CHAPTER 1

Introduction

This chapter embodies a general introduction to the experimental technique used in the work presented in this thesis and the materials under investigation. Part A of this chapter outlines the principles of photopyroelectric technique, theory of the signal generation from solids and applications of the technique to different solids. Part B of this chapter describes the features and theory of ferroelectric phase transitions with a special reference to the variation of thermal parameters during a ferroelectric phase transition. Part C gives an overall review on the metal-insulator transition in solids, with focus being mainly on the mixed valence perovskite systems. The various theoretical models, to explain the metal-insulator transition and the magnetic and transport properties of mixed valence perovskites are reviewed.

Part A: The Photopyroelectric effect and its applications

1.1 Introduction

In recent years there has been a surge of interest in investigations of materials - solids and liquids, using photothermal diagnostic techniques, which use lasers as precisely controlled optical heat sources. The development of lasers as convenient and powerful sources of localized energy has contributed greatly to the success of
photothermal techniques over the conventional methods. The photothermal effects are generated by the deposition of energetic beams via direct heating provided by thermal deexcitations or by other non-thermal deexcitation processes like photoelectric, photochemical, luminescence and energy transfer processes, which result in indirect heating of the sample. If the excitation is modulated, the corresponding time and space dependent temperature variations developed in the sample gives rise to a variety of effects and most directly to temperature increase of the sample, which constitutes the basis of a distinct experimental technique, known as photopyroelectric (PPE) effect.

The pyroelectric effect consists in the induction of spontaneous, rapid polarization in a non-centrosymmetric, piezoelectric crystal as a result of temperature changes in the crystal. The measurements of the pyroelectric effect first appeared shortly before World War I [1-3]. The use of pyroelectric detectors for the detection of infrared radiation was suggested early by Yeou [4] and Chynoweth [5]; however the practical pyroelectric detectors have been developed only over the last two decades [6, 7]. Historically, the search for pyroelectric materials has been focused on their infrared radiation detectivity [8, 9] and their efficient high frequency responsivity [7, 10]. It is surprising that the sensitivity and the unique intrinsic capability of thermal sensors based on the pyroelectric effect to respond very rapidly to thermal excitations have not been exploited with photothermal phenomena until recently.

The impetus for an exploitation of the capabilities of the pyroelectric detection technique has come from the need for a spectroscopic technique that would provide reliable information about samples, which are difficult to examine by
conventional optical transmission or reflectance spectroscopy in the UV-Visible and 
near IR regions of the electromagnetic spectrum. The combined use of the quick 
response to radiation and temperature measurement capabilities of a pyroelectric 
detector led to the development of a new spectroscopic technique for solids, 
designated as photopyroelectric spectroscopy in 1984 [11-13].

The PPE technique consists of the measurement of the temperature increase 
of a sample due to the absorption of radiation, by placing a pyroelectric transducer in 
thermal contact with the sample. Both in PPE experiments and pyroelectric 
radiometry, one needs essentially a radiation source and a sensor composed of a 
pyroelectric element and an absorber. The PPE technique is the only photothermal 
technique based on the direct detection of photothermal heating (the temperature 
change) and therefore it has a number of advantages over other detection schemes 
involving secondary mechanisms [14, 15]. In all other techniques, each conversion 
step in the signal-generation chain degrades the overall signal-to-noise ratio, 
sensitivity and bandwidth performance and complicates the theoretical interpretation 
of the results. A PPE experiment is rather simple to design and the specimen needs 
no preparation, the material that can be investigated range from weakly absorbing 
solids like thin films [11, 16-18] or liquids [19], semiconductors [20], surfaces and 
absorbates [14, 17, 21, 22] to strongly absorbing solids [13] and liquids [23, 24] or 
diffusing materials [12]. The obtained spectra are comparable to those obtained 
using pure optical methods if the nonradiative quantum efficiency reaches unity or 
wavelength independent. By comparing two such spectra, intermolecular energy 
transfer processes and non-radiative quantum efficiencies can be studied [14, 16, 25, 
26]. Due to the fact that the PPE signal depends on the optical properties and also on
the thermal properties of the sample, non-spectroscopic problems such as thermal microscopy [27, 28], depth profiling [16, 29], investigation of multilayered structures [30, 31], thermal diffusivity measurements [32-39] and measurement of temperature dependence of specific heat [40] can be investigated very effectively. Several approaches are possible in which the excitation and detection is harmonic, pulsed and modulated in a wide bandwidth [41], each having specific advantages and drawbacks.

1.2 Theory of photopyroelectric effect in solids

The first successful attempt to derive a general expression for the photopyroelectric signal voltage developed in the pyroelectric detector, in intimate contact with a sample was made by Andreas Mandelis and Martin Zver in 1985 [42]. They put forward a one-dimensional photopyroelectric model of a solid sample in contact with a pyroelectric thin film, supported on a backing material. The emphasis is placed on the conditions and / or restrictions imposed on the values of the system parameters so that the technique can produce signals linear with the optical absorption coefficient of the material under investigation. The limits of validity of photopyroelectric spectroscopy as a spectroscopic technique are also identified herewith.

A one-dimensional geometry of a photopyroelectric system, as suggested by Mandelis and Zver is shown in Fig. 1.1(a). They considered a solid sample of thickness \( L_s \), irradiated by a monochromatic light of wavelength \( \lambda \), whose intensity is modulated at an angular frequency \( \omega_m \) by a chopper. The sample has optical absorption coefficient \( \beta_s(\lambda) \) and is in intimate contact with a pyroelectric detector of
thickness $L_p$. The optical absorption coefficient and pyroelectric coefficient of the detector are $\beta_p(\lambda)$ and $p$ respectively. The detector is supported on a backing material of thickness $L_b$, large compared to $L_s$ or $L_p$. The incident light is assumed to illuminate the sample surface uniformly. Light absorption by the sample surface and non-radiative energy conversion to heat causes the temperature increase of the pyroelectric thin film. This temperature increase results in a potential difference between the upper and lower surfaces of the pyroelectric detector. This voltage $V[\omega, \beta(\lambda)]$ causes an electrical signal, which is measured in the external circuit through the connections to the pyroelectric detector as in Fig. 1.1(b).

The charge accumulated in the pyroelectric, due to a change $\Delta T$ in temperature is given by

$$Q = p \Delta T \quad (1.1)$$

For a pyroelectric film of thickness $L_p$, the average charge induced due to the pyroelectric effect is

$$\langle Q \rangle = p \Delta T = \left( \frac{p}{L_p} \right) \int_{\text{thickness } L_p} T(x) e^{i\omega t} \, dx$$

$$= \left( \frac{p}{L_p} \right) \Re \left[ \int_{L_p} T(x) \, dx \right] e^{i\omega t} \quad (1.2)$$

The average pyroelectric voltage is then given by

$$V = \frac{\langle Q \rangle}{C} \quad (1.3)$$

where $C$ is the capacitance per unit area of the thin film.
Fig. 1.1(a): One-dimensional geometry of the photopyroelectric set up. $g$, $s$, $p$ and $b$ stand for the gas medium in front of the sample, sample, pyroelectric detector and backing respectively.

Fig. 1.1(b): Electrical equivalent circuit of the photopyroelectric set up.
For two parallel charged plates of thickness $L_p$ and dielectric constant $K$, Eq. (1.3) becomes

$$V(\omega_o) = \left[ \frac{pL_p \theta_p(\omega_o)}{K \varepsilon_o} \right] \exp(i\omega_o t)$$

(1.4)

where $\theta_p(\omega_o) = \frac{1}{L_p} \int T_p(\omega_o, x) \, dx$

(1.5)

Here, $\varepsilon_0$ is the permittivity constant of vacuum ($8.854 \times 10^{-12}$ C/Vm).

$T_p(\omega_o, x)$ is the temperature field in the pyroelectric detector as a result of heat conduction processes through the solid. For the geometry shown in Fig. 1.1(b), $T_p(\omega_o, x)$ can be found from the solution of one-dimensional thermal transport equations. Assuming that there is negligible optical reflection and radiative heat transfer coefficients on the sample surface and pyroelectric-sample interface [9], the appropriate heat diffusion equations have the form

$$\left( \frac{\partial^2 T_p(\omega_o, x)}{\partial x^2} \right) - \left( \frac{i\omega_o}{\alpha_p} \right) T_p(\omega_o, x) = 0; \quad x \geq 0$$

(1.6a)

$$\left( \frac{\partial^2 T_s(\omega_o, x)}{\partial x^2} \right) - \left( \frac{i\omega_o}{\alpha_s} \right) T_s(\omega_o, x) = \left( \frac{I_o \beta_s \eta_s}{2k_s} \right) \exp(\beta_s x); \quad -L_s \leq x \leq 0$$

(1.6b)

$$\left( \frac{\partial^2 T_p(\omega_o, x)}{\partial x^2} \right) - \left( \frac{i\omega_o}{\alpha_p} \right) T_p(\omega_o, x) = \left( \frac{I_o \beta_p \eta_p \exp(-\beta_p L_p)}{2k_p} \right) \exp(\beta_p (x+L_p)); \quad -L_p - L_s \leq x \leq -L_s$$

(1.6c)

$$\left( \frac{\partial^2 T_b(\omega_o, x)}{\partial x^2} \right) - \left( \frac{i\omega_o}{\alpha_b} \right) T_b(\omega_o, x) = 0; \quad x \leq -(L_p + L_s)$$

(1.6d)

The subscript $j$ refer to the respective media $j = s, p, b$ or $g$ as in Fig. 1.1(a). The various terms in the above equations are defined as follows.
\( I_0 \) = Intensity of light source

\( k_j \) = Thermal conductivity of the respective media \( j (= s, p, g \) or \( h) \)

\( \alpha_j \) = Thermal diffusivity of \( j \)

\( \eta_n, \eta_p \) = Non radiative conversion efficiencies for the absorbing solid and pyroelectric.

The boundary conditions of temperature and heat flux continuity at all interfaces are given by

\[
T_j(\omega_0, \text{boundary}) = T_j(\omega_0, \text{boundary}) \quad (1.7a)
\]

\[
k_j \frac{\partial}{\partial x} T_j(\omega_0, \text{boundary}) = k_j \frac{\partial}{\partial x} T_j(\omega_0, \text{boundary}) \quad (1.7b)
\]

The complex solutions to equations (1.6) are

\[
T_s(\omega_0, x) = C_s \exp(-\sigma_s x) \quad (1.8a)
\]

\[
T_s(\omega_0, x) = \left( \frac{I_0 \beta s \eta_s}{2k_s (\sigma_s^2 - \beta_s^2)} \right) \exp(\beta_s x) + C_2 \exp(\sigma_s x) + C_3 \exp(-\sigma_s x) \quad (1.8b)
\]

\[
T_p(\omega_0, x) = \left[ \frac{I_0 \beta_p \eta_p \exp(-\beta_p x)}{2k_p (\sigma_p^2 - \beta_p^2)} \right] \exp \left[ \beta_p (x + L_p) \right] + C_4 \exp(\sigma_p x) \quad (1.8c)
\]

\[
T_s(\omega_0, x) = C_s \exp(\sigma_s x) \quad (1.8d)
\]

where \( \sigma_j = (1+i) a_j \) and \( a_j = \left( \frac{\omega_0}{2\alpha_j} \right)^{1/2} \quad (1.9) \)

and \( a_j \) is the thermal diffusion coefficient of the respective media.

