CHAPTER I - INTRODUCTION
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1. Dielectrics:

Major part of the present day research in solid state is devoted to the defect structure of solids, as this may provide a way to synthesise the apparently different fields of investigation such as luminescence, electrets, conductivity, dielectric behaviour, etc. (1-19). Prior to Heaviside (1928) the subject of ionic or electrolytic conductivity in solids was considered only a descriptive study, but now it can properly be regarded as an integral part of the subject of imperfections in crystals (20, 21). Similarly according to Maxwell's theory, a dielectric could neither sustain a persistent polarisation nor persistent surface or space charges. But in practice charges are found in the dielectrics and polarisation is out of phase with the field (22). The question of spontaneous polarisation is also a current problem and is related to the pyroelectric, piezoelectric and ferroelectric properties of the substance (23-27). As a result, investigation of the problem of charge storage and persistent polarisation in solid state, has interesting possibilities regarding the theories of dielectric behaviour and structure.

2. Definitions:

(a) Dielectric and Semiconductor. Dielectric is an insulator which under
the influence of an electric field exhibits only a charge

displacement whereas a semiconductor has an intrinsic conductivity

in the range $\sim 10^2$ to $10^9$ mhos/cm. However, the distinction

between an insulator and a semiconductor is more of a quantitative

nature according to the concepts of the modern theory of solids

(28). Addition of an appropriate impurity to an insulator can

make it behave like a semiconductor showing what is known as

impurity conductivity — a phenomenon which is becoming

increasingly important in recent years.

(b) Polarisation of Dielectrics. A dielectric is said to

be polarised if the

centroids of the negative and positive charge distribution in it

do not coincide. An external applied field might affect the

separation,

(i) by attracting electrons and nuclei in the opposite
direction,

(ii) by attracting negative and positive ions,

or (iii) by aligning the molecules having permanent dipole

moment.

These are known as electronic polarisation,

ionic polarisation and polarisation due to dipole orientation

respectively.

Static charges on a dielectric can be produced

without an external electric field as well. In addition to the

well known contact electrification these may be produced by phase
change. Reversible currents are produced during the orderly solidification and melting of dielectrics — an effect known as "Thermoelectric effect". A separation of charges takes place at the phase boundary depending on the rate processes. This leads to frozen-in space charge and production of macroscopic space charge field (29, 30).

(c) Electrets. An electrical analogue of a magnet, i.e. a dielectric body with a permanent dielectric volume polarisation, was termed an "Electret" by O. Heaviside (31). Various workers have since defined electret in different ways (32). However, the definition due to Robillard as "a dielectric which can give rise to a sensibly permanent external electric field" appears to be fairly appropriate (33).

Electrets may further be subdivided depending on the physical agency which produces polarisation in a dielectric under the influence of an external electric field. Thus we have thermoelectrets (34), photoelectrets (35, 36), radioelectrets (37) etc. Two exceptions to above classification are (i) electrolelectrets (38) obtained from ceramics under the influence of electric field only, and (ii) magnetoelectrets (39) obtained from carnauba wax at an elevated temperature under the influence of a magnetic field.

(d) Homo and Heterocharge. A charge on the electret of
the same sign as the polarity of the adjacent electrode was
called by Gemant as a homocharge, while that of sign opposite
to the polarity of the forming electrode, a heterocharge (40).

3. Certain properties of electrets:

The experimental investigation of electrets
has mainly been confined to the study of the nature of the
charge developed, its magnitude and life.

Nature of charge:

It was generally believed that only polar
dielectrics are capable of exhibiting permanent electrification
(40). This view had to be modified after the successful
attempts of a number of workers in making electrets from a
variety of nonpolar substances, such as naphthalene (41),
sulphur (42) and ceramics (43). Now it is generally
believed that any dielectric under suitable conditions is
capable of being transformed into an electret (44).

Mikola classified dielectrics into two
categories depending on whether they are capable of producing
only heterocharge or both hetero and homocharges (45). The
initial charge is invariably hetero (32) though in some cases
initial homocharge is also reported (46). Further, dielectrics
exhibiting heterocharge have a comparatively higher
conductivity (45).
A characteristic of the thermoelectret state is the variation of charge as a function of polarising field. It was found that if the polarising field is below 10 kV/cm, the thermoelectrets acquire only a heterocharge and if the polarising field is considerably higher a homocharge is obtained. At intermediate field intensities the initial heterocharge decays within a few days and a steady homocharge appears on the surface (46). If the field is fixed, it was found that the nature of the charge depends on the polarising voltage (47).

