

Chapter - 1

INTRODUCTION

1.1 General Introduction

Extensive research devoted to the physics of semiconductors has led to a more complete understanding of the physics of solids in general. The semiconducting properties of the elements of the fourth group of the periodic system germanium and silicon have been the object of intensive study since the mid-Forties and this resulted in discovery of the transistor. It should be remembered however that the first observation of negative temperature coefficient of resistance, a recognizable semiconductor property, was made on a I-VI compound Ag_2S by Faraday in 1839. Since then it was realized that the III-VI compounds such as ZnS and the I-VII compounds such as CuI also possess semiconducting properties. Thus it is to be noted that the III-V compounds which have now become next in importance to silicon are relatively newcomers in that their semiconducting properties were predicted on the basis of the periodic table by Welker as recently as 1952.

The III-VI compounds In_2Te_3 and Ga_2Te_3 , whose preparation and properties are the object of study in this thesis, have been considered to be intermediate between the III-V and III-VI compounds. However there are significant differences because of the presence of stoichiometric vacancies in the cation sub-lattice. This imbues these compounds with special properties such as radiation stability which are responsible for their applications in particle detectors.

In 1926 Grimm and Sommerfeld⁽¹⁾ formulated a rule stating that all compounds which crystallize with diamond or zincblende structures are related to diamond, not only in respect to tetrahedral coordination, but also in their characteristic chemical binding. Each of the electrons on a given atom forms a covalent bond with one of the electrons in a neighbouring atom. These bonds having a saturated character do not contribute to the electrical conductivity even when the atoms in the lattice are not chemically identical. Hence the compounds exhibit semiconducting behaviour. An electric current is only possible when the bonds are broken by some type of defect or disturbance. This can occur either as a result of thermal excitation of the lattice, or as a result of an incorporated defect which alters the "integral combining proportions of the electrons". In 1960 Hooser and Pearson⁽²⁾ formulated a criterion for the formation of semiconducting bonds in a solid, known also as the $A^m B^{8-N}$ rule. This states that saturated covalent bonds occur when the number of s and p valence electrons in elements A and B add upto 8.

As one proceeds from the group IV elements which were the first to be prepared as high quality single crystals, to the III-V and II-VI compounds, new properties become available for study and exploitation. The availability of a large number of compounds with a wide variety of band gaps and band structures enabled the discovery of new phenomena

and also the development of novel devices depending on larger and sometimes direct energy gaps (as required for LED and heterojunction lasers) or high mobilities (such as Hall effect, photoelectromagnetic (PEM) and magnetoresistance devices) which cannot be made from elementary semiconductors. Some completely new devices like those based on the Gunn effect also became possible. Much of the progress has been made possible by significant advances in material preparation techniques.

II-VI compounds provide a wide variety of band gaps. ZnS and CdS for example are large band gap semiconductors used for their luminescent properties. But these materials though studied earlier are more difficult to grow in the form of large high quality crystals because of their high vapour pressure. Many of them occur with only one type of conductivity e.g. ZnS, CdS and ZnSe are only n type while ZnTe occurs only as p type. Hence homojunction formation is not possible. Further carrier mobilities are also low. Most III-V semiconductors on the other hand can be grown from the melt, have high carrier mobilities and can be doped both n-and p-type (exceptions are large band-gap materials such as AlN, GaN). These properties have given greater technological importance to III-V compounds as a new group of semiconductors with GaAs, InP and GaP occupying positions next only to silicon.

A natural extension in the search for new semiconductors is to examine III-VI compounds exhibiting diamond-like or tetrahedral coordination. The III-VI binary compounds with cation A = Al, Ga or In and anion B = S, Se or Te generally have one of the two chemical formulae AB or A₂B₃. While the AB compounds crystallize in layer structures, the A₂B₃ compounds occur in several phases having different structures as shown in Table 1.1.1.

Table 1.1.1

Compound	Al ₂ S ₃		Ga ₂ S ₃		Ga ₂ Se ₃	Ga ₂ Te ₃	In ₂ S ₃		In ₂ Se ₃	In ₂ Te ₃	
		(α)	(β)				(α)	(β)		(α)	(β)
Structure	Wurtzite	Zincblende	Wurtzite	Zincblende	Zincblende	Zincblende	NaCl	Spinel	h.c.p. (r.t)	Zincblende	Zincblende

A₂^{III}B₃^{VI} compounds may be considered to be intermediate between the II-VI and III-V compounds. Their semiconducting nature is maintained during melting, in contrast to the structurally related elements (Ge, Si) and A^{III}B^V compounds. This is because of the substantially greater degree of ionic character of their chemical bonds which preserves short range order on melting.