The quantity of interest is the function for the temperature variations in the pyroelectric \( T_p(\omega_0, x) \). The coefficients in Eq. (1.8c) can be determined using the
boundary conditions (1.7a) and (1.7b). So after a considerable amount of algebraic manipulation, the general expression for $\theta_p(\omega_d)$ is obtained as

$$\theta_p(\omega_d) = \left( \frac{I_0}{2\sigma_p\omega_0} \right) \left( \frac{\beta_p}{k} \right) \left( \frac{\eta_p}{\beta_p^2 - \sigma_p^2} \right) \left\{ \left[ \exp(\sigma, L_p) - 1 \right] \left[ (b_{\nu,1} - 1) \exp(-\beta_p L_p) \right] - \left[ 1 - \exp(-\sigma_p L_p) \right] \right\} \left[ (b_{\nu,1} + 1) \exp(\beta_p L_p) \right] \left[ (b_{\nu,1} - 1) \exp(-\beta_p L_p) \right]$$

Further, substitution of Eq. (1.10) into Eq. (1.4) gives the expression for the complex pyroelectric voltage as a function of modulation frequency of light and optical, thermal and geometric parameters of the sample/pyroelectric system.
Special cases

Equation (1.10) demonstrates explicitly that the thickness averaged photopyroelectric signal is a function of both the optical and thermal parameters of the sample under investigation. The complicated dependence of the signal on the sample parameters makes it difficult to give a physical interpretation to the general case. Therefore several special cases are considered according to the optical opacity and transparency of the sample. The classification scheme used here is adopted from Rosencwaig and Gersho [43]. All cases considered here have been classified according to the relative magnitudes of three characteristic lengths in the solid and

\[ H, \quad \text{Optical absorption depth} \quad \mu_\beta \text{ or } \mu_\beta'] \]

\[ J, \quad \text{Thermal diffusion length} \quad \mu_\gamma \text{ or } \mu_\gamma' \]

\[ \mu_j = \mu_j^{-1} = \left( \frac{2\alpha_\gamma}{\omega_\alpha} \right)^{1/2} \]

For the special cases of the photopyroelectric signal discussed below, the time dependent factor \( \exp(i\omega t) \) in Eq. (1.4) has been omitted, as it does not affect the amplitude or the phase lag of the complex envelope of the signal.

A. Optically opaque and thermally thick pyroelectric

This case occurs experimentally at high chopping frequencies \( \omega_\alpha \) or for thick detectors.

For this limit \( \mu_\beta' \ll L_p, \mu_\beta < L_p \) and \( \mu_\beta' < \mu_\beta' \). So in Eq. (1.10), we set...
\[ \exp(-\beta p L_p) \equiv 0, \exp(-\sigma_p L_p) \equiv 0 \text{ and } |\gamma_p| > 1 \]

Then

\[ V(\omega_0, \beta_\gamma) = \left( \frac{p I_0}{2k \varepsilon_0} \right) \left( \frac{\beta \eta_p}{k^2 (\beta_p^2 - \sigma_p^2)} \right) \left( 2(b_{\eta} \gamma + 1) \right) \left( 2(b_{\gamma} + 1) \exp(\sigma, L) \right) \]

\[ + (\gamma, -1)(b_{\eta} - 1) \exp(-\sigma, L) \right) J \exp(-\beta, L) J + \left( \frac{\eta_p \exp(-\beta, L)}{k \beta_p \sigma_p} \right) \]

\[ \left( (b_{\eta} + 1)(b_{\eta}, \gamma - 1) \exp(\sigma, L) + (b_{\gamma}, \gamma - 1) \exp(-\sigma, L) \right) J \]

\[ + \left( (b_{\eta} + 1)(b_{\eta}, \gamma + 1) \exp(\sigma, L) + (b_{\gamma} - 1)(b_{\gamma}, \gamma - 1) \exp(-\sigma, L) \right) \]  

(1.13)

**A. 1: Optically opaque sample \((\mu_\beta, << L_s)\)**

In Eq. (1.13), we set \( \exp(-\beta, L) \equiv 0 \)

**Case A.1(a): Thermally thin sample \((\mu, >> L_s, \mu >> \mu_\beta)\)**

In Eq. (1.13), set \( \exp(\pm \sigma, L) \approx 1 \) and \( |\gamma| >> 1 \)

So \( V(\omega_0) = A \left( \frac{\eta_p \alpha_p}{k_p (1 + b_{\eta}) \omega_0} \right) \exp(-i\pi/2) \)

(1.14)

where \( A = \frac{p I_0}{2k \varepsilon_0} \)  

(1.15)

Eq. (1.14) shows that the photopyroelectric signal voltage is independent of \( \beta \). This behaviour is termed as photopyroelectric saturation. The signal depends on the thermal properties of both the gas and the pyroelectric and it varies with the chopping frequency as \( \alpha_\beta \) and its phase lags by 90° to that of the reference signal.

**Case A.1 (b): Thermally thick sample \((\mu, << L_s, \mu > \mu_\beta)\)**

In Eq. (1.13) we set \( \exp(-\sigma, L) \equiv 0 \) and \( |\gamma| > 1 \)

Assuming that \( |\gamma| > b_{\eta} \), Eq. (1.13) reduces to
$$V(\omega_0) = A\left(\frac{\eta, \alpha_{\gamma}}{k_p (1 + b_{\gamma}) \omega_0}\right) \exp\left[-\left(\frac{\omega_0}{2 \alpha_{\gamma}}\right)^{1/2} L_s\right] \exp\left[-i\left(\frac{\pi}{2} + \left(\frac{\omega_0}{2 \alpha_{\gamma}}\right)^{1/2}\right)\right]$$

In this limit the photopyroelectric signal, initially saturated with respect to the thermal properties of the contact gas, have now been replaced with those of the solid. Eq. (1.16) indicates that in this limit the photopyroelectric signal can be in principle to determine its thermal diffusivity $\alpha_{\gamma}$ if the thickness $L_s$ is known.

**Case A.1(c): Thermally thick sample ($\mu, << L_s$, $\mu, < \mu_\theta$)**

In Eq. (1.13), set $\exp(-\sigma, L_s) \equiv 0$ and $|\gamma,| < 1$

Here two possibilities can occur

(i) $|\gamma,| < b_{\gamma} < 1$, then

$$V(\omega_0, \beta_s) = A\beta_s\left(\frac{\eta, b_{\gamma}, \alpha_s, \sqrt{\alpha_{\gamma}}}{k_p (1 + b_{\gamma}) \omega_0^{3/2}}\right) \exp\left[-\left(\frac{\omega_0}{2 \alpha_{\gamma}}\right)^{1/2} L_s\right] \exp\left[-i\left(\frac{\omega_0}{2 \alpha_{\gamma}}\right)^{1/2} L_s - \frac{\pi}{4}\right]$$

(1.17)

This is called thermal transmission spectroscopy. As long as $\mu, < \mu_\beta$, the exponential tail of the heat wave generated within $\mu_s$ in the sample is communicated to the pyroelectric transducer, thus producing a signal linear in $\beta_s$ and of small magnitude. Therefore, the technique can be used in this limit as a spectroscopy, yielding signal information similar to the absorption spectra.

The other possibility considered is

(ii) $b_{\gamma} < |\gamma,| < 1$

So Eq. (1.13) becomes

12
\[ V(\omega_0, \beta_s) = A \beta_s^3 \left( \frac{n_s \alpha_s \alpha_p}{k_p (1 + b_{sp}) \omega_0} \right) \exp \left[ -\left( \frac{\omega_0}{2 \alpha_s} \right)^2 L_s \right] \exp \left[ -i \left( \frac{\omega_0}{2 \alpha_s} \right)^2 L_s \right] \] (1.18)

Eq. (1.18) predicts a spectral nonlinearity, i.e., \( V(\omega_0, \beta_s) \propto \beta_s^2 \). This dependence will distort the spectral information from the sample. Therefore it is regarded as undesirable.

A. 2: Optically transparent sample (\( \mu_s > L_s \))

In this limit, \( \exp(-\beta_s L_s) \equiv 1 - \beta_s L_s \)

Case A. 2(a): Thermally thin sample (\( \mu_s >> L_s, \mu_s > \mu_{p_s} \))

In Eq. (1.13), we set \( \exp(\pm \sigma_s L_s) \equiv 1 \) and \( |\gamma_s| > 1 \)

So Eq. (1.13) becomes

\[ V(\omega_0, \beta_s) = A \left( \frac{n_p + (n_s - n_p) \beta_s L_s}{k_p (1 + b_{sp}) \omega_0} \right) \exp(-i \pi/2) \] (1.19)

The photopyroelectric voltage is proportional to \( \beta_s L_s \), provided that \( n_s \neq n_p \).

In the experimentally common case, where \( n_s \sim n_p \sim 1 \) and \( b_{sp} < 1 \), the signal carries neither optical nor thermal information about the samples and it is entirely generated by the light absorption in the pyroelectric.

Case A. 2(b): Thermally thin sample (\( \mu_s > L_s, \mu_s < \mu_{p_s} \))

In Eq. (1.13), set \( \exp(\pm \sigma_s L_s) \equiv 1 \pm \sigma_s L_s \) and \( |\gamma_s| < 1 \)

Further, if we assume that

(i) \( |\gamma_s| >> \sigma_s L_s \) i.e., \( \mu_s^2 > \mu_{p_s} L_s \)

So Eq. (1.13) reduces to
\[ V(\omega_0, \beta_s) = A\alpha_p \left( \frac{\eta_p + (\eta_s - \eta_p)\beta_s L_s}{k_p \omega_0} \right) \exp\left(-i\frac{\pi/2}{2}\right) \]  

(1.20)

This case is similar to A. 2(a), in that for \( \eta_s \sim \eta_p \sim 1 \), no optical or thermal information about the sample is obtained.

