CHAPTER 1

GENERAL INTRODUCTION
1.1. HISTORICAL

Since the discovery of superconductivity by Kammerlingh Onnes in 1911 in Hg at 4 K, one of the primary objectives of superconductivity research has been to raise the transition temperature $T_C$. By almost any criterion, progress was slow. The discovery of $T_C$ above 10 K in NbC and NbN was one breakthrough; the discovery of the A15 compounds, with $T_C$ finally breaking through the 20 K barrier in the late 1960s and early 1970s, represented the culmination of two decades of intense search for higher transition temperatures. This research involved extensive investigations into materials properties and gave rise to "Matthias's Rules"\(^1\) for promoting higher values of $T_C$:

1. Cubic transition metals are best.
2. Niobium is the best transition metal.
3. Certain values of electron/atom (e/a) ratio are special
4. High $T_C$'s lie in the regime of lattice instabilities.

Certain aspects of these rules have been understood on a basic level; for example, in the cubic transition metals, the transition-metal carbonitrides, and the A15 compounds, the special e/a ratio (roughly 4.7 and 6.5) corresponds to the regions of high density states $N(E_F)$ at the Fermi level $E_F$. Niobium not only tends to lead to e/a ratios near 4.7, but also lies near the centre of the transition metal series where the electron-phonon interaction is strongest. These trends have been reviewed by Klein and Pickett\(^2\). In addition, it became clear that both high $T_C$ and lattice instabilities arise from strong electron-phonon interactions so they tend to occur together; there is no definite casual relationship between lattice instability and high $T_C$. Contrary to early speculations, the best estimates now seem to indicate that low phonon frequencies contribute little to high values of $T_C$. 

1. Klein and Pickett (1976)
The breakthrough in higher $T_c$'s resulted from Bednorz and Müller\textsuperscript{3} discovery in the copper oxide system. They were convinced that it was necessary to move beyond the standard high $T_c$ classes to obtain a real breakthrough. They chose to work on transition metal oxides, both because they were different and because they often displayed polaronic effects typical of extremely strong electron-phonon interactions. In 1986 they found evidence of a superconducting transition occurring near 30 K in the La-Ba-Cu-O system, a result that was rapidly confirmed and refined by a number of laboratories in the US, Japan and Europe. It was established that $T_c$ in the range 20-40 K occurs for La$_{2-x}$M$_x$CuO$_{4-y}$ with M = Ba, Sr, Ca and that application of pressure leads to a large pressure coefficient of $T_c$ and drives $T_c$ above 50 K in the M = Sr system. The crystal structure was identified and it has since become clear that high temperature superconductivity is only the most astounding of a number of unusual properties of this system.

Since pressure was so effective in increasing $T_c$, Wu et al.\textsuperscript{4} simulated "chemical pressure" by replacing atoms in the La 214 system by smaller isovalent ones. The replacement of La by Y in LBCO produced in early 1987 a 90 K superconductor, later identified as YBa$_2$Cu$_3$O$_{7-y}$. Like the initial system, this material was prepared by ceramic processing techniques. High temperature annealing in an oxygen containing atmosphere was necessary to produce the oxygen content and the crystalline phase necessary to give high $T_c$. Although other group techniques have now been found that result in the high $T_c$ phase, already it was clear from preparations considerations that the new copper oxides were completely different from the previous high temperature superconductors.

Although there were numerous reports of resistive and magnetic anomalies, at much higher temperatures, the next breakthrough came in early 1988 with the discovery by Maeda et al.\textsuperscript{5} and Chu et al.\textsuperscript{6} of Bi$_2$Sr$_2$CaCu$_2$O$_{8-\delta}$. This bismuth based
compound not only showed onsets around 110 K but also contained no rare earth element. It was also distinguished by its highly micaceous nature, indicating more pronounced layering than its predecessors. This breakthrough was followed rapidly by the discovery of Sheng et al.\textsuperscript{7} of onsets at 115 K in the Tl-Sr-Ca-Cu-O system. The superconductor phase was identified as Tl\textsubscript{2}Ba\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8-y} and this was soon improved to above 120 K by several groups. The crystal structures of this systems were identified and found to share certain features in common with the La-M-Cu-O and Y-Ba-Cu-O materials, particularly the existence of square Cu-O layers separated by more or less ionic regions.

This period of rapid discovery may well continue for some time. While it is certainly early to review any aspects of this novel materials, intense effort has been turned towards the understanding of their electronic structures and properties, and it is useful to collect the results and contemplate their implications. Developing the clear understanding of the structure of these high $T_c$ materials is central not only to identifying the pairing mechanism, but also to describing the host of other essential and often unusual properties displayed by these materials. Although a complete understanding of the important electronic properties would include the electronic response to perturbations of various kinds, this is an area in which little detailed work has been done.

It is far too early to draw any firm conclusions about the best way to picture, and to begin to describe the electronic structure of copper oxide high temperature superconductors. In fact, it may well be appropriate to describe the magnetic insulating state from one point of view and the metallic regime from another viewpoint. The metal insulator regime will in any case be a long time in being unraveled.

Within the metallic regime, a number of properties seem to be described rather well by the local-density version of density-functional theory. Probably the most quantitative example
is that of the calculations of the static structural properties, the lattice instability and the phonon frequencies of La$_2$CuO$_4$. To a great extent the electrical transport properties in the metallic regime look typical of quasiparticles, and the calculations appear encouraging in this respect, although many questions remain. Even many of the diverse spectral data can be interpreted in terms of the band structure density of states and corresponding characters of the states.