The heteropolar or ionic nature of the binding of the compounds can be demonstrated by studies of cleavage planes.

Whereas diamond cleaves along (111) planes, the cleavage plane for the zincblende lattice is (110). The difference in cleavage is due to the fact that diamond is purely homopolar whereas the compounds contain a heteropolar component in the binding. When two parts of a crystal are displaced relative to a (110) lattice plane, the coulomb repulsion of neighbouring like-charged ions reduce the energy required for cleavage. On the other hand, the ions on opposite sides of a (111) plane always have opposite sign and attract one another strongly.

Several $A_2^{III}B_3^{VI}$ compounds such as Ga_2S_3 , Ga_2Se_3 , Ga_2Te_3 , In_2Te_3 have tetrahedral bonding. They completely satisfy chemical valencies but have one-third of the cation sites vacant. Hence they may be termed defect semiconductors. On the average there are 2.66 neighbouring A atoms for each B atom, while each A atom is surrounded by 4 B atoms. Tetrahedral positions of the atoms and the valence angles close to 109° are characteristic of chemical bonds formed by electrons in the state of sp^3 -hybridization.

The electron states of free A and B atoms and a possible scheme of bond formation in A_2B_3 are shown in fig. 1.1.1. The arrows denote conventional direction of spins; dashed arrows indicate possible electron transfer; continuous straight lines indicate chemical bonds. Each free B atom has 6 valence electrons; 2 s-electrons and 2 p-electrons are paired, while 2 other p-electrons have

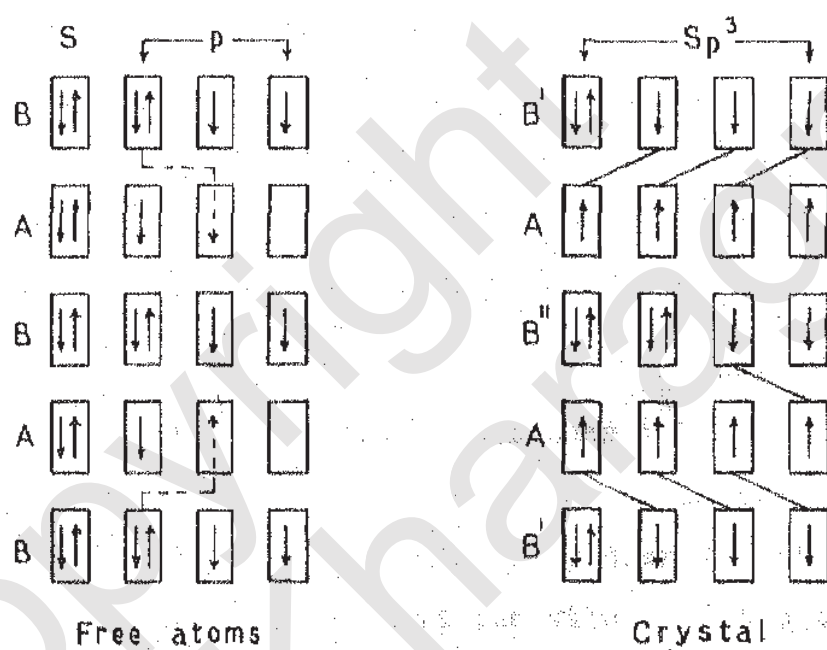


Fig. 1.1.1 Possible scheme of bond formation in A_2B_3 compound

parallel spin. The ground state of In valence electrons is s^2p .

When an A_2B_3 crystal is formed, two B atoms transfer one electron to two A-atoms. In this way each A-atom has now 4 electrons which may be in the sp^3 -hybridization state and may form bonds with the unpaired B-electrons. All the B-electrons, both paired and unpaired, are also in the state of sp^3 -hybridization. In an isolated atom the sp^3 -state is energetically higher than the pure s- and p-states. Bond formation in a crystal lowers the energy of the system and the sp^3 -states become energetically favored.