Now, if we assume that

(ii) \(|\gamma_s| \ll |\sigma_s L_s|\), then

\[ V(\omega_0, \beta_s) = A\alpha_p \left[ \frac{(\eta_p + \eta_s \beta_s L_s) (1 - \beta_s L_s)}{k_p \omega_0} \right] \exp\left(-i\frac{\pi/2}{2}\right) \]  

(1.21)

Here, if \( \eta_s \sim \eta_p \sim 1 \), the photopyroelectric output will be proportional to \([1 - (\beta_s L_s)^2]\) with a \( \omega_0^{-1} \) frequency dependence. This limit is nonlinear in \( \beta_s \) and the spectral information from the system will be similar to distorted transmission spectra.

Case A. 2 (c): Thermally thick sample \( (\mu_s < L_s, \mu_\beta < \mu_\beta, ) \)

The approximations in Eq. (1.13) are \( \exp(-\sigma_s L_s) \equiv 0 \) and \(|\gamma_s| \ll 1\). The photopyroelectric output is

\[ V(\omega_0, \beta_s) = A(1 - \beta_s L_s) \left( \frac{\eta_p}{k_p (1 + b_{sp}) \omega_0} \right) \exp\left(-i\frac{\pi/2}{2}\right) \]  

(1.22)

In this limit, the technique is equivalent to optical transmission spectroscopy.

This is of great experimental interest, because the photopyroelectric signal is proportional to \([1 - \beta_s L_s]\). Therefore the technique can yield information similar to the transmission spectrum.
Cases A. 1 (c, i) and A. 2 (c) are the only spectroscopically important cases which give direct information about the optical absorption coefficient of the sample material as a result of thermal and optical transmission respectively.

B. Optically opaque and thermally thin pyroelectric

This case is likely to occur at low chopping frequencies $\omega_0$ and/or very thin pyroelectric films. Under this condition, $\mu_\beta, \gg L_p$ and $\mu_p, \gg \mu_\beta$.

On setting $\exp(-\beta_p L_p) \simeq 0$, $\exp(\pm \sigma_p L_p) \simeq 1 \pm \sigma_p L_p$; $|\gamma_p| \gg 1$ in Eq. (1.13), we get the expression as

$$V(\omega_0, \beta_s) = A f \left( \frac{\beta_p \eta_p L_p}{k_p (\beta_0^2 - \sigma_s^2)} \right) \left[ 2 \left( b_{\gamma} \gamma_s + 1 \right) - \left( \gamma_s + 1 \right) \exp \left( \sigma_s L_s \right) \right]$$

$$+ \left( \gamma_s - 1 \right) \left( b_{\gamma} - 1 \right) \exp \left( -\sigma_s L_s \right) \exp \left( -\beta_s L_s \right) + \left( \frac{\eta_p \exp (-\beta_s L_s)}{k_p \beta_p \sigma_p} \right)$$

$$\left[ \left( b_{\gamma} + 1 \right) \left( b_{\gamma} - 1 \right) \sigma_p L_p - \gamma_p^{-1} \left( \left( b_{\gamma} + 1 \right) + \left( b_{\gamma} + b_{\gamma} \right) \sigma_p L_p \right) \exp \left( \sigma_s L_s \right) \right]$$

$$+ \left( \frac{\eta_p \exp (-\beta_s L_s)}{k_p \beta_p \sigma_p} \right) \left[ \left( b_{\gamma} + 1 \right) \left( b_{\gamma} + 1 \right) + \left( b_{\gamma} + b_{\gamma} \right) \sigma_p L_p \right] \exp \left( \sigma_s L_s \right) + \left( b_{\gamma} - 1 \right) \left( b_{\gamma} - 1 \right) \exp \left( -\sigma_s L_s \right) \right) \right] \right]$$

There are six spectral limits of Eq. (1.23) involving relationships between $\mu_\beta$, $\mu_\gamma$, and $L_s$, identical to cases A.1 and A.2. For each limit, in the case of a thermally thin pyroelectric transducer, the simplified expression for $V(\omega_0, \beta_s)$, which results from Eq. (1.23) is similar to the respective expression in the case of the thermally thick detector previously discussed, with the substitutions $-1/\sigma_p$ replaced by $L_p$ and $k_p \sigma_p$ with $k_p \sigma_p$. According to these substitutions, the cases of spectroscopic interest in the limit of a thermally thin pyroelectric are
Case B.1 (c, i): Thermal transmission mode

\[ V(\omega_n, \beta_0) = -A \left( \frac{\eta, \beta, L_p b_{\omega} \exp(-\sigma, L_s)}{\sigma_s (k_s \sigma_h + k, \sigma_s)} \right) \]  

(1.24)

Case B.2 (c): Optical transmission mode

\[ V(\omega_n, \beta_1) = A \left( \frac{\eta, \beta, L_p (1 - \beta, L_s)}{k_s \sigma_h + k, \sigma_s} \right) \]  

(1.25)

The frequency dependence of the photopyroelectric voltage in all cases (B) is consistently with a factor \( \omega_0^{-1/2} \) lower than all cases in (A).

The results obtained show some trends familiar from other thermal wave spectroscopies, such as photoacoustic and photothermal deflection spectroscopy, as well as some unique features. The calculations show that the photopyroelectric voltage is governed by the interplay between the optical absorption in the sample and in the pyroelectric transducer itself. This suggests that it is experimentally advantageous to work with optically opaque transducers whose flat (i.e., photopyroelectrically saturated) spectral response does not interfere with the spectral measurements on the sample. Opaqueness can be achieved through coating the photopyroelectric surface with metallic thin layers (e.g., nickel) [44] or black absorbing materials [9].

The present theoretical considerations help to establish photopyroelectric spectroscopy as a valid spectroscopic technique, with high promise in the realm of flexible in-situ non-destructive probing of samples and in applications at very high frequencies as piezoelectric or pyroelectric thin films (such as PVF₂) [45]. These features set this technique ahead of photoacoustics and photothermal spectroscopies.
Mandelis, in his theory assumed total absorption of radiation by the pyroelectric sensor. Chirtoc and Mihăilescu [46] in 1989 put forward another theory to understand the role played by the finite reflectance at the sample-pyroelectric interface and the mechanisms responsible for the peak inversions observed in the reflection-mode PPE spectroscopy [24, 47], since these questions have found no satisfactory answers in the framework of the former theory. It has been shown that the assumption of an arbitrary value for the reflectance completely changes the physical nature of the PPE effect, featuring simultaneous optical absorption and transmission characteristics. Hence it creates very diverse experimental opportunities for optical and thermal investigations of solid, liquid or even gaseous substances. So the full potential of the PPE technique for the investigations of optical and thermal properties of materials remains to be demonstrated by future experiments.

1.3 Experimental set up

There are three main types of photopyroelectric analysis depending on the signal generation and detection mode.

1. Frequency domain scheme (FD) – Harmonic modulation of the incident light at a single frequency and simple pyroelectric calorimetric detection [42]

2. Frequency multiplexed excitation – spectral analysis of input and output signal channel [48].

3. Time domain measurements – pulsed optical excitation of the sample and pyroelectric detection [49-53].
Of the three, frequency domain PPE instrumentation is the simplest of the three modes. The experimental set up of this technique does not present any particular problems. The cost of the instruments is relatively low. Fig. 1.2 shows a general set up of the frequency domain PPE experimental set up. As it is shown, either a broadband source or a CW laser can be used [54].

![Block diagram for the Frequency domain PPE experimental apparatus](image)

**Fig.1 2:** Block diagram for the Frequency domain PPE experimental apparatus

Frequency domain photopyroelectric measurements can be divided into two main groups.

i) The back detection technique (BDT)

ii) The front detection technique (FDT)
This thesis deals only with the back detection technique. However, for completeness, we first describe the front detection technique.

Marinelli et al., [55] were the first to use the PPE technique in the front detection mode. The configuration of the technique is given in Fig. 1.3.

**Fig. 1.3 (A):** One-dimensional geometry for the photopyroelectric technique in the front detection configuration

**Fig. 1.3 (B):** Experimental configuration of the sample and detector for photopyroelectric front detection
Fig. 1.4(A): One-dimensional geometry for the photopyroelectric technique in the back detection configuration

As it is seen in Fig. 1.3, one side of the detector is in contact with the sample, while the opposite side is illuminated. In this case, light strikes directly on the
defector and not on the sample. In back detection technique, one side of the sample is in contact with the detector, while the opposite side is illuminated. The configuration for the technique is shown in Fig. 1.4. The advantage of the FDT is that it can be used in a wide frequency range and it can attain a large signal at a high frequency limit, which allows a high depth resolution in the sample.

1.3.1 Frequency response characterization

Christofides et al. [56] used two different thickness of polyvinylidene difluoride (PVDF), 28 μm and 52 μm as pyroelectric detectors in order to obtain thermally thick pyroelectric conditions. The thickness of the detector and the modulation frequency must be such that the condition

$$f \gg f_c = \frac{\alpha_p}{\pi L_p^2}$$

(1.26)

is satisfied according to the definition of the thermally thick limit. $\alpha_p$ and $L_p$ are the thermal diffusivity and the thickness of the detector respectively [42]. In Eq. (1.26), $f_c$, the critical frequency equals 22 Hz and 5 Hz for the PVDF film of thickness 28 μm and 52 μm respectively. The thermal time response of the PVDF film depends upon its thickness, since a longer time is needed for a thicker detector to reach thermal equilibrium within the pyroelectric after excitation [44]; yet for a range of low frequencies (0.5 to 600 Hz) this dependence is significant. The frequency response characterization experiments is necessary to work in a frequency range greater than 25 Hz or so in order to satisfy the conditions of the theoretical models.

So we can say the PPE spectroscopy is technically less complex and less expensive than any other photothermal methods. The necessary condition for the experiment depends only on the thermal thickness of the detector, which is very easy
to satisfy. However, one disadvantage of PPE spectroscopy is its susceptibility to acoustic noise [57]. This problem can be partially alleviated by isolating the mechanical chopping system from the optical table that supports the rest of the instrumentation.

1.4 Applications of the technique

The pyroelectric (PE) property offers the possibility to use PE materials for a number of applications. In fact PE sensors present five main advantages that make them suitable for many applications.

1. Sensitive in a very large spectral bandwidth
2. Sensitive in a wide temperature range without the need of cooling
3. Low power requirements
4. Fast response
5. Generally low cost materials

In this subsection, we briefly describe the state of the art of the pyroelectric sensors in the field of measurement science. In the beginning, the pyroelectric effect has employed mainly in the detection of infrared radiation and in laser power measurements. The pyroelectric phenomenon has led to many applications in recent years. In fact, since the beginning of the 20th century pyroelectricity has been exploited in different areas, especially for the detection of radiation. In an excellent review, Putley has described the use of pyroelectricity for the detection of radiation [7].

