
Chapter V
D.C. electrical resistivity

CHAPTER V

D.C. ELECTRICAL RESISTIVITY OF $\text{NiAl}_x\text{Fe}_{1-x}\text{O}_2$ SYSTEM

5.1 INTRODUCTION

Many physical and chemical properties of solids can be understood from the measurements of electrical conductivity. The information of interest for an empirical analysis of conduction process is the density and mobility of charge carriers as a function of temperature and the types of energy level which the carriers occupy.

The room temperature of some ferrites exceeds 10^{10} ohm . cm, that they can be regarded practically as insulators. For oxides which contain a substantial concentration of metal ions, in two different valence states, on crystallographically equivalent sites, require relatively small activation energies and this is reflected in low resistivities.

The spin alignment and electrical conduction relationship can be inferred from comparison of conductivity versus temperature studies observed below the Neel temperature. With high temperature paramagnetic region, the spontaneous magnetisation does not affect the electrical transport properties for many oxides. Certain oxides exhibit a marked change in the slope of the $\log \rho$ versus $1/T$ relationship, where as

Fe_3O_4 undergoes a semiconductor to metal transition (3). The anomaly observed in the conductivity near the magnetic transformation results to lower resistivity.

In high resistivity oxides a very small change in activation energy takes place near the magnetic transformation temperature. In certain cases negative results have also been reported for some materials (5).

The electrical conductivity is given by the product of charge and mobility of all the ions in a unit volume. The significant contribution to electrical conductivity below the melting point is due to the transport of electrons. The allowed energy states for such electrons are grouped into bands separated by forbidden energy regions. Electrons in partially filled energy bands acquire energy from an externally applied electric field and thus contribute to the conductivity.

Magnetic oxides are technological important because of their high specific resistivity and consequent absence of eddy currents. The room temperature resistivity of high magnitude may be achieved using many ferrites and garnets and hexaferrites.

5.2 CONDUCTION IN FERRITES

Ferrites belong to a class of semiconductors having the resistivity of 10^{-2} Ohm.Cm to 10^{11} Ohm . Cm at room temperature (6). The low conductivity in ferrites is associated with the simultaneous presence of ferrous and ferric ions usually on octahedral sites. Van Uitert (7) resistivities of the order of 10^{11} Ohm .Cm of certain polycrystalline ferrites, whereas Smolenski et al (8) observed values of 10^{12} ohm. cm in a single crystal material.

A great deal of work about the mechanism of conduction was done by Verwey et al (9). The extra electron on Fe^{2+} ion requires very small amount of energy to move towards adjacent Fe^{3+} ion. The valence states of the two ions get interchanged under the influence of an electrical field. These extra electrons can be considered to constitute the conduction current.

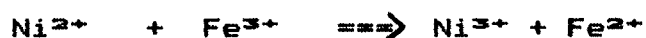
Ferrites being semiconducting in nature, their resistivity decreases with increasing temperature according to the relation

$$\rho = \rho_0 \exp (- \Delta E/kT) \quad \dots \quad 5.1$$

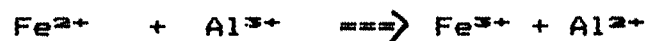
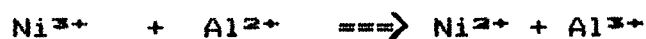
where ΔE is known as the activation energy and can be interpreted as the energy required to cause the electron jump.

The variation of $\log \rho$ vs $1/T$ plots shows breaks in the curves at the transition temperatures corresponding temperature is called Curie temperature. The change in slopes is due to disordering of electron spin at that temperature. These breaks suggest that there is some predominant change in conduction mechanism due to magnetic phase transition. The high activation energy is associated with a high resistivity at room temperature. The dependence of resistivity on the stoichiometry was studied by van Uiter (11) and Jonker (12).

In stoichiometric Ni ferrites there is some tendency for valency changes, according to



both the Nickel and iron ions, having two different valencies, provided conductivity mechanisms. On the other hand the presence of Al makes the valency changes



Both the divalent iron and trivalent nickel will be suppressed. When Al ions are present in two valence states, these will be widely separated and thus division of electrons through the lattice will require considerable activation energy.

5.3 ELECTRON HOPPING AND POLARONS

An electron in a crystal lattice interacts through its electrical charge with the ions or atoms of the lattice to create a local deformation of the lattice. The deformation further follows the electron as it moves through the lattice. The combination of the electron together with its strain field is known as polaron.

The electrostatic interaction between a conduction electron or hole and nearby ions may result in a displacement of the ions and hence in polarization of surrounding region so that the carriers becomes situated at the centre of the polarization potential well. If this well is considered deep enough, the carrier may be trapped at a lattice site and its translation to a neighbouring site can be determined by thermal activation. This process has been considered as the hopping mechanism. Heikes and Johnston(15) have derived an expression for the mobility of a charge carrier during the hopping mechanism as

$$\mu = e^2 a^2 w_0 / kT \exp(-q/kT) \quad \dots 5.2$$

where a is the distance between nearest neighbour cations, w_0 is the frequency of vibration of crystal lattice, q is the activation energy.

With the development of polaron theory it has become evident that eqn. 5.2 represents a special case of much more complicated relationship between and the parameters of the ionic lattice.

The strength of the electron-lattice-interaction is measured by the coupling constant defined as

$$-\alpha = \frac{1}{2} \frac{\text{Deformation energy}}{h W_1}$$

Where W_1 is the longitudinal optical phonon frequency near zero wave vector.

Treat the term $1/2\alpha$ as the number of phonons which surround a slow-moving electron in a crystal. The energy of lattice vibration is quantised. This quantum of energy is called a Phonon in analogy with the photon corresponding to the electro-magnetic wave. The effective mass of the polaron is greater than the bare mass of the electron.

In reality for the calculation of the mobility a study of the spatial extent of the potential well is essential. If the potential well extends over many lattice units in the crystal, the excess charge can be considered to interact with a dielectric continuum. This particular model has been developed by Frohlich (16) in order to formulate the interaction Hamiltonian for the large polaron. For a small polaron the well is

being confined to a volume comparable to the ionic volume.