It is naturally expected that such a high ($\sim 10^{21} \text{ cm}^{-3}$) concentration of stoichiometric vacancies in the lattice will have an effect on the physical properties of the compound. One example is that the values of the carrier mobilities have been reported to be considerably smaller than in the neighbouring compounds in the isoelectronic series because of carrier scattering by these neutral cation vacancies⁽³⁾. The presence of the large number of stoichiometric vacancies in the lattice leads to a strong tailing of the band edges. In fact their absorption spectra did not reveal a sharp fundamental absorption edge⁽⁴⁾ nor did the reflection spectra show sharp reflection peaks.

These compounds, particularly In_2Te_3 and Ga_2Te_3 have recently become of interest as radiation-stable semiconductors^(5,6) which can be used as high energy neutron and gamma radiation detectors. This application obviously depends on the high mass numbers of the elements resulting in high stopping power and large atomic displacement energies. Their relatively high band-gaps ~ 1.0 eV compared with their isoelectronic neighbours such as InSb and GaSb permit the preparation of high resistivity materials which can be used as detectors without cooling. In fact it has been shown that the optimum band-gap for semiconductor particle detectors is 1.0 eV since this provides low background currents and at the same time high carrier multiplication ratio. The high density of cation vacancies already present in the structure and the low activation energies for atomic diffusion are responsible for their high radiation stability.

Amorphous Ga_2Te_3 has been shown to exhibit hopping conduction. Both $\text{a-In}_2\text{Te}_3$ and $\text{a-Ga}_2\text{Te}_3$ have also attracted attention demonstrating both threshold switching and memory effect in the sample^(7,8) with the possibility of future applications.

However as the following review will show the fundamental properties of In_2Te_3 and Ga_2Te_3 have not been subject

to nearly the same intensive investigation as the III-V and III-VI compounds. There was contradictory evidence about the nature of the band-gap; plasmon energies were unknown and hence calculations of high frequency dielectric constant had not been carried out. Although photoconductivity in In_2Te_3 had been reported, there was no indication of the role of native defects. Even the variation of carrier mobility with temperature, which provides information about scattering mechanisms had not been examined in detail. These were some of the questions that motivated the present investigations on β - In_2Te_3 and Ga_2Te_3 single crystals and about which some information and understanding was sought.

1.2 A review of the Earlier Work

In_2Te_3 and Ga_2Te_3 are $\text{A}_2\text{B}_3^{\text{III-VI}}$ semiconducting compounds with band-gaps approximately equal to 1.1 eV. The sign of Hall effect and thermoelectric power in α - In_2Te_3 and Ga_2Te_3 indicated n-type conduction for these compounds; corresponding measurements carried out on β - In_2Te_3 indicated p-type conductivity. It is worth noting that the cation sublattices of α - In_2Te_3 and Ga_2Te_3 are ordered and the corresponding sublattice in β - In_2Te_3 is disordered. The change in the sign of the majority carriers could be due to reduction in the mobility of electrons resulting from disorder in the cation sublattice. Tables 1.2.1 and

1.2.2 give at a glance the important physical and chemical properties of the compounds.

Table 1.2.1

Physical Properties of In_2Te_3 and Ga_2Te_3

	Space Group	Density gn/c.c.	Lattice Parameter in Å	E_g (eV) (300°K)	E_g (eV) (0°K)	dE_g/dt $\times 10^{-4}$ eV/ °K	m_e^*	Thermal Expansion $\times 10^{-6}$ /°K	Thermal conductivity Watts/cm ² °K
In_2Te_3	$\bar{F}43m$	5.79(α)	13.54(α) ⁽⁹⁾	1.1 ⁽³⁾	1.2 ⁽¹¹⁾	(-1.0-5.5) ⁽¹²⁾	0.7 ⁽³⁾	(9.0 \pm 0.5) ⁽¹³⁾ (77 °K)	0.014 ⁽¹³⁾
	$\bar{F}43m$	5.73(β)	6.150(β) ⁽¹⁰⁾					(9.2 \pm 0.2) (300 °K)	
Ga_2Te_3	$\bar{F}43m$	5.75	5.899 ⁽¹⁴⁾	1.15 ⁽¹³⁾	1.55 ⁽¹⁵⁾	(-4.8-7.7) ⁽¹²⁾		(9.2 \pm 0.3) ⁽¹³⁾ (77 °K) (8.3 \pm 0.3) (300 °K)	0.013 ⁽¹³⁾