With these added advantages of PE detectors make the photopyroelectric technique an ideal one for the thermal and optical characterization of samples
ranging from metals to insulators. Now we will discuss some of the important applications of the photopyroelectric technique.

### 1.4.1. PPE spectroscopy in semiconductors

In 1984, Coufal and Mandelis [11, 12] used for the first time, thin polyvinylidene difluoride (PVDF) films for photothermal wave spectroscopic detection. Shortly thereafter, Coufal showed that photopyroelectric spectroscopy can be a very sensitive qualitative tool for thin film spectroscopic applications [16]. Mandelis et al. [58] used the PPE spectroscopy for electronic defect center characterization of crystalline $n$-CdS. These authors performed several experiments in open circuit as well as in conjunction with photocurrent spectroscopy in the presence of a.c. or d.c. transverse electric field. This study [59] showed the potential of the technique to give information concerning the non-radiative de-excitation mechanisms at defect centers. Tanaka [60] and Tanaka et al. [61] showed that frequency domain PPE spectroscopy is also very promising for qualitative analysis.

PPE spectroscopy was also used for the characterization of thin semiconducting films. Mandelis et al. [61] have performed spectroscopic measurements of an $\alpha$-Si:H thin film on quartz. These authors further compared their experimental PPE spectra with similar spectra obtained by conventional widely used photothermal deflection spectroscopy (PDS). It was shown that PPE spectroscopy has the ability for easy and consistent experimental acquisition of non-radiative quantum efficiency spectra, a property not shown by PDS. It is the necessity for a coupling fluid that is partly the cause of the lack of spectroscopic applications of PDS at cryogenic temperatures. Another disadvantage is the pump-
probe beam alignment requirement for PDS detection. This frequently led to the need for three-dimensional models to interpret the data quantitatively. The consideration of these advantages led to the development of PPE spectroscopy.

1.4.2. PPE spectroscopy in paramagnetic and ferromagnetic materials

In 1982, Melcher and Arbach [62] reported the use of pyroelectric sensors to detect the temperature gradients associated with magnetic resonance absorption in thin films and layers of paramagnetic and ferromagnetic materials. Photopyroelectric technique to study the magnetic phase transitions in ferroelectrics and itinerant electron antiferromagnetic materials were first done by Dădarlat et al., [63] in 1990. In their paper these authors have reported the application of PPE technique for the study of magnetic phase transitions in Ni_{100-x}Cu_x alloys with x = 28 to 33%. The samples were found to exhibit magnetic phase transitions (ferromagnetic-paramagnetic). According to Dădarlat et al., [63] due to the features of the PPE method, the high signal to noise ratios that were obtained allowed higher sensitivities for monitoring phase transitions in itinerant electron antiferromagnets than classical magnetic and electronic measurements.

In another work, Dădarlat et al., [64] demonstrated the ability of the PPE method to detect the phase transitions in solids. He made measurements on TGS, which exhibited a ferroelectric-paraelectric phase transition at 49 °C and NiCu_{30} had a ferromagnetic-paramagnetic phase transition at 50 °C. It has shown that the PPE voltage amplitude clearly reflects the phase transition. He made the inference that the thermally thin and thick conditions largely influence the results.
1.4.3. PPE spectroscopy in liquid crystals

Marinelli [55] used the photothermal front detection configuration (Fig. 1.4) to perform measurements on liquid crystal samples in the range 0.2 Hz to 200 kHz. The sample was 9CB liquid crystal and the author studied the PPE signal as a function of modulation frequency. It has been proved that with the PPE technique, it is possible, at a given frequency, to obtain the temperature dependence on the thermal parameters of the sample, which is particularly interesting in the case of phase transition studies.

Marinelli et al. [65] have also performed several experiments comparing the photoacoustic and photopyroelectric technique for the characterization of liquid crystal second order phase transitions. In their measurements they evaluated simultaneously thermal conductivity, specific heat and thermal diffusivity of 9CB liquid crystal that undergoes a second order phase transition at 47.9 °C from Smectic-A (SA) to Nematic (N) phase [66]. The variation of PPE signal amplitude and phase as a function of temperature for the liquid crystal sample has been plotted. It is seen that in the plot, the obtained dip for the PPE phase at the phase transition temperature, because of the “critical slowing down” of thermal fluctuations [65, 67] is about 160°, while in PA it was only 4°. This proves the superior sensitivity of the PPE technique over PA. Apart from the sensitivity factor, the PPE technique presents a better signal-to-noise (SNR) ratio, which makes this an ideal one for studies in liquid crystals.
1.4.4. PPE gas sensors

Photothermal and photoacoustic techniques have been used successfully in optical and thermo physical characterization of solids [68-72]. Recent developments in monitoring and measuring the properties of gases using photothermal techniques have attracted much attention for environmental quality control and manufacturing safety reasons [73-77]. Christofides and Mandelis [78] used the photopyroelectric gas sensor, a new type of solid-state devices for the detection of minute concentrations of hydrogen gas under environmental flow-through conditions. Sensitivity to exposures in a hydrogen partial pressure has been demonstrated down to concentrations as small as 40 ppm, in a flowing H₂ + N₂ mixture.

A newly developed [79] thermal wave resonant cavity (TWRC) sensor using a pyroelectric thin film transducer (polyvinylidene fluoride), proved to offer a powerful method for measuring thermal diffusivities of gases with very high precision and gas species resolution [76, 77, 80].

This section on photopyroelectric effect would not be complete if we do not emphasize the fact that high sensitivity of the PPE detector in temperature change is a great challenge for measurement scientists. Juhl and Bimberg [81] have recently proved that with calorimetric absorption and transmission spectroscopy one can achieve spectroscopic sensitivities of $\beta l = 10^{-8}$. So we can say that from an experimental and instrumental point of view, the progress of the experimental technique has been consistent and encouraging. However, the full potentiality of the PPE technique for optical and thermal material characterization remains to be demonstrated by future experiments.
Part B: Ferroelectric phase transitions

1.5 Introduction

The cross-disciplinary subject of phase transition is of great interest in the study of condensed matter. This is a very interesting phenomenon found to occur in a variety of ways in many physical systems. Literature abounds in theoretical and experimental studies of phase transitions in solids and newer kinds of phase transitions in newer systems are constantly reported [82, 83]. In the following paragraphs, a brief outline of the basic facts regarding phase transitions in solids are presented.

A homogenous assembly of atoms or molecules called a phase is characterized by thermodynamic properties like volume, pressure, temperature and free energy. The stability of the isolated phase is determined by whether its energy more generally, its free energy - is a minimum for the specified thermodynamic conditions. If the phase is present in a local minimum of free energy instead of a unique minimum and is separated by still lower minima (under the same thermodynamic conditions) by energy barriers, the system is said to be in a metastable state. If the barriers do not exist, the states of the system become unstable and the system move into a stable or equilibrium state characterized by the lowest value for free energy. As the temperature, pressure or any other variable like electric or magnetic field acting on the system is varied, the free energy of the system changes smoothly and continuously. Whenever such variations are associated with
changes in the structural details of the phase (atomic or electronic configuration) a phase transition is said to occur.

During a phase transition, even as the free energy of the system remains continuous, thermodynamic quantities like entropy, volume, specific heat etc. undergo discontinuous changes. Ehrenfest [84] classified phase transitions depending on the relation between the thermodynamic quantity undergoing discontinuity and the Gibb’s free energy function. According to this scheme, a Gibb’s function shows a discontinuous change at the transition. Thus if there is discontinuity in quantities such as volume and entropy, which are first order derivatives of the Gibb’s free energy, the transition is said to be of first order. whereas if specific heat, compressibility, thermal expansion etc. are the quantities undergoing discontinuity, which are second order derivatives of Gibb’s free energy function, the transition is said to be of second order and so on. However, several of the known transformations do not strictly belong to any one kind [85, 86] as described above. For example the phase transition in BaTiO$_3$, which has second order character, also shows a small latent heat effect. The ferroelectric transition in KH$_2$PO$_4$ should theoretically be of first order, but conforms more closely to the second order. There is superposition of second order behaviour in many first order transitions and vice versa. It is possible that many of the transitions are really of mixed order.

Phase transitions are always associated with configurational changes within the system. Magnetic phase transitions are driven by the alignment of unpaired spins in a specified direction and one usually does not observe any changes in the atomic configuration. On the other hand, several other types of phase transitions like para-
ferroelectric transitions are generally associated with atomic rearrangement or structural changes. The change of structure at a phase transition in a solid can occur in two distinct ways. Firstly, there are transitions where the atoms of a solid reconstruct a new lattice as in the case of amorphous solid to crystalline state. Secondly, there are transitions where a regular lattice is distorted slightly without in any way disrupting the linkage of the networks. This can occur as a result of small displacements in the lattice position of single atoms or molecular groups or the ordering of atoms or molecules among various equivalent positions. Most of the ferroelectric phase transitions belong to the second group. The displacive type transitions are often driven by the freezing out of a vibrational mode called soft mode. In the case of ferroelectric transition, the soft mode is an optical phonon belonging to the centre of the Brillouin zone while in the case of an antiferroelectric transition, is a zone boundary phonon. Soft acoustic phonons are associated with ferroelastic transitions.

Since all the phase transitions involve configurational changes, one can identify a physical quantity that is characteristic of a new ordered configuration. Such a concept of an order parameter was introduced by L. Landau [87] in his thermodynamic theory of phase transitions. The order parameter has a non-zero value in the ordered phase below the transition temperature \( T_c \) and is zero above \( T_c \). Thus in a ferroelectric transition, the order parameter is the spontaneous polarization while in a ferroelastic transition, it is the spontaneous strain. Landau assumed that Gibb's free energy can be expanded in powers of the order parameter is which is assumed to be very small. The results of Landau theory support Ehrenfest's classification and reveal many basic features of phase transitions.
1.6 Landau theory of second order ferroelectric phase transitions

It was pointed out earlier that during a second order transition, the entropy and volume of the system remain continuous, while the heat capacity and thermal expansivity undergo discontinuous changes. Landau [87] proposed an account for this behaviour. He suggested that the transition from a high temperature to a low temperature corresponds to the onset of an ordering process. In the ordered, less symmetrical (low temperature) phase of the material, there exists an order parameter, which decreases continuously with temperature and becomes zero at the transition temperature. The disordered high temperature phase will have high symmetry.