The electrification of a true electret is a volume effect as distinct from that of other electrified bodies which acquire surface charges only (34). This volume aspect of the thermoelectret state as suggested initially by Eguchi, has since been confirmed (48). Volume distribution of charge as a function of polarising field has also been studied. Thus it was found that when the polarising fields were less than 10 kV/cm, the volume distribution represented a heterocharge and negative charge occupied more than half the volume. Whereas for polarising fields greater than 10 kV/cm, the volume distribution represented a homocharge narrowly concentrated near the electrodes (46).

Electret lifetime:

Suitably prepared and properly preserved electrets show an appreciable permanence of polarisation (40, 49).
Thus in the absence of short circuiting of the two electrodes of an electret, the charge was found to decay very rapidly. Short circuiting of electrodes even after a lapse of time effects a recovery of charge (50). The short circuiting decreases the internal field of the electret which is responsible for the rapid decay. The motion of free charges under the action of the internal field causes the depolarisation (51, 52).

An anomalous stability was found in some inorganic thermoelectret crystals. In such cases the life time was found to be independent of the condition of storage. The explanation that a thin film of moisture short circuits the electrets in such cases is not considered to be very convincing (53, 54).

Another parameter which affects the life time is humidity (32). The charge can, however, be recovered on drying, if the humidity is less than 80%. If this limit is exceeded irreversible change in the magnitude of the charge takes place probably due to the penetration of moisture into the fissures which are formed inside the electrets (55).

Electrification of Electrets:

Surface charges ranging from 4 e.s.u/cm² to 10 e.s.u/cm² have been reported by various workers (40, 46, 56). An electric field upto 20,000 V/cm. on the surface of the electret has been reported. The field was
found to decrease exponentially with the distance from the surface (57, 58).

Other properties of Electrets:

Depolarisation of an electret occurs on its remelting and this is accompanied by a displacement current in the external circuit. It was found that the discharge current \( i \) depends only on the electret charge \( \sigma \), the temperature \( T \) at which the electret is depolarised and the rate of change of temperature with time. It is independent of the time that has elapsed between the polarisation and refusion (loc. cit.). The temperature of complete depolarisation, however, depends on the temperature at which the polarisation began originally (51, 59, 60). By heating electrets, a discharge of the order of \( 10^{-3} \) amp/cm\(^2\) is caused at a temperature equal to half the melting point. Eguchi has shown that the electrification of the electret is destroyed by X-ray irradiation. However, it reappears progressively after the irradiation has been stopped.

Piezoelectric effect has also been reported by Adams (50), but a number of later workers failed to find this property in thermoelectrets (40, 61, 62). They have accounted for the effect on the basis of the change in capacitance. However, a clear sign of piezoelectric effect was reported by Gubkin in ceramic electrets (63).
Thermoelectrets are reported to have an anomalously high thermal conductivity along the direction of polarisation, probably due to the oriented dipole molecules. Groetzinger is of the opinion that a change in thermal conductivity is more typical of thermoelectrets than their external or internal fields (64). Depolarisation of thermoelectrets by A.C. field and ultrasonics is also reported (51, 32). Simultaneous application of constant and alternating electric fields were found to give remarkably stable thermoelectrets (65). The value reported for permittivity and loss angle are however conflicting. Thus some workers found no change in the value of $\varepsilon$ (43, 66, 67) whereas an increase as large as three times is also reported (68, 69).

4. Electrical Conductivity

As has been already pointed out, the difference between an insulator and a semiconductor is quantitative rather than qualitative. Thus at absolute zero a pure and perfect crystal of any semiconductor would behave as an insulator. The semiconducting properties are invariably brought out by thermal agitation, lattice defects or impurities. The conductivity exhibited by a highly purified substance is called "intrinsic conductivity" as distinguished from "impurity conductivity" which depends on the impurity content to a very large extent. The temperature range in which electrical properties of a semiconductor
are not much influenced by the impurity content is known as "intrinsic temperature range".