Table 1.2.2

Chemical properties of In_2Te_3 and Ga_2Te_3 *

	Mol. wt.	M.P. in °K	Heat of formation in K cal.mol ⁻¹		Entropy S_{298}^0 cal K ⁻¹ mol ⁻¹	G_p in cal K ⁻¹ mol ⁻¹	Nature
			H_f^{298}	H_f^{944}			
In_2Te_3	612.44	944	-45.8 \pm 1	19.5 \pm 0.2	56.0 \pm 4	22.7 \pm 44.5 $\times 10^{-2}$ \times	black, hard & brittle
Ga_2Te_3	522.24	1063	-65.7 \pm 5	-	51.6 \pm 4	-	black, hard & brittle.

* Ref. (16)

1.2.1 Indium Telluride (In_2Te_3)

Structure :

In_2Te_3 has a zincblende f.c.c. structure with one-third of its cation sites vacant. The phase diagram (fig. 1.2.1) of In-Te system shows that In_2Te_3 has two phases, a high temperature disordered β -phase which transforms reversibly at $(617 \pm 10)^\circ\text{C}$ to a low temperature α -phase. Inuzuka and Sugaike⁽⁹⁾ obtained α - In_2Te_3 by slowly cooling the material while Hahn and Klinger⁽¹⁰⁾ obtained the disordered β -phase by quenching the material from the 617°C . X-ray diffraction studies for β - In_2Te_3 showed diffuse scattering at places where the superstructure spots of α - In_2Te_3 are expected. This indicates that at the transformation temperature a short-range ordered arrangement of vacancies probably prevails and the crystal exists in a "transition" state. The experimental and theoretical reasonings of Bleris et al.⁽¹⁷⁾ indicated that the state at the transformation temperature is actually a transition state, lying between the states of complete randomization of the vacancies and that of long range order which is stable at low temperature.

According to Hahn⁽¹⁰⁾ and Zaslavskii⁽¹⁸⁾, β - In_2Te_3 has a f.c.c. cell with $a_0 = 6.158 \text{ \AA}$. The space group is $F\bar{4}3m$. The α - In_2Te_3 superstructure has been studied by