The free energy can be written in terms of the order parameter $\xi$. (for the ferroelectric phase transition, the order parameter is the spontaneous polarization). For small values of $\xi$ (near the transition temperature) the free energy $\phi(P, T, \xi)$ can be written as

$$\phi(P, T, \xi) = \phi_0(P, T) + a\xi + b\xi^2 + c\xi^3 + d\xi^4 + \ldots$$

(1.27)

where $\phi_0(P, T)$, $a$, $b$, $c$ and $d$ are constants. Now, if the value of $\phi(P, T, \xi)$ to remain unaltered by the change of sign of $\xi$, coefficients of odd powers of $\xi$ should be zero. Therefore,

$$\phi(P, T, \xi) = \phi_0(P, T) + b\xi^2 + d\xi^4 + \ldots$$

(1.28)

The equilibrium value of the long-range order parameter is obtained by the following conditions

30
\[
\left( \frac{\partial \phi}{\partial \xi} \right)_r = \xi \left( b + 2d \xi^2 \right) = 0 \quad (1.29)
\]

\[
\left( \frac{\partial^2 \phi}{\partial \xi^2} \right)_r = b + 6d \xi^2 \geq 0 \quad (1.30)
\]

From Eq. (1.29) we obtain the solutions as \( \xi = 0 \) and \( \xi^2 = -\frac{b}{2d} \). Since \( \xi = 0 \) corresponds to the disordered state, it follows from Eq. (1.30) that \( b > 0 \) on one side of the transition temperature. Similarly on using the value \( \xi^2 = -\frac{b}{2d} \) in Eq. (1.30), we get \( b < 0 \) for the ordered phase. So \( b \) should change sign through a second order transition. Since \( b \) is negative for the ordered phase in the vicinity of a transition, \( d \) should be positive (since \( -\frac{b}{2d} = \xi^2 > 0 \)).

Assuming \( b \) to vary linearly with temperature near the transition point

\[ b(P,T) = B \left( T - T_c \right) \quad (1.31) \]

where \( T_c \) is the 'critical' or transition temperature. \( \xi^2 \), then becomes

\[ \xi^2 = -\frac{b}{2d} = -\frac{B}{2d} \left( T - T_c \right) \quad (1.32) \]

Neglecting higher order terms, entropy is given by,

\[
S = -\left( \frac{\partial \phi}{\partial T} \right)_{\xi, T} = S_0 - \xi^2 \left( \frac{\partial b}{\partial T} \right)_{\xi, T} \quad (1.35)
\]

In the symmetrical phase (above the transition temperature), \( \xi = 0 \) and \( S = S_0 \). Below the transition temperature, using Eq. (1.32) we get

\[
S = S_0 + \frac{b(P,T)}{2d} \left( \frac{\partial b}{\partial T} \right) = S_0 + \frac{B^2}{2d} \left( T - T_c \right) \quad (1.34)
\]

This guarantees the continuous nature of the entropy during a second order transition.
Since \( C_r = T \left( \frac{\partial S}{\partial T} \right)_{\rho, \xi} \), we have two phases at the transition

\[
C_r = \left( \frac{\partial S_0}{\partial T} \right)_r = C_r^0 \quad \text{and} \quad C_r = C_r^0 + \frac{B^2 T_c}{2d} \quad (1.35)
\]
on either side of the transformation. So the change in heat capacity during a second order transition will have a finite value given by

\[
\Delta C_r = \frac{B^2 T_c}{2d} \quad (1.36)
\]

So we see that Landau theory provides the basis for Ehrenfest’s second order transition. Extension of Landau treatment has been attempted by various workers in conjunction with fluctuation theory [88].

1.7 Variation of thermal conductivity and heat capacity during ferroelectric phase transitions

Phase transitions in solids are often accompanied by interesting changes in their properties. Several techniques are employed to investigate phase transitions, depending on the nature of the solid and properties of interest. Such studies are not only of academic value in understanding the structural and mechanistic aspects of phase transitions, but can also be of technological importance. The literature abounds in studies of phase transitions in solids using a wide range of techniques, including diffraction, thermal, optical, electrical, magnetic, dielectric, spectroscopic and other measurements [86, 89-93].

It would be difficult here to describe all the techniques and material properties that have been employed to study phase transitions. We shall therefore
limit our discussion to the thermal properties namely thermal conductivity and heat capacity of solid materials.

Thermal measurements have been widely used to identify and characterize transitions. Heat capacity measurements provide enthalpy changes and indicate the thermodynamic order of transitions. Differential scanning calorimetry (DSC) is a popular technique for obtaining heat capacity data and $\Delta H$ of transitions. Another technique that is widely used for the phase transition studies is the photothermal technique.

Photoacoustic technique has been gained wide interest as a powerful tool for the study of phase transitions in solids. The wealth of information contained in the PA signal can be used to investigate the variation in the optical and thermal properties of materials during phase changes. Florian et al., [94] were the first to publish results of measurements of PA effect in the temperature region of first order phase transitions in solids. In their paper, results of measurements of the PA signal at the liquid-solid transition of gallium and of water and the structural phase transition in $K_2SnCl_6$ were reported.

Pichon et al., [95] examined the specific heat anomaly of thermally thick dielectric samples in the neighbourhood of a magnetic phase transition using PA technique. R.G theory has been used to obtain relative values of the specific heat. Results obtained with CrCl$_3$ and MnF$_2$ are given therein. In case of MnF$_2$ the observed anomaly is comparable to that observed using conventional calorimetric techniques.

By exploring the dependence of photoacoustic signal in the thermal properties of the sample, Siquerra et al., [96] demonstrated the usefulness of PA
effect for investigating phase transitions in solids. Their studies have been on aluminium doped VO$_2$. A theoretical model for the PA effect during a first order phase transition has been described by Korpiun and Tilgner [97]. Bibi and Jenkins [98] have reported observations of a first order phase transition in CoSiF$_6$. $6\text{H}_2\text{O}$ using photoacoustic technique. The PA technique has been applied for the study of series of phase transitions in tetra methylammonium tetrachloride cobaltate (TMTC-CO) by Fernandez et al. [99]. But in practice gas coupled PAS at high frequencies is virtually impossible due to very poor signal-to-noise ratios and microphone frequency response limitations.

Extebarria et al. [100, 101] have shown theoretically, using the Jackson and Amer's theory [102] and experimentally that the piezoelectric photoacoustic signal is a function of sample specific heat only, and independent of thermal conductivity, in the optically and thermally thick limits. This observation is indicative of further restrictions on the opacity of the sample, in addition of high modulation frequency requirements similar to the gas coupled PAS.

The PPE technique has been employed by different authors for the study of phase transitions in solids [11, 12, 42, 103].
Part C: Metal-Insulator transition in solids

1.8: Introduction

An early success of quantum mechanics was attributed to the explanation by Wilson [104, 105] for the sharp distinction between metals and non-metals. In crystalline materials, the energies of the electron states lie in bands, a non-metal is a material in which all bands are full or empty, while in a metal, one or more bands are party full. Any metal-insulator transition in a crystalline material is identified as a transition at zero temperature from a situation in which bands overlap to situations when they do not overlap.

Interest in a metal-insulator transition arose long way back in 1937. de Boer and Verwey pointed out [106] that nickel oxide, a transparent non-metal, according to the Wilson model, should be metallic because of the eight electrons of the Ni\(^{2+}\) ions would only partly fill one of the \(d\)-bands. Peierls said this must be due to the correlation and gave a satisfactory explanation of how this could occur. At the time, it wasn’t known that nickel oxide was antiferromagnetic, as Slater pointed out in 1951 [107]. Slater suggested that an antiferromagnetic lattice can split the \(d\)-bands, allowing all bands to be full or empty, making them insulators.

Mott [108-110] described a metal-insulator transition by imagining a crystalline array of hydrogen-like atoms with a lattice constant ‘\(a\)’ that could be varied. The example of nickel oxide suggested that for large values of ‘\(a\)’, the material would be insulating, while the example of monovalent metal like sodium showed that for small values it would metallic. To satisfactorily explain the values
of ‘$\alpha$’ at which a metal-insulator transition can occur, Mott [108] made an assumption that this would occur when the screened potential around each positive charge

$$V(r) = \frac{e^2}{r} e^{-\alpha r}$$  \hspace{1cm} (1.37)

with the screening potential calculated by the Thomas-Fermi method, was just strong enough to trap an electron. The transition would be discontinuous with varying $n$ and $q$ and there would be a discontinuous transition from the state with all electrons trapped to that where all are free. It was found that this would occur when

$$n^{1/3} a_H = 0.2$$  \hspace{1cm} (1.38)

where $n$ is the number of electrons per unit volume and $a_H$ is the hydrogen radius. The Eq. (1.38) was applied with success to the metal-insulator transition in doped semiconductors and the disorder resulting from the random positions of the centers being neglected. The disorder was believed to be the cause of the absence of a discontinuous change in conductivity. However the success of Eq. (1.38) was fortuitous if the many valley nature of the conduction bands of silicon and germanium is taken into account, and also the central cell corrections, totally different results are obtained [111-113].

The next important step in the development of the theory was the introduction by Hubbard [114, 115] of a model in which the interaction between electrons is included only when they are on the same atom, long-range Coulomb forces being neglected. For large values of ‘$\alpha$’, this model leads to an antiferromagnetic insulator which splits the band, so that an electron’s energy lie in a full band and an empty one [107]. However, Hubbard’s work was criticized by
Herring [116] for lack of clear recognition that low-density form is antiferromagnetic. But work on 'resonating valence bond' materials by Anderson [117] has shown that an antiferromagnetic lattice is not essential in the insulating state.

When two bands exist, they are named as lower and upper Hubbard bands. The metal-insulator transition then appears as a band crossing transition, from an antiferromagnetic metal to an antiferromagnetic insulator. There is another antiferromagnetic metal to normal metal transition and is one which is highly correlated and this leads to the great enhancement of the electronic specific heat and Pauli susceptibility, as first pointed out by Brinkman and Rice [118] and observed in vanadium oxides. The Hubbard model, which does not include long range forces, does not predict a discontinuous change in $n$, the number of carriers when long range forces are included, as first shown by Brinkman and Rice [119]. For a crystalline system, a discontinuity will always occur when a full and an empty band cross, as a result of the long-range electron-hole interaction and whether the bands are of Hubbard type or those generated by the crystal structure. Mott [120] has discussed the conditions under which disorder can remove the discontinuity. Actually, in many doped semiconductors, the transition is of Anderson type and not directly a consequence of short-range (intra atomic) interaction, both disorder and long-range interaction contributing to an equation similar to Eq. (1.37).

For disordered systems, a quite different form of metal-insulator transition occurs - the Anderson transition. In these systems, a range of energies exists in which the electron states are localized, and if at zero Kelvin, the Fermi level lies in this range then the material will not conduct even though the density of states is not
zero. The Anderson transition can be discussed in terms of non-interacting electrons though in real systems, electron-electron interaction plays an important part.

Many systems are known to exhibit metal-insulator transitions. Mixed valence perovskites are an important class of materials. In this subsection we give an outline of properties of mixed valence perovskites and various theoretical models to better understand the phenomena of metal-insulator transition found in these materials.