On the negative side, there are spectral features, particularly the valence band satellite indicating that self energy effects are strong in certain regions of the spectrum. Even for the ground state of the antiferromagnetic insulators, it is clear that there are crucial correlations that are missing from the local density treatment. How one should try to describe quantitatively the gaps in this materials is also still an open question; the local density approach does not predict them to be either antiferromagnetic or insulators. To what extent these correlations and self energy effects are important for the very-low-energy carriers and for the 0.1 - 5 eV excitations which are widely speculated to be active in these materials, is a monumental task to be addressed in the future, hopefully the near future.

1.2. THE PROCESS OF X- RAY ABSORPTION

The interaction of X-rays with matter$^8,9$ results in a number of interesting phenomena, such as, scattering, photoelectron absorption, radiation damage, pair production (in the case of X-rays of energy $>$ 1.02 MeV), secondary emission, Auger emission etc. The analysis of attenuation, generally logarithmic of X-ray intensity requires, therefore, the segregation of the various processes involved, of which the photoelectric absorption is usually the most important and is referred to as the true absorption.

When an X-ray beam passes through a medium, the intensity of
the transmitted beam \( I \) is attenuated logarithmically. According to the classical absorption equation, if the incident beam of intensity \( I_0 \) has traveled a distance \( x \), then the absorption coefficient

\[
\mu_l = -\frac{1}{x} \ln \frac{I}{I_0}
\]  

(1.1)

It follows from equation (1.1) that the dimensions of \( \mu_l \) are reciprocal centimeters so that it represents the attenuation of the beam per unit length traveled and is called the linear absorption coefficient. It turns out to depend on the energy (wavelength) of the X-rays, the atomic numbers of the constituent atoms, and on their state of aggregation.

Calculation of the linear absorption coefficient is complicated by this last fact so that it is more convenient to use a mass absorption coefficient

\[
\mu_m = \frac{\mu_l}{\rho}
\]  

(1.2)

where \( \rho \) is the density of the absorbing medium and \( \mu_m \) is the absorption cross section of the mass unit.

In the analysis of the dependence of \( \mu \) on wavelength and atomic number, it is most convenient to define an atomic absorption coefficient

\[
\mu_a = \frac{A}{N_o} \mu_m
\]  

(1.3)

where \( A \) is the atomic weight of the element and \( N_o \) is Avogadro's number. A plot of \( \mu_a \) against wavelength, for any element, has the general appearance of the curve shown in Figure 1.1. The
Figure 1.1: Variation of absorption coefficient of lead as a function of X-ray wavelength
absorption increases with increasing wavelength (decreasing energy of incident X-rays) until an abrupt discontinuity occurs. After this discontinuity, called an absorption edge, the absorption increases with wavelength until new discontinuities are encountered. An empirical study of the relation between the atomic absorption coefficient and the X-ray wavelength and atomic number of the absorbing atoms shows that curve like that in Figure 1.1 can be described by

$$\mu_a = C Z^m \lambda^n + \sigma_a(Z,\lambda)$$  \hspace{1cm} (1.4)

where the coefficient C takes on different values on each side of an absorption edge and the "best" values for the two exponents are $m = 4$ and $n = 3$. The second term in equation (1.4) is called the atomic scattering cross section $\sigma_a$ and represents the intensity lost due to the scattering in directions other than that of the incident beam. For wavelengths that are large compared to electron-electron distances in atoms ($\lambda > 0.5$), $\sigma_a$ is nearly independent of wavelength and increases in proportion to $Z$. Since the first term in (1.4) increases with both $Z$ and $\lambda$ much more rapidly, the second term may be neglected by comparison. At shorter wavelengths, the $\lambda$ dependence becomes more complex but, because of severe experimental difficulties in measuring the scattering part of (1.4), an accurate dependence has not been established. Since the second term is small (typically, $\sigma/\rho \sim 0.10$ to 0.20 cm$^2$/gm), it is normally neglected in the discussion of absorption coefficients. This is an acceptable practice for all but the lightest elements, for which the total absorption coefficients may have commensurate magnitudes (For carbon $\mu_m < 4.0$ cm$^2$/gm for $\lambda < 1.5$ Å$^0$).

The first term in (1.4) is of primary interest, not only because it is relatively much large but also because it represents the wavelength and $Z$ dependences of the photoelectric
absorption process for X-rays. As can be seen in Figure 1.1, as the wavelength of the transmitted X-rays increases, the photoelectric absorption increases $\propto \lambda^3$ until a critical wavelength is reached. For wavelengths longer than that at the absorption edge, the incident X-rays have insufficient energy to knock out a particular kind of bound electron in the atom, and the photoelectric ejection of such electrons no longer contributes to the absorption process. The absorption edges in Figure 1.1 are called K, L_I, L_{II}, and L_{III} edges, respectively, according to the inner electron whose binding energy equals the energy at the absorption edge. Following the photoelectron ejection of an inner electron, the excited atom typically emits an X-ray photon, as an outer electron falls into the newly created hole, so that the first term in (1.4) is called the fluorescence term.