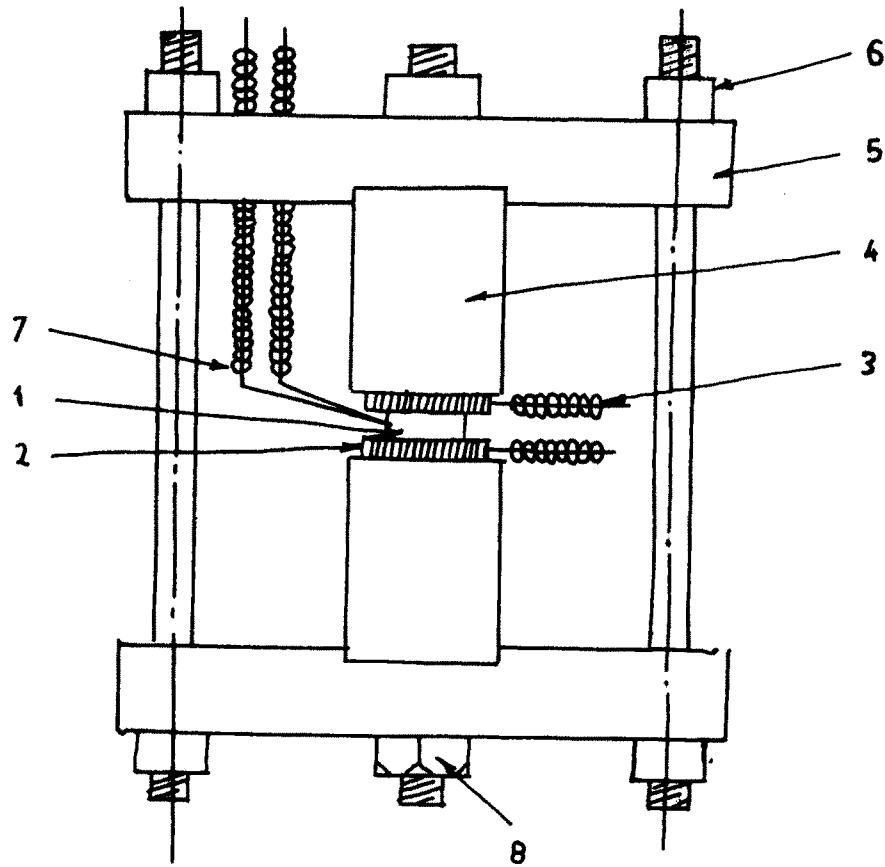
The real size of the polaron can be understood from a consideration of the free energy. Small polaron formation is favoured in solids which combine a large coupling constant with a narrow conduction band.

A small polaron is being considered to behave as a particle moving in a very narrow band at considerably low temperature. On the other hand, at higher temperature small polaron motion may result from the absorption of one or more phonons leading to the hopping mechanism. There is a strong experimental evidence for the existence of small polarons and for the hopping process (17,18).

5.4 EXPERIMENTAL

The experimental set up used for the measurement of d.c. electrical resistivity consists of electrically heated furnace, a digital d.c. micro-volt^{meter} (VMV 15), Temperature controlling arrangement and transistorised power supply unit (TPSU, type LVA 30/1) to provide the d.c. electric field.

Two probe method is used to measure the resistivity of the sample in the pellet form the experimental circuit diagram is shown in Fig. 5.2 and



- | | |
|--------------------------------------|---|
| 1 Ferrite specimen (pellet). | 5 Porcelain discs. |
| 2 Silver discs. | 6 Holding screws. |
| 3 Silver wires with porcelain beads. | 7 Chromel Alumel thermocouple. |
| 4 Brass cylinders. | 8 Screws holding the brass blocks to porcelain discs. |