1.9 Mixed valence perovskites: An overview

Mixed valence manganites with the perovskite structure has been studied for almost 60 years. The system offers a degree of chemical flexibility that permits the relation between the oxide’s structure, electronic and magnetic properties to be examined in a systematic way. Research on the manganites have revealed new phenomena such as colossal [121] and dense granular magnetoresistance [122] and has led to the formulation of important physical concepts such as double exchange [123, 124] and the Jahn-Teller polaron [125, 126]. Early research was motivated by a need to develop insulating ferromagnets with a large magnetization for high frequency applications. More recent work has been driven by a desire to understand and exploit the large negative magnetoresistance effects that appear above and below the Curie temperature. The manganites also have potential as solid electrolytes, catalysts, sensors and novel electronic materials.

Mixed valence oxides are represented by \( R_{1-x}A_x\text{MnO}_3 \) (where \( R = \text{La, Nd, Pr} \) and \( A = \text{Ca, Sr, Ba, Pb} \) have been the materials of intense experimental interest. Besides manganese, many perovskite structure oxides form with Al, Ga or other
3d elements such as Chromium, Iron, Cobalt or Nickel. The rare earth orthoferrites RFeO₃ is one example of a series of perovskite structure oxides. An exhaustive compilation of data on perovskite-structure compounds by Goodenough and Longho [127] was published in a 1970 *Landholdt-Börnstein* volume. The mixed valence oxides can be considered as solid solutions between end members such as RMnO₃ and AMnO₃, with formal valence state states R³⁺Mn³⁺O₃²⁻ and A²⁺Mn⁴⁺O₃²⁻ leading to mixed valence compounds such as \((R_{1-x}A_x)\)(Mn_{1-x}Mn_{x})O₃. The nominal electronic configurations of Mn³⁺ are Mn⁴⁺ are \(3d^4\) and \(3d^5\) respectively. Chemically, the system is characterized by the wide range of cations, which can occupy the A-site in the perovskite structure, which may be set at the body centre or the cube corner. The structure of mixed valence oxides can be considered as a cubic close packed array formed of \(O^{2-}\) anions and large A cations with small B cations in the octahedral interstitial sites as shown in Fig. 1.5. The ideal cubic structures is distorted by cation size mismatch and the Jahn-Teller effect, where by a distortion of the oxygen octahedron surrounding the B site cation splits the energy levels of a 3d ion such as Mn³⁺, thus lowering the energy. The distorted structures are frequently orthorhombic.

![Fig. 1.5: Ideal cubic perovskite structure ABO₃ for the mixed valence perovskites](image)

\[a = b = c = 0.388 \text{nm}\]
The broad feature of mixed valence perovskites were described by polycrystalline ceramic samples by Jonker and van Santen [128], van Santen and Jonker [129] and Jonker [130] in the late 1940s. They discussed the preparation, crystal structure and magnetic properties of the (La$_{1-x}$Ca$_x$)MnO$_3$ series [128] and gave an account for the electrical conductivity [129]. Similar results were found for the (La$_{1-x}$Sr$_x$)MnO$_3$ and (La$_{1-x}$Ba$_x$)MnO$_3$ series, but the range of solid solutions was limited to $x < 0.7$ or $x < 0.5$ respectively. Magnetoresistance and other transport properties were first described in 1954 by Volger [131] who showed that the magnetoresistance of La$_{0.6}$Sr$_{0.2}$MnO$_3$ is negative with a peak near the Curie temperature.

The crystallographic and magnetic structure for the (La$_{1-x}$Ca$_x$)MnO$_3$ compounds were determined in 1955 by Wulcan and Koehler [132] in a remarkably complete neutron and X-ray diffraction study as a function of Mn$^{4+}$ content. In particular, the neutron data revealed a very rich magnetic phase diagram where, for different doping levels, there are three main regions. For small amounts of Mn$^{4+}$, the compounds have essentially antiferromagnetic properties. For $x \approx 0.3$, they become ferromagnetic, but for $x > 0.5$ they revert to antiferromagnetism up to the end member CaMnO$_3$. From magnetization and susceptibility results, Jonker [130] concluded that the exchange is weakly positive (ferromagnetic) between the two 3$d^4$ Mn$^{3+}$ ions, negative (antiferromagnetic) between two 3$d^3$ Mn$^{4+}$ and positive between a 3$d^4$ Mn$^{3+}$ and 3$d^3$ Mn$^{4+}$ ion, these measurements provided a first clear evidence for a ferromagnetic exchange interaction in an oxide. Resistivity measurements also revealed a strong correlation between electron transport and magnetic properties. The resistivity is lowest for the $x \sim 0.3$ compounds corresponding to best
ferromagnetism, where as high resistivity is associated with the antiferromagnetic compositions.

An extensive study of flux grown single crystals of (La$_{1-x}$Pb$_x$) MnO$_3$ with $0.2 < x > 0.4$ was carried out by Searle and Wang [133, 134], Morrish et al. [135] and Leung et. al. [136] in 1969 and 1970. They found metallic conductivity below the Curie point $T_c$ and a large negative magnetoresistance effect of about 20% at 1 T in the vicinity of $T_c$, similar to that in polycrystalline (La$_{1-x}$Sr$_x$) MnO$_3$.

Interest in the mixed valence manganites revived in the 1990s, following the preparation of high quality thin films with large magnetoresistance by von Helmholdt et. al. [137] and Chahara et. al. [138]. Optimised films show remarkable magnetoresistance effects near $T_c$ that were epitomised by Jin et al. as the 'colossal magnetoresistance' (CMR) [121]. The Curie point coincides with the metal - insulator transition and there are associated anomalies in various physical properties. It is seen that the $x \approx 3$ corresponds to the best ferromagnetism, where high resistivities are associated with the antiferromagnetic compositions.

Despite intensive investigations of the CMR phenomenon, the nature of the metal-insulator (M-I) transition remains an open question. The manganese oxides are usually modeled by the double-exchange Hamiltonian that describes the exchange of electrons between neighbouring Mn$^{3+}$ and Mn$^{4+}$ ions with strong on-site Hund’s coupling. So the inquisitiveness as to the origin of the mechanism of the effect, a great deal of effort is being devoted. Zener [123] paved the way by offering first satisfactory explanation for this phenomenon. In the next subsection, we will give an outline of the double-exchange model put forward by Zener to explain the M-I transition.
1.10 Double exchange model

Zener in 1951, offered an explanation for the behaviour of mixed valence manganites with doping, in terms of his theory of indirect magnetic exchange between 3d atoms. Starting from the insulating antiferromagnetic RMnO$_3$ end member whose electrons are localized in the atomic orbitals, he gave an explanation how the system should gradually become more ferromagnetic upon hole doping (introduction Mn$^{4+}$). He suggested that there will be an exchange of electron between Mn$^{3+}$ and Mn$^{4+}$ ion via oxygen and introduced the concept of simultaneous transfer of an electron from the Mn$^{3+}$ to the oxygen and from the oxygen to the neighbouring Mn$^{4+}$ as in Fig. 1.6. Such a transfer is called double exchange.

![Diagram of double-exchange mechanism](image)

Fig. 1.6: Schematic diagram of the double-exchange mechanism. The two states Mn$^{3+}$-Mn$^{4+}$ and Mn$^{4+}$-Mn$^{3+}$ are degenerate if the manganese spins are parallel.

In the case of magnetic ions, the configurations Mn$^{3+}$ - O$^{2-}$ - Mn$^{4+}$ and Mn$^{4+}$ - O$^{2-}$ - Mn$^{3+}$ are degenerate if the spins of the 2d shells are parallel and the lowest energy of the system at low temperature corresponds to parallel alignment of the
spins of the two adjacent cations. Double exchange is always found to be ferromagnetic unlike super exchange interaction that involves virtual electron transfer and is frequently antiferromagnetic.

He considered that the interatomic Hund rule exchange was strong and that carriers do not change their spin orientation upon hopping from one ion to the next, so that they can only hop if the spins of the two ions are parallel. On minimizing the total free energy of the system, Zener found that ferromagnetic interactions are favoured when the magnetic atoms are fairly well separated and conduction electrons are present. If the manganese spins are not parallel or if the Mn-O-Mn bond is bent, the electron transfer becomes more difficult and the mobility decreases. It follows that there is a direct connection between conductivity and ferromagnetism and a qualitative relation with Curie temperature has been proposed.

\[
\sigma = \left( \frac{x e^2}{ah} \right) \left( \frac{T_c}{T} \right)
\]

(1.39)

where \( x \) is the doping and \( a \) is the Mn-Mn distance, which agreed with the available experimental results of Jonker and van Santen in the limited region \( 0.2 < x < 0.4 \).

Anderson and Hasegawa [139] generalized the double exchange mechanism by considering interaction between a pair of magnetic ion with general spin direction. They calculated the transfer integral \( t \) to be

\[
t = t_n \cos \left( \frac{\theta}{2} \right)
\]

(1.40)

where \( t_n \) is the normal transfer integral which depends on the spatial wave functions and the term \( \cos \left( \frac{\theta}{2} \right) \) is due to the spin wave function and \( \theta \) is the angle between two spin direction. This is quite unlike super exchange when the coupling is proportional to \( \cos \theta \). They also considered the problem of high temperature
paramagnetic state of the manganites where the exchange energy is much larger than the transfer integral and predicted that $\chi$ should be Curie like, which contradicted the experimental results showing Curie-Weiss behaviour. The point was corrected by deGennes [140] who pointed out that the prediction is erroneous when the carrier bandwidth is large with respect to $kT$. Double exchange therefore leads to normal Curie-Weiss behaviour of the susceptibility $\chi = \frac{C}{T - T_p}$ with $\theta_p > 0$.

It is seen that even though double exchange plays an important role for metallic conductivity and ferromagnetism in these materials, it alone can't explain all the aforementioned phenomena. It has been pointed out by various workers [141-143] that other effects such as localization, electron-electron correlation, electron magnon scattering, electron-phonon interaction etc., strongly modify the temperature dependence of many physical properties. It will be an uphill task to give details of all effects mentioned above. So we will give an outline of the localization phenomena and describe the Anderson transition in detail, in the next subsection.