For free atoms, such as in the case of monoatomic gases, the processes of X-ray emission and absorption are simple and are well understood. However, these processes become rather complex when the atom is no more free, such as in solids and chemical compounds. The mechanism of X-ray emission and absorption in a solid is shown in Figure 1.2. In a solid the valence electrons of the neighbouring atoms interact with each other and the energy levels are no longer discrete as in the case of free atoms but are broaden, the outer ones being more broad than inner ones and from quasi-continuous valence and conduction bands. The X-ray emission band spectrum results from the transition of the electrons from the valence band to a inner level. It provides information about the distribution of the occupied electron states in the valence band, since the inner level is generally sharp and well-defined. The X-ray absorption spectrum, on the other hand, corresponds to the transitions of the ejected photoelectron to empty states, bound or unbound of proper symmetry, and provides complementary information about the density of unoccupied electronic energy states.
Figure 1.2: The mechanism of X-ray absorption and emission
1.3. THE POSITION, SHAPE AND FINE STRUCTURE OF AN X-RAY ABSORPTION DISCONTINUITY

In the X-ray emission process, if \( I(\nu) \) denotes the intensity per unit frequency range, then \( I(\nu)d\nu \) is the intensity of X-rays emitted with frequencies in the range \( d\nu \) corresponding to the energy range \( dE \) and the expression for \( I(\nu) \) is given as

\[
I(\nu) = \frac{n e^2 h^3 \Omega \nu^3}{3 \pi^3 m^2 c^3} \int |M_{fi}|^2 \frac{ds}{|\text{grad } E|}
\]

where \( \Omega \) is the volume of the unit cell, \( n \) is the number of radiators per unit volume, \( M_{fi} \) is the matrix element or the transition probability, subscript \( i \) and \( f \) correspond to the initial and the final states respectively and the integration is carried out over a constant energy surface in \( k \)-space. Equation (1.5) represents the observed frequency distribution within an emission band.

In the X-ray absorption process, if \( A(\nu)d\nu \) denotes the energy absorbed per unit time by an atom in the electron transition from a sharp inner level to a band of empty states in an energy range \( dE \) and \( I_0(\nu) d\nu \) is the incident intensity (energy per unit area per unit time), then the linear absorption coefficient (in \( \text{cm}^{-1} \)) is given by

\[
\mu = \frac{n A(\nu) d\nu}{I_0(\nu) d\nu}
\]

where \( n \) represents the number of atoms per \( \text{cm}^3 \).

On the basis of Dirac's radiation theory, the energy absorption per second per unit frequency range by one atom may be expressed as
\[ \alpha(\nu) = \frac{e_0 h}{2\pi n^2 c \nu} |M_{fi}| I_0(\nu) \quad (1.7) \]

Furthermore, \( E = h\nu - h\nu_0 \), where \( h\nu \) is the energy of the incident photon and \( h\nu_0 \) is the energy interval between the initial X-ray level and the unoccupied state of lowest energy. Upon averaging over the three directions of the electron momentum, the power absorbed in transitions into a number of closely grouped states spread over an energy interval \( h\nu \) becomes

\[ A(\nu) d\nu = \frac{e^2 h^2 \Omega I_0(\nu) d\nu}{6 \pi^2 m^2 c \nu} \int_s \frac{|M_{fi}|^2}{|\text{grad} E|} \, ds \quad (1.8) \]

Hence by (1.8)

\[ \mu(\nu) = \frac{n e^2 h^2 \Omega}{6 \pi^2 m^2 c \nu} \int_s \frac{|M_{fi}|^2}{|\text{grad} E|} \, ds \quad (1.9) \]

The above expression can be approximated\(^{14}\) to

\[ \mu(E) \propto \nu \, P(E) \, N(E) \quad (1.10) \]

where \( N(E) \) is the density of unoccupied states at energy \( E \) and \( P(E) \) is the transition probability for a transition involving the two states concerned, with the initial state being the core state (or \( s \) state) and the final state being one in which an electron is excited to a normally unoccupied level in the valence or conduction band. It is very difficult to calculate theoretically \( P(E) \) for such transitions in the case of solids. However, the selection rules often help in giving a rough estimate of the
transition probability. Assuming the dipole approximation to be valid for solids, one can assume the K, L_I, ... absorption spectra to reflect the density of unoccupied p-like states in the conduction band, and the L_{II}, L_{III}, M_{III}, ....... spectra to reflect the density of d and s electron states. In a given band the transition probability is generally assumed\textsuperscript{15} to be a monotonous function of energy.

The first significant attempt towards the explanation of the shape of an X-ray absorption discontinuity in a solid was that of Richtmyer, Barnes and Ramberg\textsuperscript{15} who described the absorption edge in terms of a series of absorption lines with equal widths and having equal transition probabilities. In their work, Richtmyer et al. employed the following expression for the intensity distribution function $J_{AB}(\nu)\,d\nu$ for an absorption line, given by Weisskoff and Wigner\textsuperscript{16}.