Fig. 5.1 (C): THE CONDUCTIVITY CELL

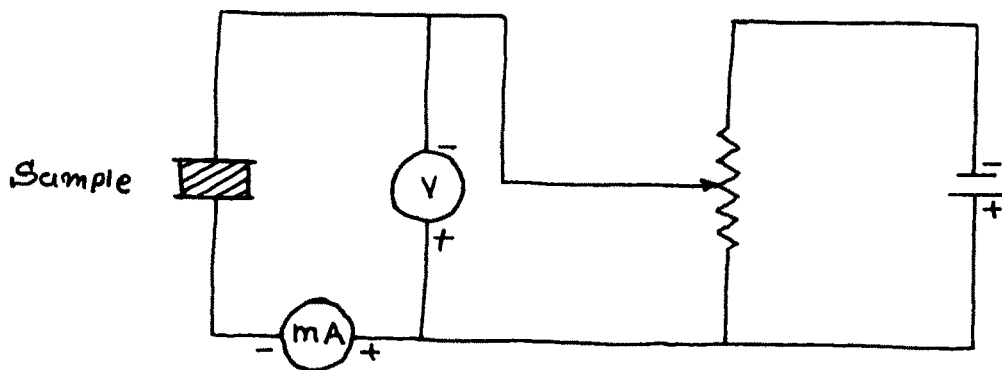
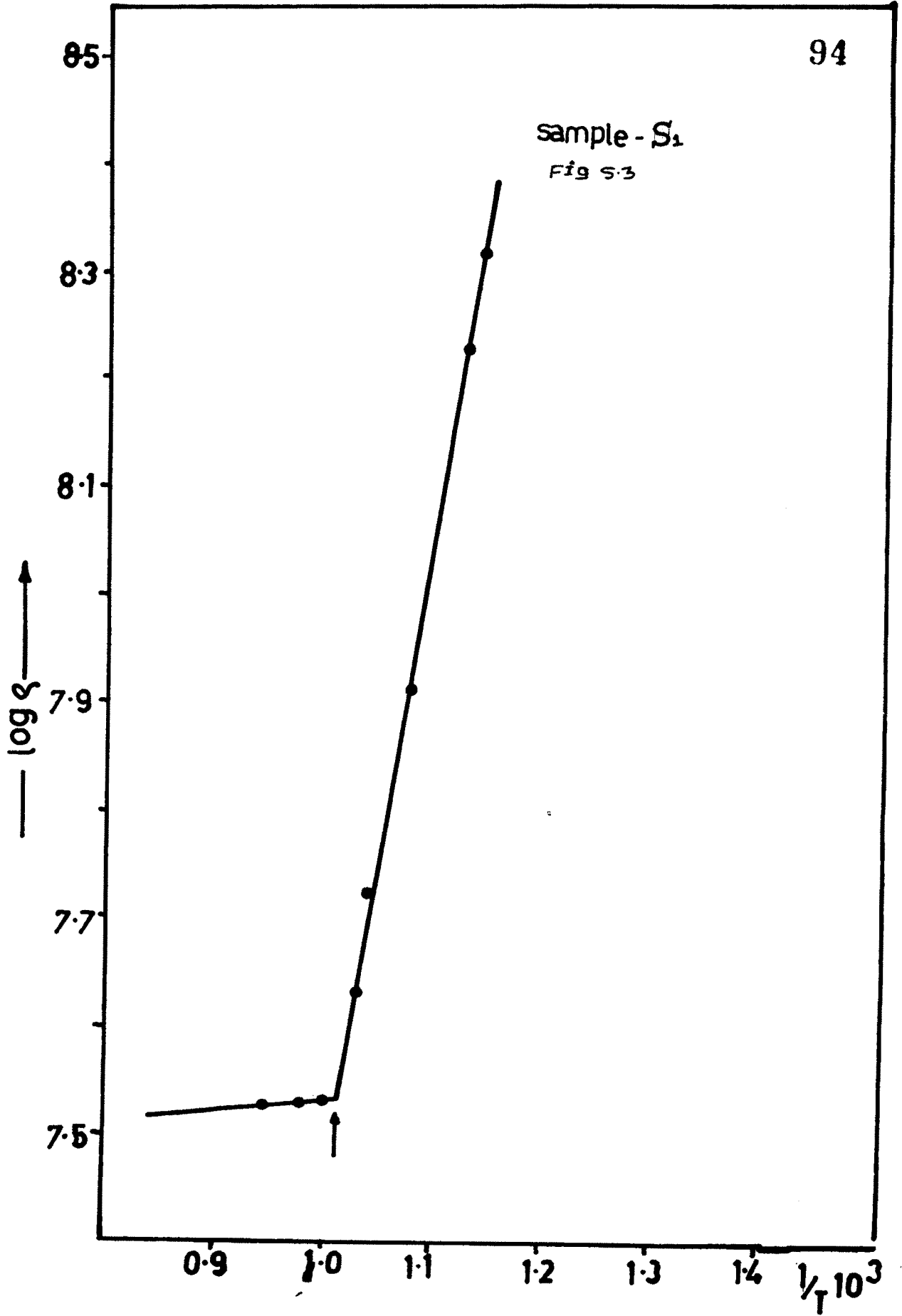
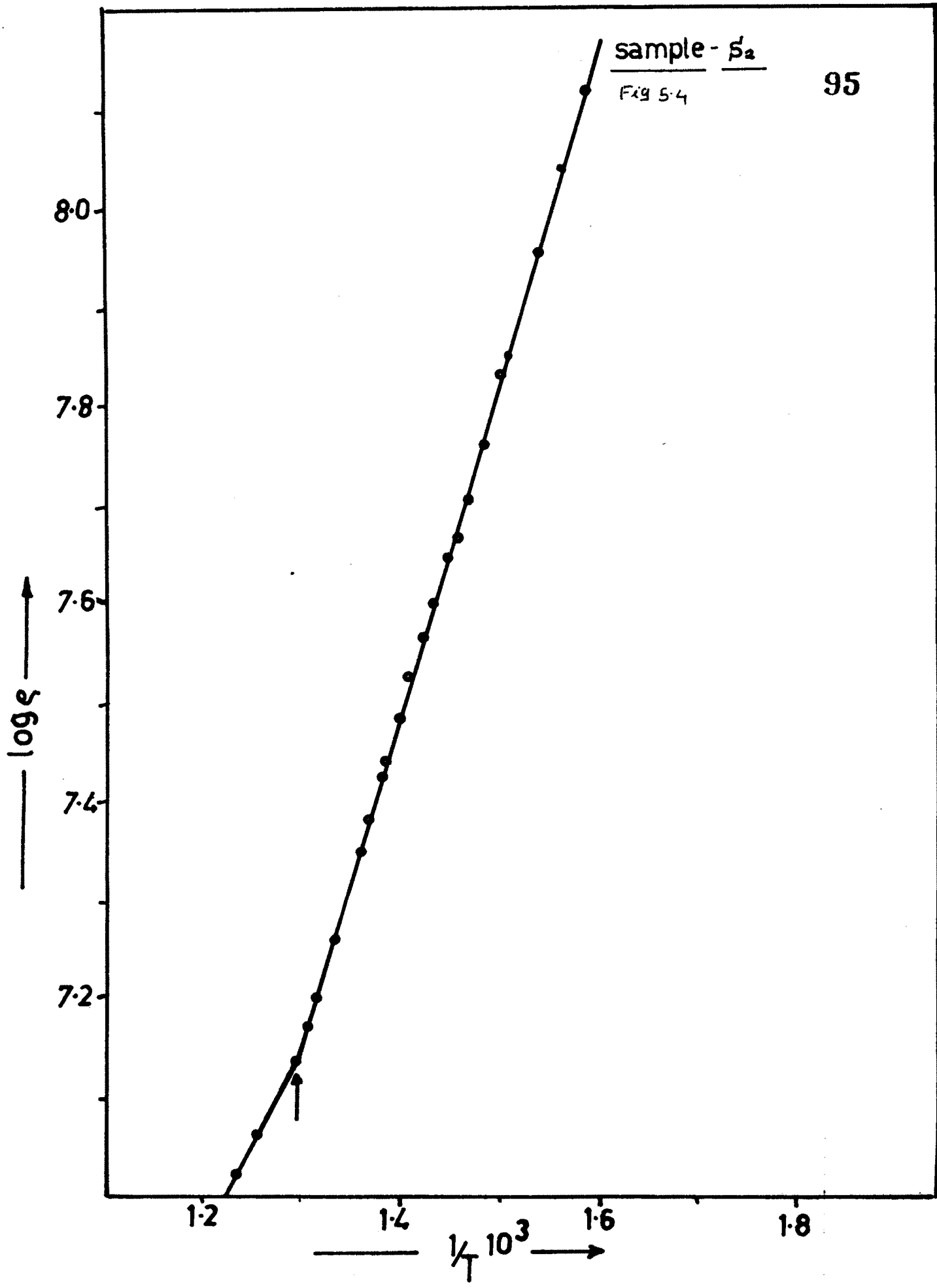


Fig. 5.2 (L): Circuit diagram for electrical resistivity and switching.