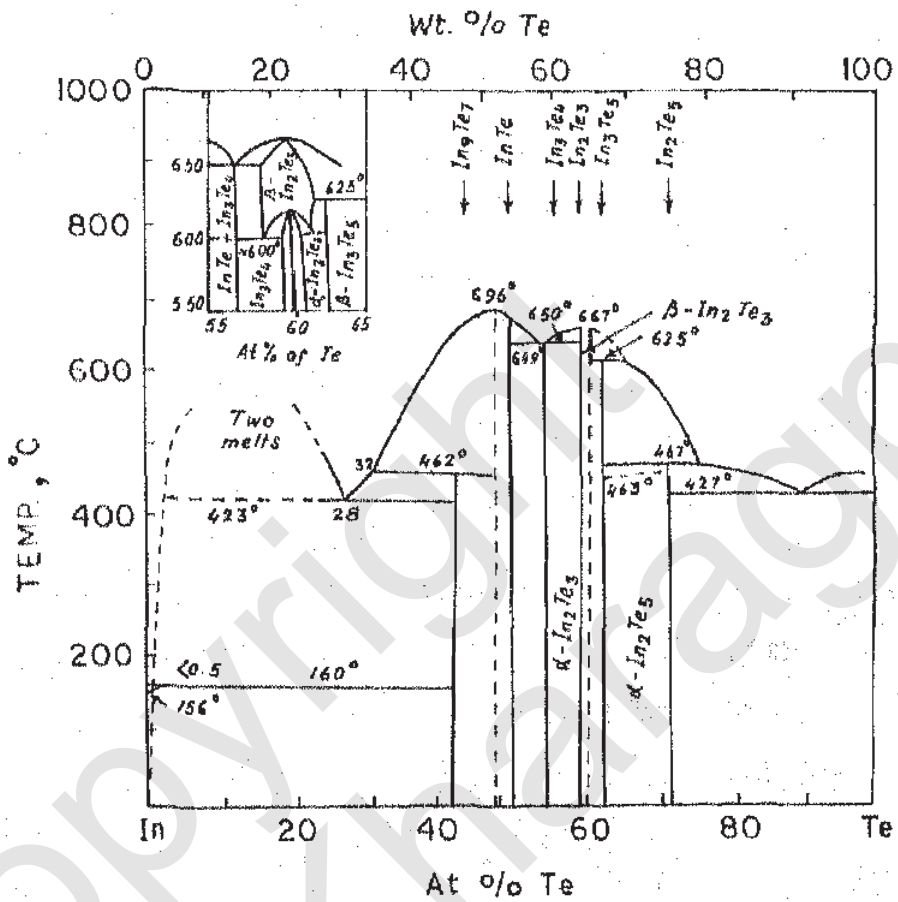


Fig. 1.2.1 Phase diagram of In-Te system

x-ray methods by different workers but the published results are contradictory. Inuzuka and Sugaike⁽⁹⁾ studied a single crystal of α - In_2Te_3 and established that it has a cubic f.c.c. cell with $a = 18.40 \text{ \AA}$. The parameter of such a unit cell is approximately $3a_0$. A possible space group is $F\bar{4}3m$. The indexing of the powder diagrams of the α -form on Inuzuka and Sugaike cell had shown that for all the reflections in question, at least one of the hkl indices was divisible by three. This has suggested to Woolley et al⁽¹⁹⁾ that there was a reduction in the symmetry of the ordered modification compared with β - In_2Te_3 . The same powder patterns established two distinct unit cells and space groups : (1) a b.c.c. unit with $a = a_0 \sqrt{2}$, $b = 3 a_0 \sqrt{2}$ and $c = a_0$, space group $I\bar{4}m2$ and (2) a tetragonal b.c.c. unit with $a = 3a_0$, $c = a_0$ and the space group $I4mm$.

This data was not in agreement with the results on single crystals by Inuzuka⁽⁹⁾ and Zaslavskii⁽¹⁸⁾. In order to remove the contradictions, Woolley et al⁽¹⁹⁾ proposed a domain structure for the α -form. According to this hypothesis, there are domains in the ordered modification with orthorhombic or tetrahedral symmetry. These domains are regularly oriented along three mutually perpendicular directions. The result of spatial arrangement is the pseudocubic symmetry of α - In_2Te_3 .

Zaslavskii et al.⁽²⁰⁾ examined the structure of single crystals of α - In_2Te_3 by Laue, Weissenberg and rotation and oscillation techniques. The Laue diffraction pattern confirmed the cubic symmetry of the α -form of the crystal. The crystal class was found to be $m\bar{3}m$. The x-ray rotation and oscillation photograph demonstrated an f.c.c. unit cell with $a = 18.54 \text{ \AA}$. The Weissenberg photograph showed that all the reflections fitted an f.c.c. lattice. These results established the presence of this modification of a f.c.c. cell with $a = 3a_0$ and space group $Fm\bar{3}m$ as determined by Imuzuka⁽⁹⁾.

Thermal & Electrical Properties :

The presence of large number of stoichiometric vacancies ($5.7 \times 10^{21}/\text{cm}^3$ empty cation sites) in these semiconductors leads to disturbance of periodicity, vanishing of potential field at atomic sites and affects the physical properties of the compound. Woolley et al.⁽¹³⁾ found the thermal conduction of the lattice very small, only 1.4×10^{-2} watt/cm² °K over a temperature range 120°K to 400°K, considerably smaller than the corresponding III-V compounds for which lattice thermal conductivity is of the order of 10^{-1} watt/cm² °K. The electronic contribution is negligible. This suggests that thermal conduction is due to lattice vibrations and is limited by the high concentration of defects.

Zuze et al⁽³⁾ found electron mobility at room temperature for In_2Te_3 to be anomalously small, only $10\text{-}45 \text{ cm}^2/\text{V}\cdot\text{sec}$. Efforts to dope the crystal using elements such as Cu, Hg, Cd, Zn, Sn, Ge, Hg, Si, Sb did not result in any impurity conduction even at high dopant concentrations, probably because impurity atoms localised at neutral stoichiometric vacancies and remained unionised. The electrical conduction determined by Zuze et al⁽³⁾ as a function of the impurity concentration and temperature showed that in spite of the high impurity concentrations incorporated, the conduction process was intrinsic and the scattering due to ionized impurities was of little importance.

