Chapter -V

D.C. ELECTRICAL CONDUCTIVITY

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5.1 Introduction

Electrical conductivity is one of the essential characteristics of a semiconductor ferroelectric substance. But the electrical conductivity of ferroelectrics, of even the simplest viz-perovskite structure, is not well understood. It is also found that the point defects are generally responsible for many electrical properties of ABO_3 oxides belonging to perovskite family. The first step in the understanding of electrical transport, in any solid is to know whether the type of conductivity is ionic, electronic or mixed (partially electronic and ionic). There are many ways of determining the nature of conductivity. In the case of pure ionic conduction, the d.c.conductivity decreases with time and tends to become zero after sufficiently long time, where as for a pure electronic conduction it decreases with time but tends to stabilise at some finite constant value, which is termed the electronic contribution.

Greener (1) et al, measured the electrical conductivity of $KNbO_3$ single crystals. Dielectric and conductivity measurement was also carried by Deshmukh and Ingle (2) for single crystals of potassium niobates. The electrical conductivity of potassium niobates doped with various impurities was carried by Yanovskii (3) at room temperature. Timofieva (4), and Aleksandrowiz (5) investigated transport phenomena in $KNbO_3$. Roberts (6) discussed in detail the important role of electrodes in the measurement of conductivity and suggested that ohmic contact is the first strongest requirement for such a measurement.

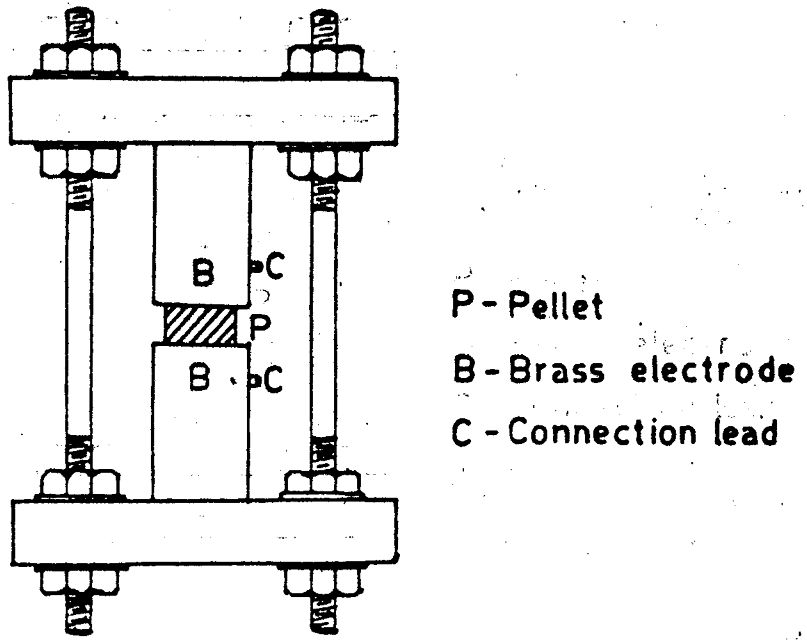
Hayne (7) reported on the electrical transport in solids and several ways of determination of nature of conductivity whether it is ionic, electronic or mixed. Maskimov (8) et al carried out experimental and theoretical investigation of energy levels of intinsic defects in ABO_3 oxides belonging to the perovskite family. Raevskii (9) et al studied the effect of polarisation, in an external field in % proportions of $BaTiO_3$ and $KNbO_3$ semiconducting ferroelectric ceramics. Handerek et al (10) observed the temperature dependence of the electrical conductivity for reduced and unreduced $KNbO_3$ monocrystals.

In the present work, investigations are carried out on the variation of d.c.electrical conductivity with temperature for the ferroelectric semiconducting ceramics $K(Ni_x Fe_y Nb_z)O_3$ system.

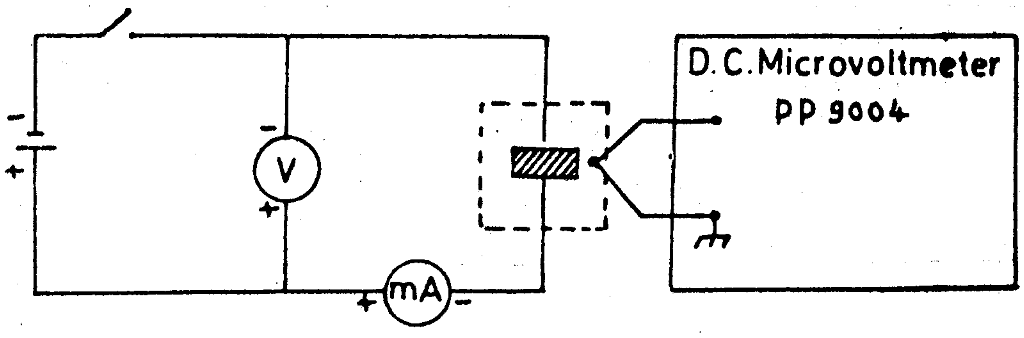
5.2 Experimental

The experimental set up used for the study of d.c.conductivity of ferroelectric potassium niobate and system $k(Ni_x Fe_y Nb_z)O_3$ $x = y = 0.02$, 0.05, 0.10 and 0.15 is schematically shown in Fig.5.1. The experimental set up consists of an electrically heated furnace, a transisterised power supply unit to provide d.c.electric field, a digital micrometer and a digital multimeter. The pellets of above $x = y = 0$, 0.02, 0.05, 0.10 and 0.15 compositions were used in the form of round discs. The two sides of these sintered disks were coated with thin layer of silver paste for a good electrical contact. The d.c. conductivity investigations were based on the d.c.resistivity data observed by the two probe method.