$$J_{AB}(\nu)\,d\nu = \frac{r_A + r_B}{2\pi} \cdot \frac{d\nu}{(\nu_{AB} - \nu)^2 + \left(\frac{r_A + r_B}{2}\right)^2} \quad (1.11)$$

where $A$ and $B$ refer to the initial and final states involved in the electronic transition, $\nu_{AB}$ is the frequency corresponding to the transition and is

$$\nu_{AB} = \nu_A - \nu_B = (E_A - E_B)/h \quad (1.12)$$

and $r_A$ and $r_B$ are related to the mean life-times $\tau_A$ and $\tau_B$ of the states $A$ and $B$ respectively through the relations

$$r_A = 1/2 \, \pi \, \tau_A, \quad \text{and} \quad r_B = 1/2 \, \pi \, \tau_B \quad (1.13)$$

Richtmyer et al have discussed using the relation (1.11) the
shape of the $L_{III}$ absorption discontinuity of gold and have shown that the variation of the absorption coefficient in the vicinity of the absorption discontinuity follows an arc-tan curve given by the formula

$$\mu(E) = \text{Constant} \left[ \frac{1}{2} \arctan \left( \frac{v_{EoA} - v}{\frac{1}{2}E \cdot r} \right) \right]$$

where $r_E$ is the full width at the half maximum of each absorption line and $v_{EoA}$ is the frequency difference between the initial state in the absorption process and the first one of the final states.

It is difficult to assess the exact importance of the above formula because of the absence of experimental verification of the assumptions leading to it and the lack of the knowledge of the transition probabilities. In spite of it, it has been found that in many cases there exists rather a close similarity between the theoretical arc-tan curve and the experimentally observed curves. Whenever such a close fit exists, the calculations leading to the above formula for $\mu(E)$ show that the inflection point on the absorption curve corresponds to a transition of the inner electron to the first available empty level in the solid.

A detailed study by Parratt of the K-absorption discontinuity of gaseous argon ($Z=18$) has led to a further step in the understanding of the X-ray absorption process. He has decomposed the observed absorption curve, duly corrected for experimental distortions, into a series of resonance absorption lines corresponding to the transitions $1s \rightarrow np$, where $n > 3$. The wavelength positions of these absorption lines were calculated with the help of the optical terms of potassium ($Z=19$), since an ionised argon atom can be considered to be similar to a potassium atom. This study has been extended to the other inert gases by Brogren. The approximation was further examined by Mitchell.
for neon who cautioned that this model may not hold for very light atoms. In a different approach, Vainshtein and Narbutt have calculated the relative intensities of the various absorption lines assuming hydrogenic wavefunctions for the initial and final states for the inert gases.

Soules and Shaw have studied the K-absorption spectrum of solid argon and have found that it differs very much from that obtained in the gaseous state. The absorption edge for the solid closely follows the theoretical arc-tan curve except in the region of maximum absorption. The first absorption maximum in the curve of the gas has approximately the same wavelength as the inflection point on the absorption curve of the solid. These results, together with Nilsson's measurements of the absorption coefficients with different excitation voltages, confirm the view that the inflection point on an X-ray absorption discontinuity corresponds to the transition of an inner electron to the first unoccupied level in the conduction band of the solid.

Breinig et al. have proposed a theoretical model for absorption edges and derived the following expression for absorption cross section near the edge:

\[
\sigma_{\text{nhij}} = \sum_{\text{ni}} \left[ \frac{\Gamma/2}{E - (E_{\text{ni}} - E_{\text{nhij}})} \right]^2 + \left( \frac{\Gamma}{2} \right)^2 + a \left( \frac{1}{2} + \frac{1}{\pi} \tan^{-1} \frac{1}{2} \frac{\Gamma}{E + E_{\text{nhij}} + \varepsilon'} \right)
\]

(1.15)

where \(E_{\text{nhij}}\) and \(E_{\text{ni}}\) are initial and final states in the transition, \(E\) denotes the photon energy, \(\sigma\) is the width of the excited state and \(\varepsilon(\nu-0.5 \text{ eV})\) the constant energy used for inclusion with the continuum the highest bound states whose
width exceed their separation. It is clear from this expression that the profile of the X-ray absorption discontinuity is nothing but a Lorentzian of appropriate height and width superimposed on an arc-tan curve. Breinig et al.\textsuperscript{23,24} have studied the K-absorption edge spectrum of argon and L-absorption spectra of krypton and xenon. These workers decomposed their spectra into Lorentzians and arc-tan curve. They found a good agreement between the peak position of Lorentzian corresponding to a particular electronic transition and the optical energy obtained from experiments.

Though a rigorous calculation of the shapes of absorption discontinuity have been done by Breinig et al., for argon, krypton and xenon, these have not been to date (to our knowledge) for different absorption edges in solids. However, it has been found practical to perform numerical analysis on the absorption data in terms of the positions, widths and oscillator strengths of bound-state and resonance peaks and of an edge position, width, and height for the principal continuum edge. Cramer and Hodgson\textsuperscript{25} have done such type of analysis by decomposing the Mo K-edge spectrum in [Mo\textsubscript{7}O\textsubscript{24}]\textsuperscript{6-}. These authors have shown that by fitting the absorption edge with several Lorentzians and an arctangent function, the positions and intensities of edge features may be quantitated. In this laboratory\textsuperscript{26} also, the fitting of K-edge profiles of transition metal ions and L\textsubscript{III}-edge profiles of tungsten ions in various compounds into Lorentzians and arctangent function has been done and it has been shown for the first time that the areas under different Lorentzians give a measure of extent of tetrahedral to octahedral clusters.