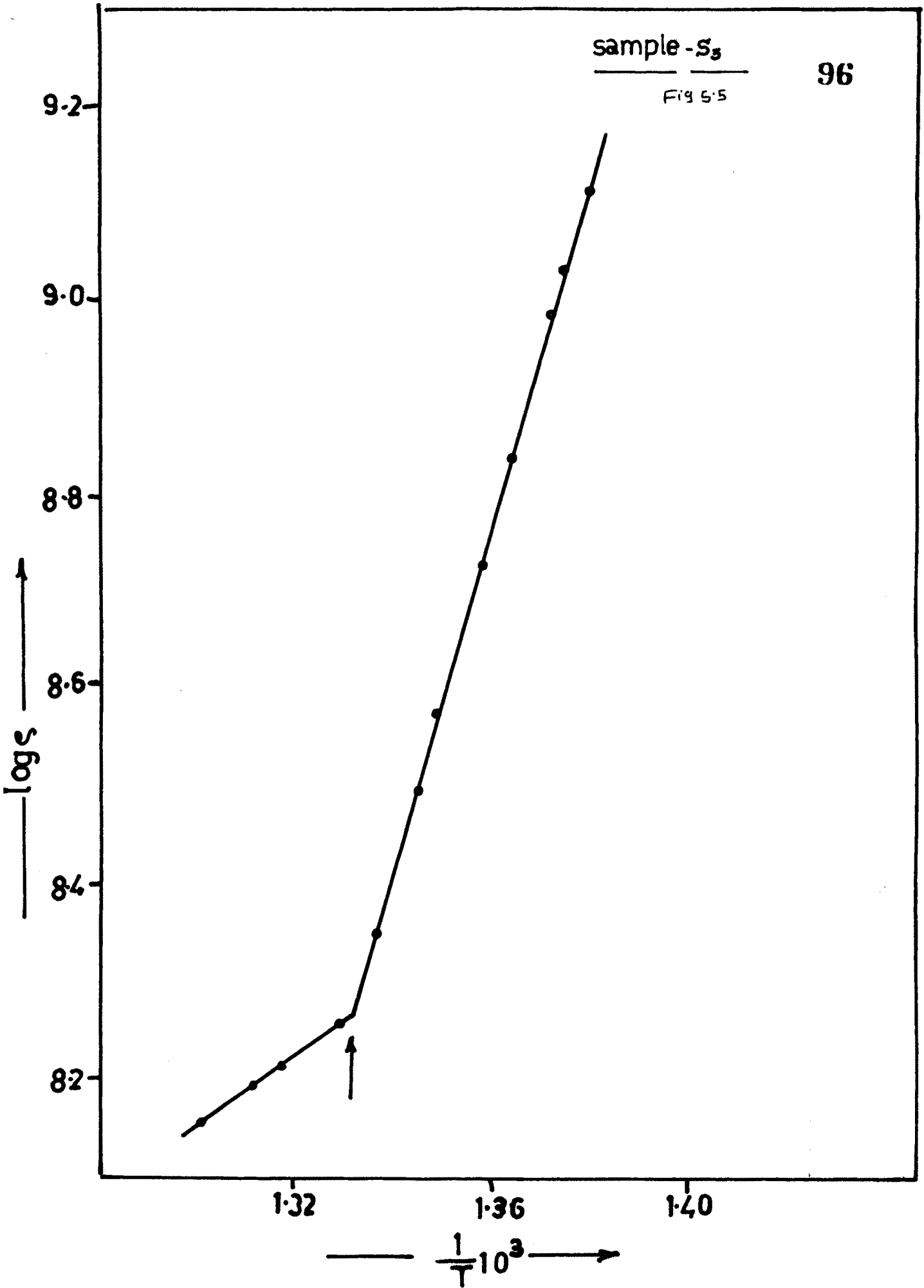




sample - S₃

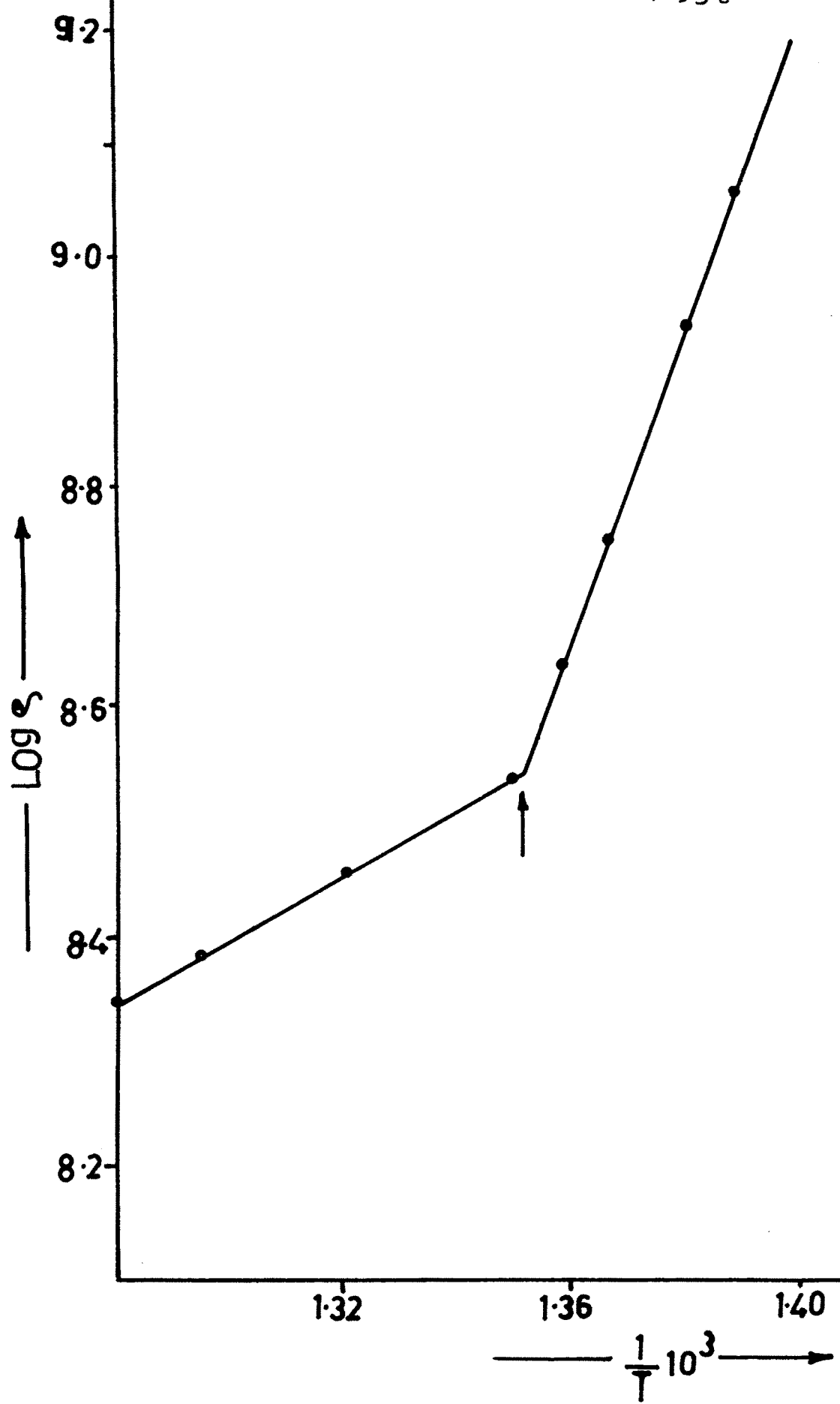
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FIG 5.5