The electrical properties of solids are now mostly explained on the basis of an energy band model (70). According to this model the forbidden zone between the normally filled valence band and normally unoccupied conduction band is too large for the electron to make a jump at room temperature in insulators, whereas in semiconductors the phonon interaction is sufficient for such a transition to take place. The electron, now in the conduction band and the vacancy left behind in valence band known as "hole", will both contribute to conductivity. Then at a particular temperature it will depend on the concentration and mobility of these two types of carriers. A variation of the type $\exp(-E/kT)$ with temperature may also be expected, where $E$ is known as the "activation energy" and comes out to be half of the band gap as the Fermi level normally lies midway in the forbidden gap. Defects of the Frenkel (71) and Schottky (72) type in crystals give rise to localised levels in forbidden zones. The population of these defects and their mobility also contribute to the conductivity. Addition of impurities also introduce localised levels (73). These lie either immediately below the conduction band or just above the valence band depending on the nature of the impurity added. The levels below the conduction band are normally empty and are known
as "donor levels", whereas those above the valence band are normally occupied and are known as "acceptor levels". The amount of impurity added determines the density of charge carriers and this impurity conductivity is not much affected by temperature beyond a certain point.

A plot of \( \log \sigma \) against \( 1/T \) is generally a superposition of the above two phenomena (74). In case two straight lines are observed with a knee in such a plot, the high temperature line corresponds to intrinsic conductivity while the low temperature one below the knee is the structure sensitive part.

5. Theories of Thermoelectrets:

Various theories of the thermoelectret state have been attempted to explain the following two basic properties:

(i) Stability of homocharge,
and (ii) Transition from hetero to homocharge.

Adams, explaining the electret effect on the basis of the pyroelectric phenomenon, assumed that the orientation of dipoles with long relaxation time is responsible for the heterocharge while the homocharge is due to free charges held in position by the internal field. Then a slow change in internal polarisation will lead to the charge reversal (50). However, the initial polarisation needed to account for the magnitude of the observed charge, if the theory is correct, cannot be attained even if all the dipoles in the dielectric were aligned (32). As a result, though it was generally accepted that the dipole
orientation was necessary (52, 61, 75), the appropriate mechanism could not be that proposed by Adams.

Gemant considered heterocharge to be purely an ionic effect while the homocharge a piezo-electric effect produced as a result of transverse stresses in the oriented dipoles (40). However, it was found that the magnitude of homocharge is independent of the stresses frozen in the electret, thus contradicting this hypothesis (46, 76, 77). But the explanation for heterocharge appears to have been confirmed experimentally (46). Attempts to explain homocharge on the basis of contact electrification were also not successful (61).

Thiessen, Winkel and Herrmann proposed two different mechanisms of thermoelectret formation. They classified the polarisation as internal and external (46). The heterocharge is supposed to be due to internal polarisation resulting from ion displacement while the homocharge is due to the breakdown of air gap between the electrode and dielectric surface. The charge reversal is then the result of a superposition of the two effects.

Gross further developed this idea (49, 59, 60, 78, 79). According to him the heterocharge is due to all processes of charge absorption in a dielectric while the breakdown at the interface of dielectric and electrodes is responsible for the homocharge. The gradual decay of internal polarisation then leads to charge reversal as the surface charges received from the electrodes are kept in
their position on account of the field due to internal polarisation. The subsequent charge decay of the electret is determined by both internal and external polarisation. This was confirmed by the observations of Wiseman and Linden on electrets of polyvinyl acetate (80).

Gemant took into account three processes to explain the thermoelectret effect (81). According to him ion displacement and dipole orientation are responsible for heterocharge while homocharge results from the corona discharge between the dielectric and electrode. The charge reversal is explained by the neutralization of displaced ions under the action of dipole field, while the long life time results from the stability of dipole orientation. This stability might even lead to a formation of domain like groups. Thus dipole orientation is an important feature of Gemant's theory.

The explanation on the basis of the above three processes was considered satisfactory till Baldus reported the formation of electrets from napthalene which is a nonpolar substance (41). Subsequently a number of workers have reported electret effect, in a variety of nonpolar materials (43). Baldus explanation of the effect as due to "freezing-in" of induced dipoles produced by the polarising field was not considered to be very likely.