It has been often found that the position of an X-ray absorption discontinuity changes with the physicochemical environment of the absorbing atom. It was Bergengren\textsuperscript{27} who first demonstrated the dependence of X-ray absorption discontinuities on chemical combination. He investigated the K-absorption edge of
phosphorus in its various allotropic forms and found slight variations in the wavelength of the edge. Lindh\textsuperscript{28}, who carried out a number of experiments to study the effect of chemical combination on the wavelengths of the K-absorption discontinuities of chlorine, phosphorus and sulphur in various compounds, demonstrated that the wavelength of the X-ray absorption spectrum of an atom varies with its chemical state in the compound. Stelling\textsuperscript{29} using spectrograph with higher dispersion than that used by Lindh has studied the K-absorption limit of chlorine in various chlorides. Aoyama, Kimura and Nishina\textsuperscript{30} have studied the K-absorption limit of chlorine in various organic compounds. Coster\textsuperscript{31} has studied the K-absorption edges of titanium and manganese in their different oxides and lent support to the earlier observations. These investigations were soon followed by many researchers who extended the study of chemical shifts to all sorts of compounds, complexes, alloys, solutions and glasses.

Considering the various factors which may affect the energy necessary to remove an electron from an ion in a crystal, Pauling\textsuperscript{32} has discussed the dependence of the wavelength of an absorption discontinuity on the chemical environment of the absorbing atom and has emphasized the importance of electrostatic potential seen by the absorbing ion due to its environment and the external screening caused by the valence electrons. The experimentally observed chemical shifts of the K-absorption edges of chlorine in LiCl, NaCl, KCl and RbCl seem to be in accordance with the theory proposed by Pauling, but the results obtained for some other compounds, e.g.\(\text{NH}_4\text{Cl}\), CsCl, CuCl and AgCl do not agree with it.

Kunzl\textsuperscript{33} made a critical examination of the experimental work concerning the displacement of the K-absorption discontinuities of atoms present in different oxidation states in their oxides. He formulated a law according to which the displacement of an absorption edge in a series of compounds depends directly upon
the valency of the element in the compound under consideration. This dependence is given by the relation $\Delta \nu / R \propto V$, where $\Delta \nu$ denotes the change in the frequency of the absorption edge for a given compound with respect to that for the pure element, $R$ is the Rydberg constant and $V$ is the valency of the absorbing atom.

This dependence of the chemical shift on valence has been supported by the work of Zinn\(^{34}\), Barton\(^{35}\), Manescu\(^{36}\), Glenn and Dodd\(^{37}\) and many others. Assuming the dependence of the position of the K-absorption limit on valency, Boehm, Faessler and Rittmayer\(^{38}\) have reported the valence of cobalt in vitamin B\(_{12}\) to be three. Kirichock and Karalnik\(^{39}\), Vainshtein\(^{40}\), Miller\(^{41}\), Mande and Chetal\(^{42}\) and Sarode et al.\(^{43}\) have determined the valence of transition metal ions in different compounds and complexes, making use of the Kunzl's law. However, several investigations\(^{44-46}\) have pointed out the limitations of the Kunzl's law. The effect of electronegativity and character of the ligands, type of hybridization, nature of chemical bond, coordination number and the other structural parameters\(^{47}\) seem to affect the chemical shift. Agarwal and Verma\(^{48}\) have given an empirical rule which states that "in general, the chemical shift is towards the high energy side of the metal edge and it increases progressively with the increase in the valence of the cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of metal-metal bonding." Dey and Agarwal\(^{49}\) have further attempted to demonstrate a linear variation of the chemical shift with the product of the ionicity of the bond and square of the valency.

Several workers\(^{50,51}\) have tried to correlate the chemical shift with effective charges on the absorbing atoms calculated by different methods. Batsanov and Ovseyannikova\(^{52}\) have investigated the position of the K-absorption discontinuity of manganese in some of its compounds and have observed its dependence on the coordination charge on the absorbing ions. Barinskii and Nadzhakov\(^{53}\) have attempted to determine the effective charges in
some transition metal compounds by this method. These attempts have been critically reviewed by Barinskii and Nefedow\textsuperscript{54} in their book. Through somewhat involved reasoning Böke\textsuperscript{55} also has tried to deduce the effective charges on the absorbing metal atoms in various complexes. Srivastava et al.\textsuperscript{56} have also shown that the variation in the K-edge shifts of copper in some complexes involving Cu\textsuperscript{I} and Cu\textsuperscript{II} follows a parallel variation in the calculated effective nuclear charge. In 1973 Mande and Sapre\textsuperscript{57} have shown that the absorption discontinuity in a compound shifts towards the higher or lower energy side with respect to the corresponding discontinuity in the pure element depending upon whether the absorbing atom is a cation or an anion and that the magnitude of the chemical shift depends upon the effective charge on the absorbing ion. They have determined the effective charges in the case of gallium selenide and gallium telluride using the X-spectroscopic technique. Mande and Kondawar\textsuperscript{58} have calculated the effective charges on cobalt ions in some of its intermetallic compounds and a correlation between the X-ray absorption shifts and the effective charges has been found. Sarode\textsuperscript{59} has investigated the L\textsubscript{III}-absorption edges of bismuth in bismuth halides. He has shown that the inflection point position of the absorption discontinuity shows variation on the partial ionic charge calculated by Sanderson's method. Sarode et al.\textsuperscript{60} have examined the K-absorption spectra of several oxides and pervoskites of manganese, iron and cobalt. These authors have found a functional relationship between chemical shifts and effective atomic charges.