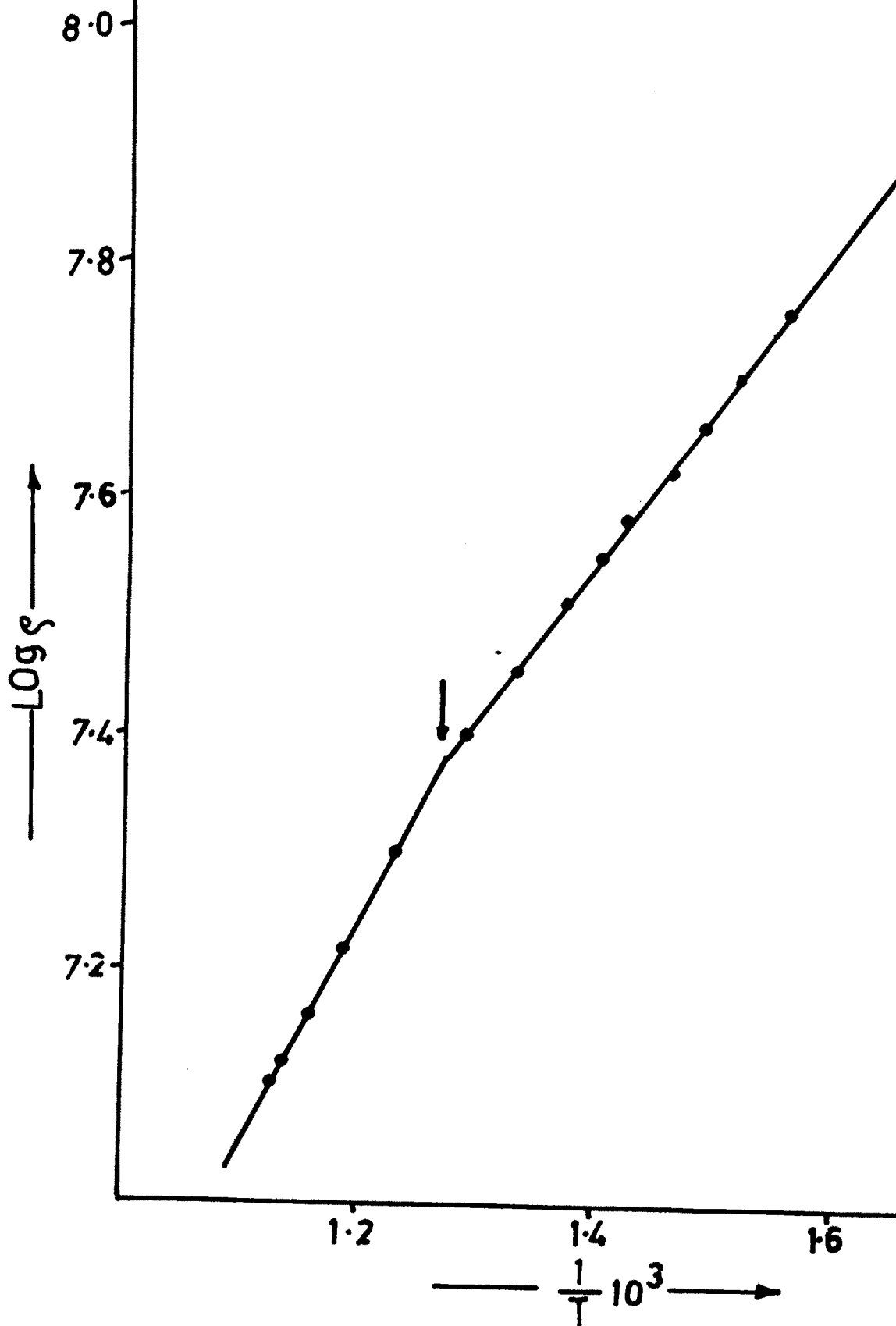
sample - S₄
Fig 5.6

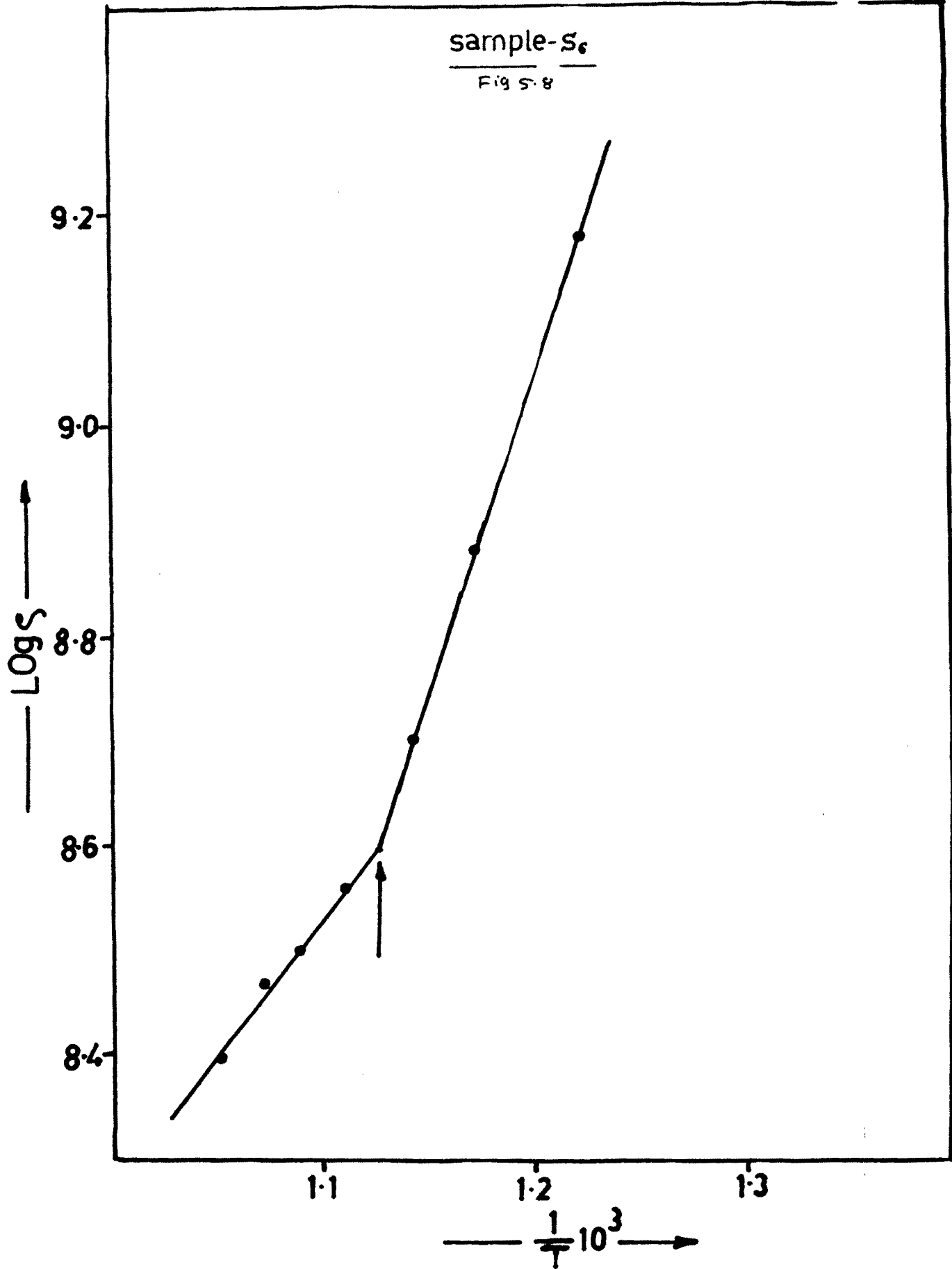