1.11 Theoretical models

Localization-delocalization phenomenon in the physics of amorphous solids concerns the motion, not of atoms, but of electrons. Liquid-glass transition that involves atomic motion can be visualized in a classical picture of molecular movements, whereas the metal-insulator transition is an electronic phenomenon and is intrinsically quantum mechanical in character. Moreover, important features of this phenomenon represent conceptual departures from the traditional quantum mechanical treatment of electrons in crystalline solids. In order to introduce some of the main ideas and to place the issue of disorder induced localization in the context
of other basic electronic phenomena, we present three popular models of atomic scale metal-insulator transitions as given in Table (1.1)

Table 1.1: Major classification of metal-insulator transitions

<table>
<thead>
<tr>
<th>Transition</th>
<th>Electron Wave functions</th>
<th>Characteristic Energies</th>
<th>Change at the M→I Transition</th>
<th>Criterion for Localization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal side of Transition</td>
<td>Insulator side of Transition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bloch</td>
<td>Extended</td>
<td>Extended</td>
<td>Bandwidth $B$</td>
<td>Partly filled→ all bands filled or empty</td>
</tr>
<tr>
<td>Mott</td>
<td>Extended</td>
<td>Localized</td>
<td>Electron-electron correlation energy $U$</td>
<td>Correlation-induced localization</td>
</tr>
<tr>
<td>Anderson</td>
<td>Extended</td>
<td>Localized</td>
<td>Width $W$ of the distribution of random site energies</td>
<td>Disorder-induced localization</td>
</tr>
</tbody>
</table>
1.11.1 Bloch theory of Metal – Insulator transitions

The first class of transition considered in Table (1.1) is one that is encompassed within the Bloch or band theory framework for electronic states in crystalline solids. Band theory is a one-electron independent particle theory that assumes that there exists a set of stationary states available to any one electron and that all of the electrons are distributed among these states according to Fermi-Dirac statistics. The states $\psi_{nk}$ are given by the solutions of a Schrödinger equation $H\psi_{nk} = E_{nk}\psi_{nk}$ in which the Hamiltonian operator $H$ is given by the sum of electronic kinetic energy term $p^2 = \left(-\frac{\hbar^2}{2m}\right)\left(\frac{d^2}{dx^2}\right)$ and a crystal potential term $V(x)$, to account for the interaction of one electron with all other particles in the crystal. Since $V$ (and therefore $H$) is periodic in space with the translational periodicity of the crystal structure, $V(x + a) = V(x)$, where $a$ is the lattice constant.

In the Bloch (or more properly the Bloch-Peierls-Wilson) theory of electrons in crystals, a solid is an insulator if each band is either completely filled or completely empty and it is a metal if atleast one band is partly filled. At zero temperature, (which is often assumed for the purpose of making a perfectly sharp metal - insulator distinction), all states lying lower in energy than the Fermi energy $E_F$ are occupied by electrons, while all states lying higher than $E_F$ are empty. For a metal, the band structure and the number of electrons are such that $E_F$ lies within a band, which is only partly filled. For an insulator $E_F$ lies between the bands and there is an energy gap separating the highest lying valence band and the lowest lying empty conduction band. This is very clearly illustrated in Fig (1.7)
The type of metal-insulator (M-I) transition envisioned in the first row of Table (1.1), is illustrated by the schematic band structure shown in Fig. 1.7. A crystalline material, composed of atoms with even number of electrons, sufficient to populate an integral number of bands, close to the Fermi level either just overlap in energy or just miss overlapping. A small change in pressure or temperature may cause the crystal's band structure to cross over to the other situation. Such a band-overlap M-I transition occurs in Ytterbium, in which a variation in pressure produces a cross over between band structures of types 'a' and 'b'.

As indicated in Table (1.1), on the both the metallic and insulating side of the above type of transition, the electronic wave function in the vicinity of \( E_F \) correspond to 'extended' states. Such wave functions have appreciable amplitude throughout the solid. For a crystal, the Bloch functions have the form as in Fig 1.8. The solid line in the figure represents the real and imaginary part of \( \psi \), while the
dashed line indicates the plane-wave envelope corresponding to the wave vector eigen value $\kappa$. For amorphous solids, $\kappa$ is not a good quantum number, since the validity of Bloch-function depends upon the presence of crystalline long-range order. Long-range order is totally absent in amorphous solids and this is an obvious way in which band theory breaks down for amorphous solids.

Fig. 1.8: A Bloch type extended wave function as in a crystal

Before proceeding to the discussion of disorder-induced localization and the Anderson transition, it is useful to introduce the concepts involved in another type of M-I transition, contributed to condensed matter physics by Sir Nevill Mott. The Mott transition [144, 145] is philosophically and physically related to Anderson transition. Philosophically both transitions are dramatic demonstrations of situations in which the conventional theory (Bloch functions, band structures etc) used for electrons breaks down. Band theory, often successful in explaining the electrical and optical properties of crystalline solids fails completely in these situations.
1.11.2 The Mott transition

The Mott transition illuminates a regime in which the one electron or independent particle theory of solids fails, within a crystalline material. In quantum mechanical calculations for electronic states in a crystal, standard procedure is to assume that the atomic nuclei are fixed in position on the sites of a crystalline lattice. But suppose we set $a'$ at a very large value, then in the independent particle theory, as the translational periodicity is retained, the one electron solutions are still Bloch functions, the highest band is only half filled and the material is still predicted to be a metal. But this is not true as we are dealing with a set of isolated atoms and the true solutions must be just the atomic solutions. The above argument shows that the band theory fails in the atomic limit $a' \to \infty$ for a system with a half-filled highest band.

The physical reason for this failure is disclosed with the aid of Fig. 1.9. There are two electronic configurations that in the independent electron picture, have the same potential energy. In configuration 'b' of Fig. 1.9, two of the outermost or valence electrons have been shifted from their positions in 'a' to translationally equivalent positions in another unit cell. Because of the translational periodicity of the crystal potential $V(r)$ which approximates the average interaction of each electron with all of the other $10^{24}$ charged particles in the solid, configurations 'a' and 'b' have the same potential energy in the independent particle picture. This is manifestly unreasonable as configuration 'b' has a substantially higher energy than 'a' because of the repulsive Coulomb interaction among the valence electrons. This energy cost associated with the electronic crowding in 'b', is
a 'many body effect' that is left out of the independent particle picture of one electron theory.

![Diagram](image)

**Fig. 1.9:** Two electronic configurations within a four-unit cell region of a crystal

One electron theory is therefore unable to discriminate against configuration as (b), since it does not perceive their extra energy vis-à-vis configurations such as in (a). In a real solid, however, the electrons definitely do tend to correlate their movements in order to avoid such energetically unfavourable mutual proximity as in Fig (1.9a). The amount by which band theory overestimates the ground state energy of the system because of this neglect of electron correlations is called the correlation energy. The point embodied by the Mott transition concept is that the correlation energy can under certain conditions cause a solid to have an insulating ground state when the neglect of correlation band picture would erroneously predict it to be a metal. Such a solid is called a Mott Insulator. An example is NiS$_2$ and the condition required for its occurrence is described in Fig. 1.10.
In this figure, the atoms are represented by potential wells and single valence electron of each atom occupies, in the isolated atom limit, a bound state energy level that is indicated on each atomic well by a horizontal line. In the crystal, the level gives rise to an energy band of band width $B$. Relative to the energy level of free atom, the crystal band extends in energy from roughly $-B/2$ to $+B/2$. This lowering in energy relative to the free atom is responsible for metallic cohesion. It arises from a lowering of kinetic energy that is achieved by the delocalization of the electrons into extended states in the crystal. Delocalization smooths the wave function oscillations and thus reduces the $\nabla^2$ kinetic energy contribution to the total energy. This energy lowering is relatively ineffective when there is little overlap between orbitals on neighbouring atoms. $B$ thus decreases with increasing lattice constant $a$, as suggested by Fig. 1.10 and the bandwidth vanishes in the $a \to \infty$ limit.
In figures 1.10(a) and 1.10(b), single horizontal line at each well denotes the energy level of the valence electron of the isolated atom. This energy level is doubly degenerate and this view neglects the $e^2/r_{12}$ interaction. In the case when two electrons occupy the same site, repulsive interaction dominates and raises the energy and this occupation number dependent feature introduced by $e^2/r_{12}$. It is represented by an equivalent two-level diagram shown in Fig. 1.10(c). Two levels are associated with each site. The lower level, which corresponds to the level used in (a) and (b) is available to the first electron to occupy the atom. The upper level exists only when the lower level is filled and is lifted by the amount $U$ and is available to the second electron to occupy the site. Hence the delocalized wave functions and the failure of electrons to maximally avoid each other, introduces an average potential energy cost per electron of $U/4$. Since the average kinetic energy incentive for band formation is $B/4$, it follows that the correlation cost exceeds the delocalization gain if $U > B$. This is the condition for the occurrence of a Mott insulator, i.e., $U > B$ represents the criterion for correlation induced localization.

If this inequality criterion is satisfied, then electrons are localized. Unlike the Bloch type of metal-insulator transition (in which extended states apply to both sides), the Mott transition is a delocalization-localization transition for electron states. It occurs as implied in a→b, when a change in interatomic separation causes a cross over in the relative importance of the two characteristic energies of the valence electron system the bandwidth $B$ and the electron-electron correlation energy $U$. The Mott transition is an exemplary embodiment of a recurrent theme in condensed matter physics. Electron localization in the low density limit signals the triumph of potential energy over kinetic energy in that regime. The kinetic energy
cost of localization becomes negligible in comparison to the coulomb interaction and the electrons from a lattice to maximally avoid each other in order to minimize the totally dominant potential energy.

1.11.3 Disorder induced localization-Anderson transition

The type of metal insulator transition that is most relevant to amorphous solids is the Anderson transition. Here the insulating side of the transition corresponds not to extended states in filled bands as in a Bloch type transition in crystals, but instead to electron states which are localized. The meaning of localized states is indicated in Fig. 1.11. The wave function is concentrated near a centre composed of just few atoms and has negligible amplitude elsewhere in the solid. Away from the small regions that contain essentially all of its integrated possibility \( \int |\psi|^2 \, dr \), the amplitude spatially decays away with distance. This behaviour is schematically shown by the dashed line wave functions envelope in Fig. 1.11, and falls off as \( e^{-\alpha R} \) at large distances \( R \) from the localization centre. The quantity \( \alpha \) is an important parameter for a given localized state known as inverse localization length.

In crystalline solids, localized states are often introduced by chemical impurities. An illustration of Anderson transition is shown in Fig. 1.12. As in the case of the Mott and Wigner transitions, electron localization in the Anderson transition reflects the passage to a regime in which the potential energy pins over the kinetic energy, while the \( a \leftrightarrow b \) delocalization-localization transition in Mott case of Fig. 1.10 occurs via the kinetic energy considerations with decreasing band width at low densities. In the Anderson case of Fig. 1.12 it occurs via the superposition of disorder-induced potential energy of sufficient depth.
Fig. 1.11: Schematic representation of a localized wave function as in amorphous solids

Fig. 1.12: One electron tight binding picture for the Anderson transition
Here the potential wells representing the atomic sites are no longer all the same. Instead, the well depths vary from sites in a random way. Such a disordered potential is present in an amorphous solid. Instead of single well depth as in a crystalline case, there is a distribution of well depths. $W$ denotes the width of this distribution, which specifies the energy range of the disorder-induced spatial fluctuations of the potential energy seen by an electron at the atomic site.