It is not always easy to locate the position of the X-ray absorption discontinuities unequivocally because their shapes often appear complicated and do not always follow\textsuperscript{61} the simple arctangent curve. Moreover, the discontinuities are frequently accompanied by\textsuperscript{62} fluctuations in the absorption coefficient on the low as well as high energy sides. These complexities in X-ray absorption spectra can be roughly classified in the following
(i) Pre-absorption: This is the structure observed on the low energy side of the absorption edge. It is usually attributed\textsuperscript{63,64} to the availability of localized unoccupied electronic levels below the conduction band. In the case of some rare earths and their systems one observes in the L and M spectra such preabsorption peaks corresponding to transitions to the unfilled atomic levels. Preabsorption structures in some insulators like CuO, ZnO, RbCl etc. have also been observed by Cauchois and Mott\textsuperscript{64}, who have interpreted their results on a model suggested earlier by Frenkel\textsuperscript{65}. According to Frenkel in the non-metallic solids the hole formed in an inner atomic level can trap the free electron in the lattice by virtue of its Coulomb field, forming a bound electron hole pair (exiton), which forms free atomic like levels in the forbidden gap. Transitions of the inner electron to these levels give rise to the preabsorption maximum on the low energy side of the absorption discontinuity.

Pre-absorption peaks have also been observed\textsuperscript{66-72} in compounds wherein the metal ions have tetrahedral, square planar and square pyramidal coordination. The intensities of these peaks are found to depend on the coordination geometry\textsuperscript{69,70} of the metal site. For example, in compounds like Ag\textsubscript{3}VO\textsubscript{4}, where vanadium ion is tetrahedrally coordinated by four oxygen ligands, the intensity of pre-edge peak is large\textsuperscript{71}, whereas in GdVO\textsubscript{3}, the vanadium ion being in octahedral coordination, the intensity is very small. The metal ions, which have square pyramidal coordination in compounds, give the pre-absorption peak whose intensity is slightly smaller than those observed for tetrahedrally coordinated compounds\textsuperscript{71}. These peaks are generally attributed\textsuperscript{67,68,72} to the core electron transition to the partially vacant conduction band. Shulman et al.\textsuperscript{66} have explained that vibronic mixing of np and nd characters makes the low energy transitions allowed. Theoretical considerations\textsuperscript{67,68} also support
this views.

(ii) Splitting of the Discontinuity and the Near Edge Structure: It has been observed\textsuperscript{73-75} that the X-ray absorption discontinuity often splits into two or more components and that their appears some fine structure in its immediate vicinity (upto about 30eV ) on its high energy side. Kossel\textsuperscript{76} has observed this structure initially in the case of gases and had suggested a model of single electron transitions to the empty atomic states for the interpretation of such structure. This type of structure was later found\textsuperscript{75} to appear in the liquids and solids also. This near edge structure in the case of metals, alloys and highly covalent compounds is usually attributed\textsuperscript{62} to the distribution of unoccupied states of appropriate symmetry in the conduction band. For gaseous molecules, molecular solids and transition metal coordination complexes it is attributed\textsuperscript{77-80} to the transitions of core electrons to the states formed due to molecular formation. In the K-absorption spectra of transition metal compounds several workers\textsuperscript{37,58,81} have observed a weak low energy peak at the threshold followed by a shoulder on a rising absorption that culminates in a strong peak. The occurrence of low energy peak corresponding to inner electron transition to nd state, has already been discussed above. The shoulder peak and strong absorption maxima are generally assigned to ns and np states.

The transition to the outer states created due to capture of another atom's electron\textsuperscript{29} (cross-over transition) as well as the creation of multiple inner vacancies\textsuperscript{82} may also give rise to some small peaks near the absorption edge.

(iii) White Line: The appearance of a strong peak just above the X-ray absorption edge for some elements and compounds has been an interesting subject in X-ray spectroscopy for many years. The strong peak is referred to as a "white line" (or "raie blanche"
in French), because such a little amount of radiation at certain wavelengths would penetrate the absorber relative even to the radiation transmitted above the edge, giving a white line on the photographic film used in the early experiments. For example, white lines have been observed at the K-edges of elements Ga and As, Ni in Ni$_2$O$_3$, Cu in CuO, and Zn in ZnO$^{64}$, but not in the 3d transition elements$^{74}$. White lines have also been observed at the L$_{II}$ and L$_{III}$ edges (but not at the L$_I$ edge) of Fe, Co, Ni$^{83,84}$, Cu in CuO$^{85}$, Ru, Rh, Pd$^{86,87}$, Sm, Gd through Lu$^{88}$, Ta, W, Re$^{89-93}$, compounds of Hg and Tl$^{92}$, and U$^{93}$. The list is by no means complete, in fact, with the enhanced intensity and improved resolution from synchrotron radiation sources$^{94,95}$, white lines have been observed in a large number of substances. Although the origin of the strong absorption has not been analyzed in detail, it is generally believed$^{64}$ to be associated with an atomic like electric-dipole-allowed transition from an inner shell to an unoccupied level with a high density of states in the vicinity of the absorbing atom. In this regard, the white line also depends on the chemical bonding because Cu in metal or Cu$_2$O does not have a white line$^{85}$ while W in WO$_3$ exhibits a broader white line than the one in metallic W$^{90}$.

