick found that the '3d' bandwidth is broad and below the '2p' band. This gives metallic nature of NiO and it is unaffected by the introduction of the exchange energy. The minority-spin '3d' band is splitted into degenerate band if the cubic crystalline field is taken into account. The eight '3d' electron per cation fillup the fivefold degenerate majority-spin bands and threefold degenerate minority-spin band. Thus NiO is an insulator. But this NiO is ferromagnetic which is contradictory to the actual antiferromagnetic NiO.

For antiferromagnetic material band structure must be modified/2/. The self-consistent potential cannot have the full translational symmetry of the lattice in an antiferromagnet. To get a sublattice magnetization, the exchange potential must have double periodicity of the sublattice.

This indicates that the Bloch states are not the correct solution as they are derived from the full lattice symmetry. The doubly periodic potential divides the Brillouin zone of the lattice in half and the exchange energy introduces band splittings. If the original, nonmagnetic band is narrow or the exchange energy is large, the band splittings could introduce a real gap in the density of states. Thus the material is an insulator.

Callaway studied the energy band structure of a body centered cubic antiferromagnet. The first Fourier component of the exchange potential shows that an insulating state results whenever an interaction parameter is sufficiently large such that the energy of the lower band state at a zone corner is below an upper band state at a zone face.

A self-consistent solution possible with $\alpha = \alpha'$ (paramagnetic state) results in a half-filled band if there is one electron per ion outside of the closed shells. Thus the material is metallic. An insulating state results for a self-consistent solution possible with $\alpha \neq \alpha'$ and if the lower band full and the upper band is empty.

For the most of the oxides, whose 'd' band is very narrow, the magnetization is virtually saturated if the bandwidth is small compared to the bandgap. On the other hand, if the bands are wide compared to the gap, the sublattice magnetization is near zero i.e. the antiferromagnetism is undetectable.

By this analysis antiferromagnetism leads to an insulating ground state for a large class of crystals which would be metallic. Thus the band calculations cannot explain the entire set of materials.

The paramagnetic solution, $\alpha = \alpha'$ leads to a metallic state for all materials which remain insulating above their Neel temperature. A lower symmetry solution of the Hartree-Fock equation for an antiferromagnet gives explanation for this. The major part of the exchange energy in all such itinerant models is the intra-atomic exchange integral. This gives a nonvanishing spin density at each lattice position as all spins line up at a site. A full lattice periodic crystal wavefunction gives a ferromagnet. But intra-atomic exchange of an isolate atoms leads to the high spin ground states of most transition metal ions by the Hund's coupling rule. An exchange splitting can be maintained by lowering the symmetry that results from transformation from a ferromagnet to an antiferromagnet. Further reduction of symmetry yields an energy gap. This type of state is a possibly excited state as the new state is not essentially the ground state of the crystal. As the degenerative state number is more, the entropy connected with them is enormous. Thus at high temperatures, the free energy associated with these paramagnetic insulating states falls below the antiferromagnetic state, resulting an antiferro-paramagnetic transition while retaining on energy gap.

The preceding theory is still incomplete, though the

suggestion is correct. All antiferromagnetism provides one extra splitting of all the bands. As the 'd' bands are highly orbitally degenerate, there are many materials that are forced to have metallic ground states.

A small crystalline distortion can produce a real gap in the density of states; e.g. CoO. A partially filled band due to cubic crystalline field gives a metallic nature for CoO. But due to 2% tetragonal distortion it is shifted in antiferromagnetic region. Such deformation is due to a Jahn-Teller effect and gives a filled lower degenerate sub-band and an empty upper nondegenerate sub-band. Thus gap is produced in density states and CoO is a low temperature insulator. As the crystalline distortion produces insulating behaviour for metallic CoO some work^{3/} on it is of interest. Consider that a distortion splits a doubly degenerate half-filled band into a valence and a conduction band. The energies of these bands depends on ' E_0 ', ' β ' and ' r '. Where $E_0 = (\alpha + d)/2$; $\beta = \int dx \phi^*(x)H(x)\phi(x-a/2)/4/$ and ' r ' is the parameter which depends on the amount of distortion. The summation of one electron energies over the filled band gives the total electronic energy of the crystal at $T=0$. In such case, for sufficiently small distortions E_g is proportional to the distortion. This is not strictly valid in the narrow band limit.

The extremely narrow band materials with partially filled bands can lower their ground state energy by a crystalline structure distortion. The energy which results from

deformation lowers the energy of all filled states and arises the energy of all unfilled states. Thus, the half filled band will split in two. As the bandwidth must be of the order of the splittings or narrower, there is a reasonable probability of obtaining such a real gap. Then all the materials will be insulating at $T=0$.

At low temperatures distortions are observed in all antiferromagnetic oxides which are insulators even though they are undeformed. Possibly these distortions help to produce real gap in these materials. The distortions disappear at or slightly below the Neel temperature and the antiferromagnetic energy gap remains above T_N . There is no theory explaining the splitting in a higher symmetry phase due to a crystalline structure change.