The competition between kinetic energy and potential energy influences on the electron states now resides on the ratio $W/B$; $W$ the magnitude of the random potential and $B$, the crystal bandwidth in the absence of disorder are the two relevant characteristic energies. Anderson showed that when the dimensionless parameter $W/B$ is sufficiently large, all of the states in the valence band are localized. i.e., $W > B$ denotes the disorder-induced localization.

Anderson's model is a quantum mechanical calculation that invokes a tight binding independent electron picture, which corresponds to Fig (1.12b). Unlike the Mott insulator, in which the extended states predicted by an independent electron picture are overturned when electron-electron correlation is introduced, Anderson localization appears as a consequence of disorder in a purely independent electron picture.

The notion of disorder-induced localization was subsequently extended by Mott and others [146, 147]. When the disorder is great enough for $W/B$ to satisfy the Anderson's criterion, all of the states in the band become localized. Mott pointed out that even for smaller degrees of disorder, states in the tails of the band are localized as in Fig. 1.13 and the energies for which states are localized (the shaded regions) correspond to the tails of top of the valence band and bottom of the conduction band.
Within each band, the states are extended. As shown in Fig. 1.13(b), the demarcation energies separating regions of localized and extended states are referred to as mobility edges. The Anderson transition then refers to a localization→delocalization transition in which a change in composition, pressure, applied electric field etc. pushes the Fermi level through such a mobility edge. The energy separation between the mobility edges of Fig. 1.13(b) is called the mobility gap [148]. It plays a role, with respect to the electrical properties of amorphous semiconductors that is similar to the role played by the energy gap in a crystalline semiconductor.

![Schematic density of states diagram for a crystalline and amorphous materials](image)

Fig. 1.13: Schematic density of states diagram for a crystalline and amorphous materials
Even these models couldn’t successfully explain the M-I transition phenomena found in mixed valence perovskites. Based on the strong electron-phonon coupling in these materials, Mills [149] et al., proposed that the M-I transition involves a cross over from a high-\( T \) polaron dominated magnetically disordered regime to a low-\( T \) metallic magnetically ordered regime. Now, some authors have concluded that M-I transition in CMR materials is the Anderson transition - a quantum phase transition, driven by magnetic order, because quantum localization effect plays an important role in the system around and above the magnetic transition.

### 1.12 Review of experiments

In the first study of mixed valence perovskites, van Santen and Jonker [129] and Jonker [150] have reported resistivity measurements on ceramic samples of \((\text{La}_1-x\text{A}_x)\,\text{MnO}_3\) (A= Ba, Ca or Sr), as a function of temperature and composition. Their main result was the striking correlation between the magnitude of the resistivity and the magnetic state of the compounds. Outside the ferromagnetic concentration range, resistivities are high and thermally activated, but a resistance anomaly appears around \( T_c \) for the ferromagnetic compositions, where there is a transition to metallic like conductivity.

When Volger [131] discovered the large negative magneto resistance effect near \( T_c \) in 1954, he showed it to be isotropic-independent of the relative orientation of the current and the field and frequency dependent. He also made the first measurements of Hall effect, thermopower and specific heat. The single crystal magnetoresistance measurements reported 15 years later for the \((\text{La}_{1-x}\text{Pb}_x)\,\text{MnO}_3\)
system [134], showed the effect to be quite substantial, with a 20% decrease in resistivity at 310K in an applied field of 1T. Twenty more years elapsed before the effect was rediscovered, at a time of interest in using magnetoresistance in sensors operating at room temperature. The largest magnetoresistance for the manganites usually appears near $T_c$ that can be above room temperature for some compositions. Examples are La-Na or La-K with $x \approx 0.15$ [151-153]; La-Ba, La-Pb or La-Sr with $x \approx 0.3$. The resistivity peak temperature $T_{mn}$ almost coincides with $T_c$ for crystals with $x \approx 0.3$. The saturation magnetoresistance in the vicinity of $T_c$ is bounded by a drop in resistivity below $T_c$, which depends in turn on $T_c$ itself [154, 155].

Volger [131] in his first measurements of the Hall effect in $(La_{1-x}\text{Sr}_x)\text{MnO}_3$, obtained a very low value for mobility in the paramagnetic state. The Hall coefficient is negative and the deduced electron concentration contradicts thermopower measurements. In the ferromagnetic state, Volger reported that the extraordinary Hall effect is small and negative and the upper limit obtained for mobility is only $10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. Thirty years later, Tanaka et al. [156] reported Hall effect measurements on polycrystalline $(La_{0.8}\text{Ca}_{0.2})\text{MnO}_3$. Because of the smallness of the signals, only an upper limit on the mobility edge could be estimated as $7 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300K. A similar mobility was measured in a crystal of $(Nd_{0.5}\text{Pb}_{0.5})\text{MnO}_3$ near $T_c$ [157] and a carrier concentration of $5 \times 10^{26} \text{ m}^{-3}$ below 100K was deduced. Liu et al., [158] reported successful Hall effect measurements on single crystals of $La_{0.65}(\text{PbCa})_{0.35}\text{MnO}_3$ at 5K where the resistivities were in the micro ohm-meter range. The inferred electron density is typically metallic with $n_{eff} \approx 10^{29} \text{ m}^{-3}$. The result is consistent with the density of states deduced from low temperature
heat capacity measurements that lead to a metallic density of states for a range of polycrystalline samples [158].

Measurement of the electric field induced by a temperature gradient across a sample provides complementary information to the resistivity. These have been many measurements of the thermopower ($S$) of samples with $x \approx 0.3$, which exhibit a metal-insulator transition [131, 159, 167]. There is strong magnetic field dependence of $S$ in the vicinity of $T_c$, which demonstrates that carriers are magnetic in character. When a large positive anomaly is observed around $T_c$, the thermopower is reduced by the field [159, 165, 168]. At higher temperatures, when the thermopower has become negative, the effect of the field is to reduce its absolute value [162]. Well above $T_c$, the magnetic field has little effect on $S$, and it is thought that transport is due to hopping and dielectric polarons [164].

The pressure dependence of $S$ has been measured by Zhou and co-workers [164, 169], who found that the large positive bump across $T_c$ is reduced in magnitude as the Curie temperature is increased by pressure. Thermopower measurements were carried out across the entire composition range for $(La_{1-x}Sr_x)\,MnO_3$ [131], $(La_{1-x}Ca_x)\,MnO_3$ [170] and $(Pr_{1-x}Ca_x)\,MnO_3$ [171] series. The Seebeck coefficient of $Nd_{0.5}(Sr. Pb)_{0.5}MnO_3$ is negative for $T > 100K$ [165]. Likewise those of $(La_{1-x}Ca_x)\,MnO_3$ and $(La_{1-x}Sr_x)\,MnO_3$ become negative for $x > 0.25$ [172-174]. Cation deficient $(LaMn)_{1-x}O_3$ shows a positive thermopower at all temperatures, indicating that the holes are produced by cation deficiency [166, 175].
1.13 Variation of thermal conductivity and heat capacity during an M-I transition.

1.13.1 Heat capacity

The heat capacity of several ferromagnetic manganite compositions with $x \approx 0.3$ have been measured at low temperature [176-178]. There are also low temperature data on $(La_{1-x}Sr_x)MnO_3$ [176] for $0 \leq x \leq 0.3$ and nonstoichiometric $LaMnO_3$ [179] as well as data as $(La_{1-x}Ca_x)MnO_3$ for $T > 50K$ [180] and $(La_{0.8}Ca_{0.2})MnO_3$ for $T > 100 K$ [181]. In compounds of magnetic rare earths, the low temperature specific heat is dominated by single ion excitations of the rare earth.

By fitting low temperature data on $x \approx 0.3$ compositions of a non magnetic rare earth to just an electronic and a lattice term, of the form,

$$C = \gamma T + \beta T^3,$$

Coey and co-workers [182] deduced $\gamma = 5-8 \text{ mJ mol}^{-1}\text{K}^{-2}$ which corresponds to a density of carriers at Fermilevel $N(E_F) = \frac{3\gamma}{\pi k_B^2}$ of about $4 \times 10^{21} \text{ m}^{-3} \text{ eV}^{-1}$.

This is a relatively high value for a metal, but the value of $\gamma$ is uncorrelated with the residual resistivity $\rho_0$ that varies by several orders of magnitude in these compounds.

The low temperature heat capacity of the stoichiometric $LaMnO_3$ and end member has been fitted with $T^{-2}$, $T^0$ and $T^3$ terms, with the latter being ascribed to two-dimensional ferromagnetic magnons. A comparison of the two cation deficient $(LaMn)_{1-x}O_3$ samples, one ferromagnetic and other antiferromagnetic, shows an unexpectedly large heat capacity at low temperatures in both cases. $\gamma$ is $> 20 \text{ mJ}$
for both cases, which has been ascribed to a high density of localized states below the mobility edge [179].

Heat capacity anomalies have been observed in the vicinity of the Curie temperatures for (La$_{1-x}$Ca$_x$)MnO$_3$ system, where a typical lambda anomaly is observed or $x \approx 0.33$ [180,181]. The associated entropy of $0.4R \ln 2$ per mole is attributed to the spin disorder entropy contribution due to charge localization above $T_c$ [180]. Heat capacity anomalies appear at the two-phase transition in samples with $x \geq 0.5$, one of which is associated with charge order and also at the $O \rightarrow O'$ structural transition [181,182].

1.13.2 Thermal conductivity

It has been reported that like the electrical conductivity, the thermal conductivity $K$ exhibits an anomaly in the vicinity of $T_c$ that can be modified by applied field [183]. It increases by 30% in 6T at 265K. An unusual positive temperature coefficient $dK/dT > 0$ above $T_c$ is associated with scattering from large dynamic lattice distortions accompanying charge transport near $T_c$ in the insulating phase. Thermal diffusivity has been measured in (La$_{0.65}$Ca$_{0.33}$)MnO$_3$ [184], where there is a broad dip near $T_c$ related to $K$ and the magnetic part of the specific heat.

Chen et al. [185] measured the magnetothermal conductivity behaviour of polycrystalline (La$_{0.8}$Ca$_{0.2}$)MnO$_3$. The temperature dependence of the thermal conductivity displays a striking dip, while the resistivity and the thermopower have a peak near 240 K. The temperature and field dependences of the thermal conductivity are attributed to the scattering of phonons by spin fluctuations.
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