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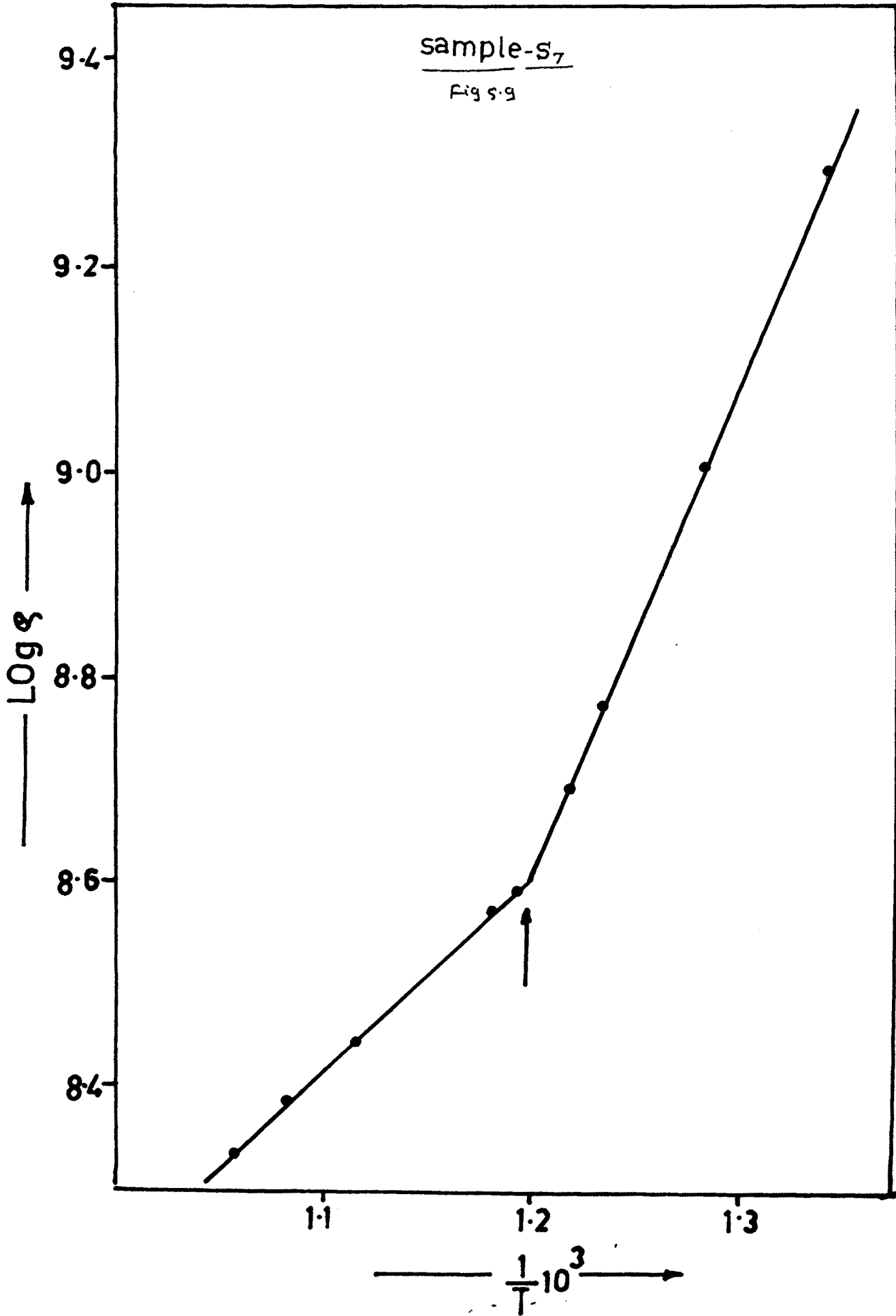