Koshkin et al⁽²¹⁾ attributed these observations to the chemically inert nature of unshared electron pairs surrounding impurity atoms located at vacancies. Drabkin et al⁽²²⁾ related this hypothesis on the basis that atomization of a metal requires an energy of the order of the heat of evaporation and if the metal atoms did not interact chemically with their environment, the neutral state would be energetically unfavourable. According to this view, the metal impurity atoms occupy stoichiometric vacancies, are not in a neutral state but have a characteristic valency. The presence of the same impurity in various charge states results in the stabilisation of the Fermi level.

Kuze et al.⁽³⁾ obtained the width of the band gap of α - In_2Te_3 from the plot of $\log RT^{3/2}$ vs. $\frac{1}{T}$ to be equal to $1.12 \pm .005$ eV. They reported that the band gap during α - β transformation, found by measurement of Hall emf and electrical conductivity with temperature, did not undergo any observable change. They also obtained $m_n \approx m_p \approx m_0$ ($m_n = 0.7 m_0$, $m_p = 1.1 m_0$) and $\mu_n \approx \mu_p$.

Kuze et al.⁽²³⁾ later found that the electrical conductivity of In_2Te_3 increased discontinuously by a factor of 17 to 20 at the melting point but above 550°C the activation energy was again 1.0 eV. The large activation energy for electrical conduction in the liquid state indicated that In_2Te_3 remains a semiconductor in this state. The similarity between the activation energies for intrinsic conduction in the solid and in the liquid state strongly suggests that there is no fundamental change in short-range order and type of chemical bond during melting because of the partly ionic nature of In_2Te_3 . This is in contrast with group IV semiconductor Ge which undergoes a change in coordination number on melting.

The above workers⁽²³⁾ reported that, with increasing temperature, the thermo-electric power retained a negative sign the same as that of electrical conductivity, but rapidly decreased in magnitude and changed its sign near the melting point to positive (hole conduction). The value

of TEI in molten In_2Te_3 was between $(20-40) \times 10^{-6} \text{ V/}^\circ\text{K}$ and depended only weakly on temperature.

The pressure dependence of conductivity has been studied by Averkin et al⁽²⁴⁾ who reported that the conductivity of polycrystalline In_2Te_3 , showing intrinsic behaviour at first, decreased with increase in pressure, passed through a minimum at pressure $P_{\sigma_{\min}} \approx 1500 \text{ kg/cm}^2$ and then increased with a further increase in hydrostatic pressure. As the temperature increased, the value of $P_{\sigma_{\min}}$ shifted in the direction of high pressure. The width of forbidden band did not change much due to pressure. The thermoelectric power was negative corresponding to electronic conduction and increased with increasing pressure. At $P_{\sigma_{\min}}$, the thermo-emf was zero and with further increase in pressure it changed sign and became positive.

Optical Properties

Gasson et al⁽²⁵⁾ investigated the optical properties of ordered and disordered In_2Te_3 using diffuse reflection spectra and found the energy gaps to be 1.12 and 1.04 eV respectively. The energy gap of disordered In_2Te_3 obtained from transmission spectra was 1.02 eV. Transmission measurements on ordered single crystals gave values for the energy gap varying from 1.04 eV for samples 1.36 mm thick to 1.14 eV for samples 6.3 μm thick. The variation

with thickness was probably due to masking of the long wavelength part of the absorption edge by some disordered material or impurity.

The observation of Zuze et al⁽³⁾ on macro-crystalline samples showed the transition to be an indirect type with forbidden energy gap for α - $\text{In}_2\text{Te}_3 = 1.026$ eV and β - $\text{In}_2\text{Te}_3 = 1.020$ eV. Koshkin et al⁽²⁶⁾ however showed the transition at the absorption edge to be of the direct allowed type with band gap value equal to 1.11 eV.

Recently a calculation was carried out by Guizzetti et al⁽²⁷⁾ based on the empirical pseudopotential method where the cation vacancy disorder was handled via the virtual crystal approximation (VCA). According to this In_2Te_3 has a direct band gap at the Γ point of the Brillouin zone with band gap energy 1.3 eV.

Anan'ina et al⁽²⁸⁾ measured photoconductivity of single crystal In_2Te_3 in the temperature range 100K-300K and found the magnitude to decrease with temperature. A study of transient behaviour showed a fast decay which had a relaxation time $\tau_f \approx 0.7 \mu$ sec at 100-300 °K and a slow decay with time-constant τ_s varying from 760 to 100 μ sec in the temperature range 120-290 °K.