Wei and Lytle$^{96}$ have studied the L$_{II}$ and L$_{III}$ edges of tantalum metal. These authors have associated the white line with an atomic like allowed transition from 2p$_{1/2}$ and 2p$_{3/2}$ states to the vacant 5d states of a high density. However, qualitative comparison with the calculated band structure was not possible because none of the existing band structure calculations has included the effect of a core hole. In an attempt to understand the white lines, Wei and Lytle presented two least-square analysis of the Ta L$_{III}$ edge in terms of (a) a Lorentzian profile and (b) a Breit-Wigner-Fano type formula. They found that the latter, which was first suggested by Cauchois and Mott$^{64}$, appeared to provide a better fit to the asymmetric line shape.

Brown et al.$^{97}$ have done rigorous theoretical calculations
of white lines and shown that the calculated weight of the absorption in the white line corresponding to a $2p_{3/2}$ to $5d_{5/2}$ transition is consistent with the experimentally determined value in platinum metal. However, experimental results for Ni and Ti do not fit into their theoretical framework.

(iv) Extended X-ray Absorption Fine Structure: The extended X-ray absorption fine structure (EXAFS) refers to oscillations in the X-ray absorption coefficient observed on the high-energy side of an X-ray absorption edge. Such oscillations can extend up to 1000 eV above the edge and may have a magnitude of 10% or more.

The phenomenon of EXAFS has been known since 1930 and the basic physical explanation has been provided by Kronig, who says that these oscillations are due to modification of the final state of the photoelectron by the crystal or, in the case of gaseous molecules, by atoms surrounding the excited atom. Since then there have been various further attempts to theoretically understand the EXAFS, but without complete success. The various theories can be classified into two categories, long-range order (LRO) and short range order (SRO). The LRO theories require the existence of long-range order to explain the fine structure. Because EXAFS is found experimentally in amorphous solids and molecules the experimental evidence favours the SRO theoretical approach. For this reason during 1970 and later the theoretical interest had centered on the SRO theories. In these theories only the environment in the vicinity of the excited atom was held responsible for EXAFS. Most SRO theories of EXAFS agree on the basic Physics. The differences occur in the various approximations made in the calculations.

However, there has never been theoretical investigation of the relationship between the LRO and SRO theories although one knows that both approaches must give the same results if correctly formulated. It is shown by Stern that the LRO theories as usually formulated are incorrect because they neglect
the dominant effects. In 1970, Sayers, Lytle and Stern derived the first successful working theory of EXAFS. This was subsequently modified by Stern to a more general form and further refined by others. According to these theories, EXAFS is regarded as resulting from interference between the photoelectron wave propagating from the X-ray absorbing atom and the wave backscattered by neighbouring atoms. Depending on whether the scattered wave returns to the origin in phase or out of phase with the outgoing wave, there is an increase or decrease in absorption.

Sayers et al. have shown that the structural information can be obtained most directly from EXAFS by taking the Fourier transform of EXAFS data. With highly symmetrical structures involving only a single absorber nearest neighbour distance in the first coordination sphere, one can use Fourier transform to obtain such distances to an accuracy of about 0.01 Å.

Besides radial distance information, EXAFS also contains information about the type and number of scattering atoms and their motion relative to the absorber. The atom type reveals itself through the EXAFS amplitude envelope. This amplitude is also affected by the static and thermal disorder of absorber-scatterer distances. Moreover, simple theory predicts that the magnitude of the fine structure will be linearly proportional to the number of scattering atoms and inversely proportional to the square of the absorber-scatterer distances. During 1975-1977, much of the amplitude information has been discarded, but in late 1978, Cramer et al. has demonstrated that using a known phase shifts and amplitude functions, one can estimate the number and identity of near-neighbours at a particular distance.

Sometimes one observes that in the extended fine structure there exists certain peaks which cannot be attributed to the states created in the above fashion. There is evidence to suggest that these peaks can be attributed to plasmons, i.e. collective
Since most of the experimental work presented in this thesis is done by using X-ray absorption spectroscopy, it would be appropriate here to mention briefly the special advantages of this technique that make it a versatile probe for electronic structure determination.

1.4. SOME SPECIAL ADVANTAGES OF X-RAY ABSORPTION SPECTROSCOPY

As is well known, the surge in interest during the last two decades in X-ray absorption fine structure, which had been an obscure phenomenon for the previous fifty years, was caused by the realization that X-ray absorption spectroscopy can be used to obtain information about the local structure of the absorbing atoms\textsuperscript{109}. Several years after this appreciation, the technique, as mentioned in section 1.1, became experimentally accessible to the general scientific community with the advent of very high intense radiation sources. Since then X-ray absorption technique has found wide applicability in many diverse areas as a tool to determine the local atomic environment in many classes of materials whose structures defied analysis by standard techniques such as diffraction or diffuse scattering\textsuperscript{109-114}. The properties of X-ray absorption technique that make it so useful for structure determination are:

1. The local atomic arrangement can be determined about each type of atom in a sample separately. By tuning the X-rays to the absorption edge energy of an atom, only its environment is probed.

2. Since EXAFS measures only short range order, there is no fundamental distinction between crystals with long range order and samples without, such as amorphous solids, liquids, and solutions. Thus aperiodic systems can be studied with the same ease as crystals.