Accurate band structure calculations show that the Bloch approximation can give ground states with the proper electrical and magnetic properties for all the oxides. To give an explanation for the finite temperature behavior of many of the materials is not possible for band theory.

The reason for the failure of band theory is inherent in any one electron approach. The Hartree-Fock equation consider one electron and all other electrons are contributing to the average potential in which the electron under consideration moves. This shows that the motion of an electron is entirely independent of the motion of all the others i.e. electronic correlation is negligible. But it does not neglect the electronic interactions. This gives a self-consistent

differential equation. This is applicable to narrow band materials i.e. to the transition metal oxides.

To explain the situation in the transition metal oxides it is required to neglect electronic correlations. On the other hand electronic correlations must be taken into account to get correct lowest excited states as well as the ground state to determine the correct optical properties and low temperature conductivity. But this account can not produce a large error in determining optical and transport behavior.

In insulators the entire band structure must be recalculated for each excited state of system. The calculation is extremely difficult to perform for 'd' band transition metal oxides as the accuracy for using the Hartree-Fock approximation for 'd' bands is extremely high.

2.2.2 Localized Electron Models :

Considering an itinerant model and by introducing techniques to include the effects of correlations the results of band theory can be improved. Thus all the electrons are considered to be localized on their particular ions. A crystal consisting of a fixed assembly of independent ions sitting at their lattice positions is important. Due to this consideration the problem of the insulating nature of the majority of the transition metal oxides can automatically be solved. A review of the localized models is taken at zero temperature.

a) Wigner Crystallization :

Consider a free electron gas having N electrons. These

electrons interact with each other by means of the Coulomb repulsion due to their charge. To keep total neutrality of the system this gas is imbeded in a uniform back-ground of fixed positive charge N_e . The Hamiltonian of this gas contains kinetic energy and potential energy. The kinetic energy is just the Fermi energy in the high-density limit. The exchange energy dominates potential energy/5/. Thus for high densities the kinetic energy is much larger than the potential energy. The potential energy may be treated as a small perturbation. The kinetic energy can not take into account the electronic correlations. Thus Hartree-Fock approximation may give good results.

For low densities, the kinetic energy is negligible as compared to the potential energy/6/. Wigner pointed out that in such case a crystal lattice is formed as in the ground state. The electrons minimized their Coulomb repulsion by spreading apart as possible. This is called the Wigner crystallization of a low-density electron gas.

b) Bloch versus Heitler-London Ground states :

For electrons in a solid in which electron-phonon effects are neglected and the ion cores are assumed to be fixed, the Hamiltonian is the same as in the case of free electron gas. In this case the positive charge is not uniformly distributed but is concentrated at definite lattice positions.

Bloch states are not always a reasonable starting point for periodic array of atoms/7/. The band contains two states

per atom due to spin degeneracy. Thus for monovalent atoms at $T=0$ the lower half of the band is filled and the upper half empty. The band is very narrow and the overlapping of atomic wave function decreases exponentially with increase in separation. Such material exhibit metallic conductivity at low temperatures according to the Bloch-Wilson theory.

The Bloch functions can not give correct ground state of a system containing noninteracting atoms whose low temperature conductivity vanishes. It was suggested by Mott that a real ground state must be made up from the localized functions; i.e. Wannier functions. These functions give actual physical state i.e. a collection of noninteracting atoms as they reduced to atomic functions localized at each lattice position. In case of a monovalent material Bloch states are double as that of Wannier states and only half of these are occupied. There is overlapping of states/8/. Then each state is independent of spin and the two states on each site are degenerate. By placing just one electron at each lattice position the ground state can be obtained. This ground state is very different from the Bloch ground state.

There is full lattice symmetry for Bloch state, each electron has equal probability to occupy unit cell of the crystal, each direction of spin has equally likely and the full periodic potential is spin independent. From this the ground state is determined by filling the lower half of the states each with two electrons with opposite spin. Due to repulsive force between them, the total energy of the state

is increased. This is nothing but a correlation effect, which is neglected in Hartree-Fock approach. The Bloch ground state will represent the true state of the system accurately if there were no other empty Bloch states of nearly the same energy. As the band is filled band, the ground state is insulating. For a monovalent solids, the band contains a sufficient number of Bloch states so that there is no need of putting two electrons in the same state. Thus for very narrow band the Bloch approximation is not appropriate.

The Heitler-London ground state is nothing but the ground states made up from Wannier functions. These states must be filled. No two electrons with opposite spin are placed on the same site though states with spin up and spin down on each site are essentially degenerate. Thus the ground state of a monovalent material has exactly one electron on each atom. Thus however the kinetic energy over the Bloch ground state is increased, the Coulomb repulsion is minimized. Bloch states are spread through the crystal and have low kinetic energy as the wavefunctions have the lowest energy. On the other hand localized states have high kinetic energies. Thus the choice of a Bloch ground state and a Wannier ground state depends on the relative importance of the kinetic and Coulomb energies.

The original Bloch state can be improved by introducing an antiferromagnetic arrangement of spins. This decreases the correlation energy. Also by modifying the Heitler-London state and decrease in the kinetic energy takes place. Both

the states describe antiferromagnetic insulators in the case of a single 's' band.