sample - S_5
Fig 5.7

98



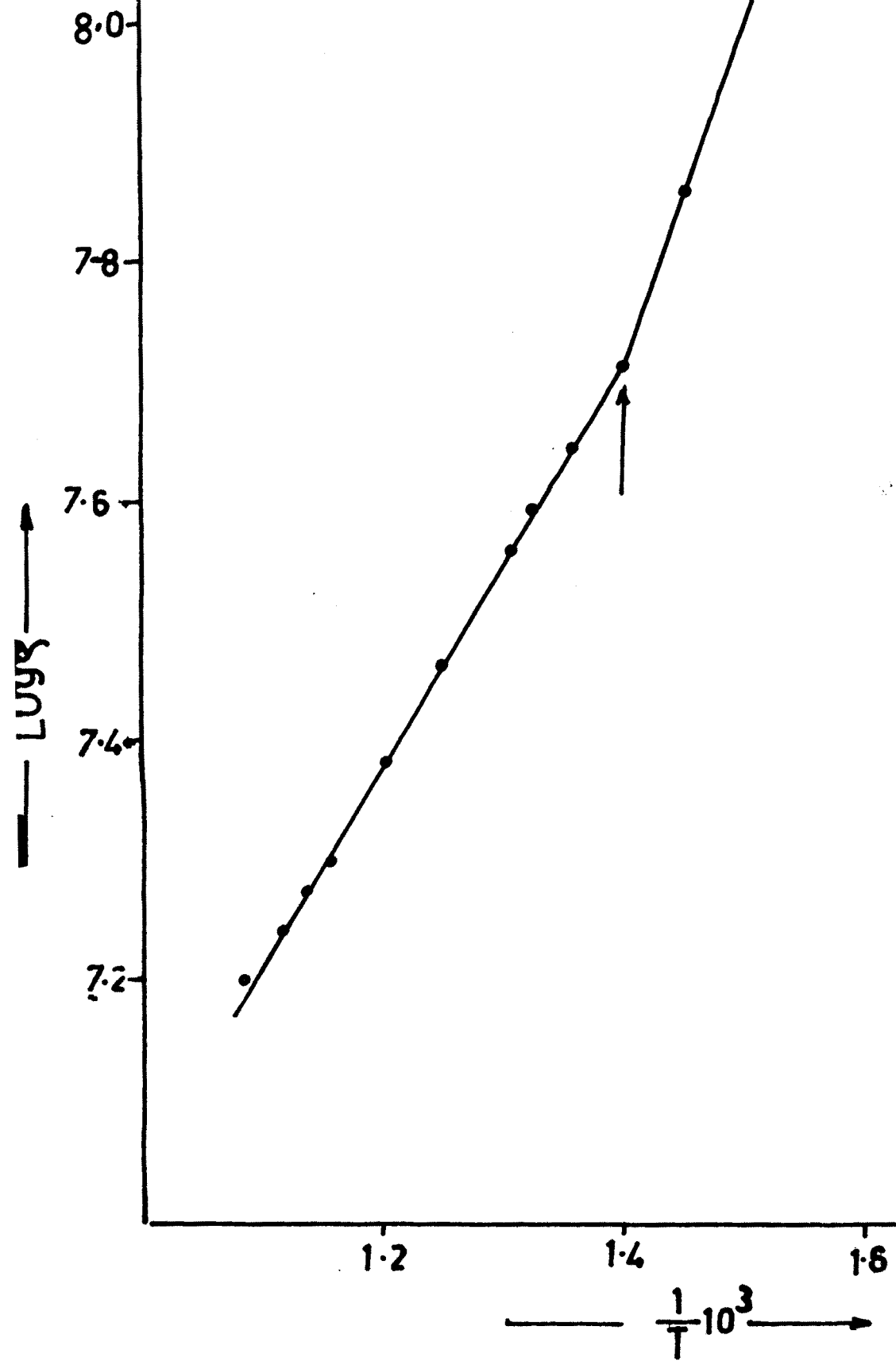




100

sample - s_0
Fig 5.10

101



sample S_9

102

Fig 5.11

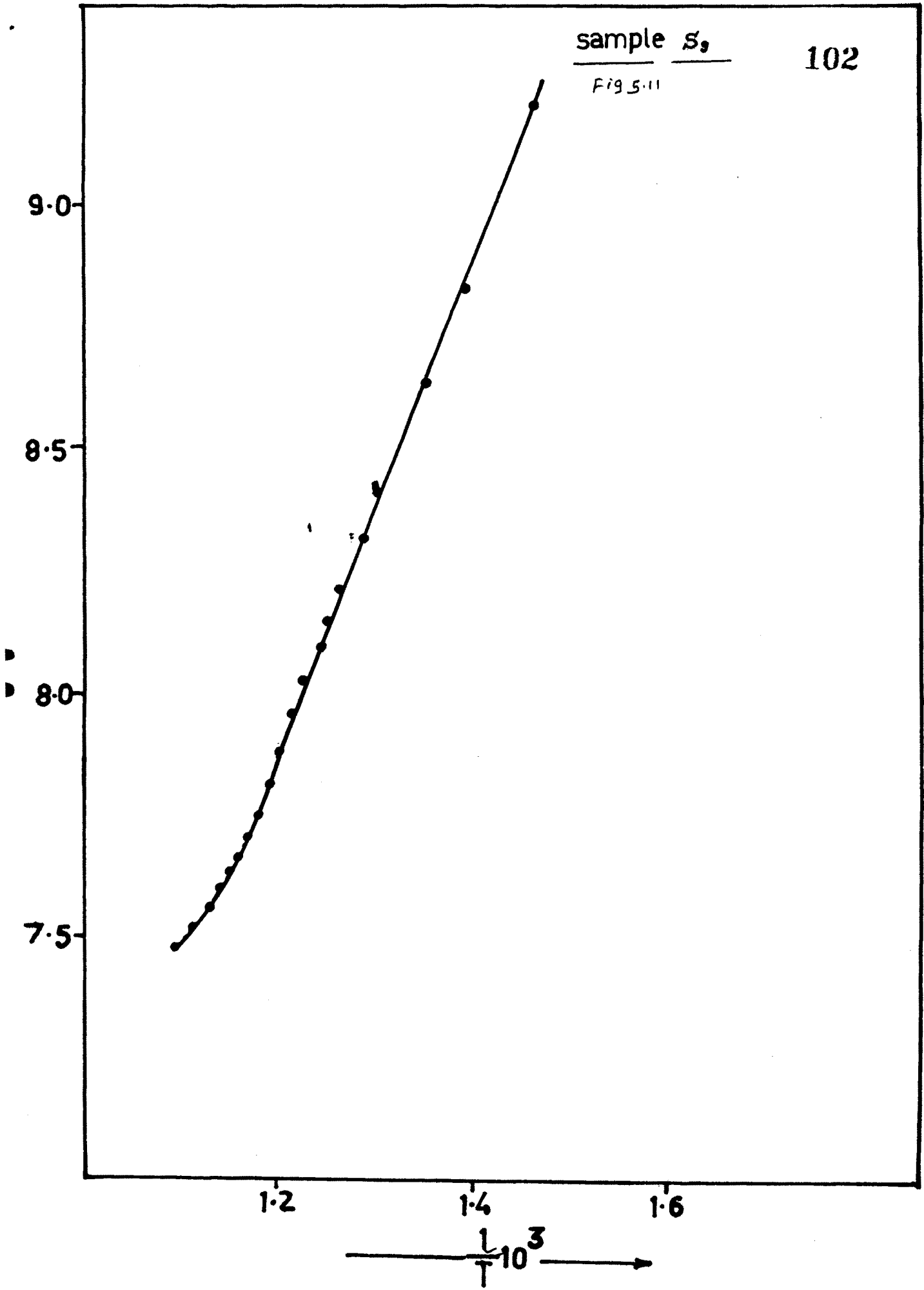


TABLE 5.1
 Activation energies of $\text{NiAl}_x\text{Fe}_{12-x}\text{O}_4$ SYSTEM

Sr. no.	Sample	x	Neel temp. o, C	Act. energy in eV	
				Ferri	Para
1	S1	2	707	1.171	0.02
2	S2	3	496	1.732	0.362
3	S3	4	475	0.623	0.43
4	S4	5	467	0.167	0.545
5	S5	6	511	0.248	0.442
6	S6	7	615	1.548	0.516
7	S7	8	560	0.95	0.357
8	S8	9	441	0.575	0.337
9	S9	10	non-magnetic		0.293

special cell in Fig 5.j. The pellet was pasted with a silver paste and sandwiched between the brass electrodes of the cell. The silver foils were introduced between the brass rods for a good contact. The wire made up of silver was insulated by ceramic beads and connected to the brass electrodes. The entire cell was then kept in the temperature controlled furnace. A calibrated Chromel - Alumel thermocouple was used to measure the temperature of the furnace by keeping the junction near to the sample. Resistivity measurements were carried out by measuring the current at constant voltage 2.5 volt for the temperature range 300°K to 850°K . Sufficient time was allowed for the sample to attain an equilibrium temperature.

5.5 RESULTS AND DISCUSSION

The present results on the measurement of d.c. resistivity of $\text{NiAl}_x\text{Fe}_{12-x}\text{O}_{19}$ series as a function of temperature are plotted in Fig. 5.3 to 5.11. The arrow on the plots indicates the temperature (T_c) at which the slope of the $\log \rho$ verses $1/T$ curves changes its value. The measurements of resistivity were carried out in the temperature region ~~200 $^{\circ}$ C~~ to ~~900 $^{\circ}$ C~~. The activation energies ΔE in the region both above and below T_c calculated by using the standard exponential

relation $\rho = c \exp(\Delta E / KT)$. Observed values of Neel temperature are tabulated in the Table 5.1

The plots of $\log \rho$ Vs $1/T$ are linear as the temperature increases the resistivity decreases. This is characteristic of the semiconducting behaviour of ferrite under study. This sort of relationship is often observed for many ferrites. The change in the slope of $\log \rho$ Vs $1/T$ plot, indicates magnetic transition. The temperature at which break occurs, corresponds closely to the observed ferromagnetic curie temperature for the ferrite.

The lowering of the activation energy has been attributed to the effect of spin ordering on conduction process in ferrites. There are few cases like those of high resistivity, where activation energy changes are very small. Negative results have also been reported for apparently similar material. It may be due to either an accidental onset of defect conduction or some secondary changes like phase transition.