Gerson and Rohrbaugh considered the hypothesis of
dipole orientation as the basis of heterocharge to be incorrect (67). Their observation was based on the reported electret effect in non-polar substances and also on lack of change of permittivity in polarised carnauba wax. Drawing a parallel between photo-electret and thermo-electret effects they believed an electron mechanism, i.e., a localisation of electrons in deep traps to be responsible for heterocharge (82). Working on their suggestion of preparing the electret without heating, under the influence of X-rays Belyaev and others studied some properties of naphthalene thermoolectrets thus prepared and found heterocharge to be due to electron localisation (83).

To sum up, Gross's explanation of homochaarge appears to be quite adequate but the heterocharge in thermoelectrets can not be explained simply by dipole orientation and ion displacement. Though dipole orientation is possible in principle, evidence of trapping of electrons in deep traps is also there. In such cases there is an intimate relationship between thermoelectret and photoelectret states. Thus the heterocharge formation remains to be explained satisfactorily.

6. **Statement of the Problem**

In view of what has been said in the foregoing paragraph the necessity of further investigations, to test the validity of the alternative idea of electron trapping
in deep traps, is evident. Inorganic crystalline substances or mixture of organic and inorganic materials appear to be quite promising in this respect. Trapping is known to be of fundamental importance in the case of electronically active inorganic crystalline substances. The mixture of organic and inorganic materials have also been tried by Herman and Minne (84).

Investigations on electret and associated effects are being carried out in our laboratories since 1953. However, it was confined to conventional waxes, known mixtures of waxes and rosins and plastics till recently (85-91). The interesting possibilities of mixture of organic and inorganic substances has led to a beginning in this direction (92). "Camel Sealing Wax", selected for the present study is known to be such a mixture.

Sealing waxes have a varied composition. In the present investigations before starting the conductivity measurements and the study of electret state, the constituents of Camel Sealing Wax No. 5 were determined by X-ray diffraction technique as the composition of this commercial product was not known. The powder pattern was recorded and 'd' values were calculated. From these the constituents were identified and 'hkl' values assigned.

Significant changes in the dielectric properties of solids are usually reported in the region of melting.
Hence an investigation was carried out to determine this region. The softening point of sealing wax was found to be in the neighbourhood of 60 °C and the melting point approximately at 75 °C. As the sample has no sharp melting point, a temperature range of 50 °C - 80 °C was chosen and all further investigations were confined to this temperature range.

Structural changes in a dielectric usually lead to a variation in its conductivity. For example, an alteration in structure can be postulated from the appearance of a discontinuity in the conductivity temperature curve (loc. cit.). Similarly the density of centres of surface recombination, the energy levels and capture probability of electron or hole by the centres can be determined by studying the variation of conductivity with field (93).

Conductivity in the present case, was studied as a function of (i) thickness and (ii) temperature, with the help of an ultrameter capable of measuring a current up to \(10^{-15}\) amp. The thickness of the sample (1 cm²) was varied from 0.1 mm. to 1.0 mm. in steps of 0.1 mm. and from 1.0 mm. to 2.0 mm. in steps of 0.2 mm., the temperature range being 50 °C to 90 °C.

Voltage-current curves exhibited an approximate linear relationship only on a log-log plot, indicating that some sort of power law is followed. The strength of linear
relationship was estimated by computing the correlation coefficient and power was calculated by the method of least squares. Activation energy was calculated from the semilog plot of conductivity and inverse temperature.

Three series of electrets were prepared by varying,

(i) thickness from 0.1 mm. to 1.0 mm. in steps of 0.1 mm.
(ii) temperature from 50 °C to 80 °C.
and (iii) polarising field from 0 kV/cm. to 9 kV/cm. in steps of 0.9 kV/cm.

The method developed in this laboratory was followed for preparing these electrets. Their decay mode was studied by measuring the surface charge with the help of Lindemann Electrometer every day for a period of one month.

Heterocharge in electrets is often associated with the orientation of crystallites with respect to field direction. In order to investigate this possibility X-ray diffraction patterns of some of the representative electrets were taken by the flat plate transmission technique. Two photographs were taken for each sample, one with the X-rays incident parallel and the other perpendicular to the polarising fields. The study was not pursued further as a visual estimate of intensity distribution of the patterns showed a complete absence of any type of orientation whatsoever.

In the end, an attempt is made to correlate the composition of sealing wax with its conductivity and electret forming property.
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