Other localized electron models are c) Mott Transitions
 d) Narrow Energy Band Theory e) Excitonic - Insulator Theory
 f) Electron-phonon Interactions and g) Polarons.

2.3 Transport Properties :

The study of electrical conductivity, Hall effect and thermoelectric coefficients as functions of temperature and composition is the main aim, since these are the properties most commonly investigated experimentally. These effects explain the insulating or conducting behavior of the materials. As the ground states of different models which are described in the section 2.2 are used to explain the insulating nature of the majority of transition metal oxides, in this section the analysis of the prediction for the transport properties of these materials according to the models is described.

Itinerant models take into account the situation of all bands whether completely filled or empty and do not take into account the correlation arising from the electron-electron interaction or from the strong electron-phonon interaction.

For metal the resistivity is given as

$$\rho = \rho_I + \rho_L \quad \dots\dots\dots 2.1$$

where ρ_I is the resistivity due to scattering by impurities and is independent of temperature and ρ_L is the resistivity due to the thermal motion of lattice.

The lattice contribution to the resistivity vanishes at temperatures much below, the Debye temperature Θ_D , as

$$\rho_L \sim K'T^5 \quad \dots\dots \quad (2.2)$$

Thus ρ_I is determined from the $T=0$ extrapolation of

ρ . The Hall coefficient is approximately

$$R_H = (NeC)^{-1} \quad \dots\dots \quad (2.3)$$

where N is the concentration of electrons in the partially filled band.

The resistivity in terms of mobility (μ) or velocity per unit electric field of a current carrying particle is given as

$$\rho = (Ne\mu)^{-1} \quad \dots\dots \quad (2.4)$$

And the Hall mobility in terms of the variable μ_H is

$$\mu_H = C|R_H|/\rho \quad \dots\dots \quad (2.5)$$

In the ordinary band theory the insulating materials are characterized by an energy gap, E_g . The conductivity is written as

$$\sigma = n_e e \mu_e + n_h e \mu_h \quad \dots\dots \quad (2.6)$$

where n_e and n_h are the concentrations of free electrons and holes, respectively, and μ_e and μ_h are the electrons and hole mobilities.

The values for mobility depend on lattice scattering and on the scattering from ionized impurities. If both scattering mechanisms are present, the mobility is given as

$$\mu = (\mu_L^{-1} + \mu_I^{-1})^{-1} \quad \dots\dots \quad (2.7)$$

where μ_L and μ_I are the mobilities due to lattice scattering and scattering from ionized mobilities respectively. The temperature dependence of these two mobilities is weaker than

the exponential dependences in n_e . Thus the conductivity equation 2.6 can be written as

$$\sigma = \sigma_0 \exp. (- E_g/2kT) \quad \dots\dots \quad (2.8)$$

where σ_0 is the conductivity at $T=0$.

If impurity levels are present the Fermi energy is determined from the neutrality condition,

$$n_e - n_h = N_d \quad \dots\dots \quad (2.9)$$

where n_e and n_h are the concentration of free electrons and free holes, and N_d is the concentration of donors.

The Hall coefficients for electrons and holes are given from the general expression for the Hall coefficient of a semiconductor as /9/.

$$R_H \approx - (r/n_e eC) \quad \dots\dots \quad \text{For electrons}$$

$$R_H \approx r/n_h eC \quad \dots\dots \quad \text{For holes.}$$

Thus the Hall mobility given in equation 2.5 is approximately equal to the electron or hole drift mobility. The Hall coefficients are derived in the absence of any magnetic order in the crystal. Most of the transition metal oxides are antiferromagnetic and in this type the Hall coefficient is a sum of a normal and an anomalous part of $R_H/10$ /.

The thermoelectric power is given by

$$\alpha = (k/e) [(E_F/kT) + a] \quad \dots\dots \quad (2.10)$$

where 'a' is a constant.

As itinerant model neglect electronic interactions it can not give correct ground state in antiferromagnet. Including the electronic interactions and the fact that interactions must vary with the population of the upper band to

get the correct ground state in antiferromagnet, a rapidly changing band structure with temperature i.e. complex behavior of $\sigma(T)$ results.

When the electron-phonon interaction is strong the electrical conductivity occurs during the thermal lattice fluctuation between a site with a self-trapped and a neighboring unoccupied site. In this case, the electron can hop between these two equivalent lattice positions. Diffusion of electrons through the crystal takes in the presence of electric field and a net current results.

According DeBoer and Verwey there is a high potential barrier between any two transition metal ions in the crystal. Thus the electrons having mean time for tunnelling through the barrier is much longer than the average lifetime of that state drop back into the ground state with participating in conduction. Then material would be insulating at low temperature. The energy required to go from the ground state to the conducting state is the activation energy (E_a) for conduction. For temperatures such that $kT \ll E_a$ the conductivity should be

$$\sigma = \sigma_0 \exp. (- E_a/kT) \quad \dots \quad (2.11)$$

This result is analogous to semiconduction with an energy gap of $2E_a$.

R E F E R E N C E S

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