The observation of lower activation energy for the conduction process in the paramagnetic region can be attributed to such an effect (sample No.2 $x = 2$). In fact such an anomaly has been observed in case of Cu - Ni ferrites and same has been recognised to be due to phase transition in these ferrites.

The observed curie temperatures are listed in Table 5.1.

It will be appropriate to note here that the resistivity measurements have been extensively used to determine Neel temperature of ferrite(21,22,23).

The Neel temperature of sample S_1 with $x = 2$ is 707°C , for S_2 Neel temperature decreases drastically to 496°C . Neel temperature decreases gradually for S_3 and S_4 . For sample S_5 , T_c is 511°C , for sample S_6 it is 615°C afterward T_c decreases for $x = 7, 8$ and 9 . The sample S_{10} , is non magnetic.

The additional contribution to resistivity in case of ferrites is expected to come from many microstructural changes brought in by the sintering conditions. Polycrystalline ferrites show higher resistivities in the presence of pores, grain boundaries and other impeding agents also play an equally important role.

The observed higher values of resistivities and activation energies in the present cases can be explained with help of above reasons and conduction mechanism in ferrites itself. Verway (24) and others have established that in magnetic oxides containing ions of the same of the same parent atom placed in crystallographically similar positions in the lattice

the conduction can take place via activation of the states involving cations of changing valance i.e $Fe^{2+} \rightarrow Fe^{3+}$ and vice - versa.

The mechanism, conveniently described as a hopping mechanism, has been successfully used by many workers to explain the electrical properties of many ferrites (25,26,27).

Electrical measurements made by Zaveta et.al (28,29) on the single crystal of hexagonal ferrites with M and W structure show a marked anisotropy in electrical resistivity. From temperature dependence of resistivity and from thermoelectric power measurement it has been established by them, that electron hopping between Fe^{2+} and Fe^{3+} ions plays a prominent role. The conduction process of hexagonal ferrites can also be attributed to such a hopping mechanism. Polarisation energy of the ions around the hopping electron, the hopping process some times involves terms like Madelung energy, strain energy etc. The observed higher activation energy is dictated by these additional energy terms along with the localised nature of hopping process involving the d wave functions of the current carriers.

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