3. In principle, the kinds of surrounding atoms can be
distinguished by the energy dependence of their contributions to
the EXAFS.
4. The numbers of atoms at a given average distance and the
disorder in their location about their average can be quantified
by EXAFS.
5. In unoriented samples only the radial distance between the
centre atom and its neighbouring atoms is determined, but in
oriented samples which have less than cubic symmetry, angular
positions are discernible.
6. Structural information is obtained from EXAFS by a simple
and direct analysis.
7. The X-ray absorption measurements are relatively easy and
rapid.
8. Determination of the chemical state of atom is possible by
determining absorption edge shift and the near edge structure.
9. Information regarding the unoccupied bound states as well
as the low-lying continuum states can be obtained from the
absorption spectrum by making use of a relatively narrow inner
state as a scanning probe.
10. It is a non-destructive technique and comparatively small
quantities of materials are required in the investigations.
11. The site symmetry of the absorbing ions i.e. the geometrical
distribution of atoms around the absorbing atom can be obtained
simply by studying the profiles of X-ray absorption edges in the
model compounds and in the unknown systems.

It is because of these properties and advantages that X-ray
absorption spectroscopy occupies an important place among the
different methods used for crystal structure determination.

1.5. ORIENTATION OF THE PRESENT WORK
As mentioned earlier, recent experimental and theoretical
advances have made X-ray absorption spectroscopy a promising new
method for the investigation of local environment around a
specific absorbing atom in simple as well as complex crystalline systems, catalysts, amorphous materials, metalloproteins and many other cases where conventional diffraction methods are not feasible. It is our intention to extend such investigations to complex oxide systems, in particular, to vanadium and thallium doped superconducting oxides and determine what correlations, if any, could be established between the changes in the different features of the X-ray absorption spectra and the changes in the electronic structures of the absorbing atom. In present thesis we report our investigations on

(i) Position and profile of vanadium K absorption edges in the model compounds viz. VO, $V_2O_3$, $V_4O_7$, VO$_2$, $V_2O_5$, NaVO$_3$, CrVO$_4$, $Zn_3(VO_4)_3$, GdVO$_4$, $Ca_3Fe_3GeVO_{12}$, $Pb_5(VO_4)_3Cl$, VOPC, VOTPP, $(NH_4)_4[VO-tart]_2\cdot 2H_2O$, VO(bzac)$_2$, VO(acac)$_2$, VOMoO$_4$, PbV$_2O_5$, $Ca_3V_{10}O_{28\cdot 16}H_2O$, SmVO$_3$, $V_2S_3$, VN, $[VO(hshed)(acac)]_2VOPO_4$, VO(OC$_3H_7$)$_3$, and in the superconducting oxides of composition Tl$_{1-x}$V$_x$Sr$_2(Ca_{0.8}Y_{0.2})$Cu$_2O_y$, ($0.2 \leq x \leq 0.5$).

(ii) Position and profile of copper K absorption edges in model systems viz. Cu$_2O$, CuO, La$_2CuO_4$ and in the superconducting oxides viz. YBa$_2Cu_{3}O_{7-\delta}$, La$_2$-x$^A_{x}$CuO$_4$ where $A = Sr, Ba$ and $0 \leq x \leq 0.3$, and Tl$_{1-x}$V$_x$Sr$_2(Ca_{0.8}Y_{0.2})$Cu$_2O_y$.

(iii) Position and profile of thallium L- absorption edges in TlCl, TlBr, TlI, Tl$_2$CO$_3$, TlNO$_3$, Tl$_2$SO$_4$, Tl(CH$_3$COO)$_2$, Tl(C$_6$H$_5$COCHCOCH$_3$)$_2$, Tl(C$_5$H$_7$O$_2$)$_2$, Tl$_2$Ta$_2$O$_6$, Tl$_2$O$_3$, Tl(NO$_3$)$_3\cdot 3H_2O$, Tl(CH$_3$COO)$_3$, Tl(CF$_3$COO)$_3$ and Ba$_2$Tl$_2$O$_5$ and superconducting oxides mentioned in (i).

(iv) Extended X-ray absorption fine structure at the thallium L$_{III}$ edge in the above superconducting oxides.

Furthermore, we have also studied the X-ray photoelectron
spectra (XPS), in particular, copper - 2p$_{3/2}$ core level spectra in Cu metal, Cu$^{1+}$, Cu$^{2+}$, Cu$^{3+}$ compounds and in a few superconductors for the confirmation of results obtained from the analysis of absorption spectra of these complex oxides.
REFERENCES


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22. A. Nilson, Ark. Physik, 6, 513 (1953).
38. G. Boehm, A. Faessler and G. Rittmayer, Z. Naturforschung, 96,


44. W.W.Beeman and J.A.Bearden, Phys. Rev. 61, 455 (1942).


64. Y. Cauchois and N.F. Mott, Phil. Mag. 40, 1260 (1949).


75. R.M. Levy and J.R. Van Wazer, Advances in analytical Chemistry


80. A.V.Pendharkar and C.Mande, Chemical Analysis 7, 244 (1975).


94. B.M. Kincaid and P. Eisenberger, Phys. Rev. Lett. 34, 1361

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100. A. Peterson, Z. Physik 80, 258 (1933).