To ensure ohmic contact between pellet and the electrode interface, the current through pellet was measured at first as a function of applied d.c.voltage at a constant temperature and current density (J) and then was plotted against the applied electric field (E). Typical plots obtained for $KNbO_3$ and $K(Ni_{0.05} Fe_{0.05} Nb_{.90})O_3$ system are presented in Fig.5.2. It is observed that the current density (J) varies linearly with E upto a critical field (E_m) and after that the variation of J becomes non-linear. Thus the contact between electrode and the pellet interface remains ohmic upto about 125 v/cm electric field. This falls well below the critical field (E_m) value. Therefore in the



Block diagram of pellet holder



A schematic circuit diagram for d.c.conductivity measurements

Fig. 5.1

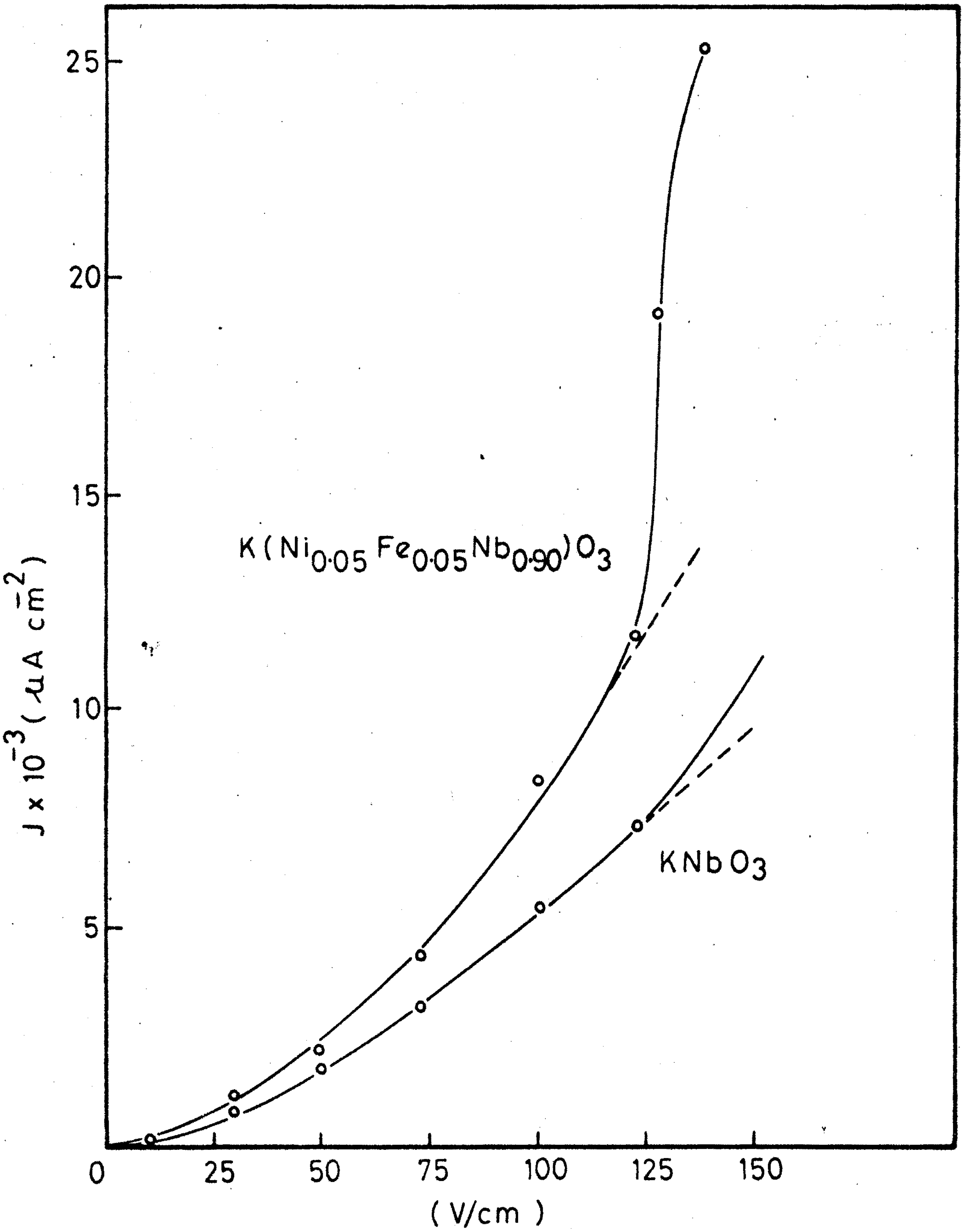


Fig. 5·2 - PLOT OF CURRENT DENSITY VERSUS APPLIED ELECTRIC FIELD FOR $K(Ni_x Fe_y Nb_z)O_3$ AT CONSTANT TEMPERATURE 348 °K.

subsequent studies of conductivity by us the applied d.c.voltage of 100 v/cm was chosen, as the upper limit.

5.3 D.C.Electrical Conductivity of $KNbO_3$ and Ferroelectric semiconducting ceramic $K(Ni_x Fe_y Nb_z)O_3$ system

The sintered pellet, of the specified composition under investigation, was placed in the pellet holder attached with stainless steel electrodes. The d.c.voltage of 10 v was applied across the pellet holder in series with a digital micrometer and the pellet holder was heated slowly. The d.c. resistivity measurements were carried out in the temperature range that covers their transition points. The resistivity data was used to calculate d.c. conductivity. The temperature variation of log σ for $KNbO_3$, $K(Ni_{0.02}\ Fe_{0.02}\ Nb_{.96})O_3$, $K(Ni_{0.05}\ Fe_{0.05}\ Nb_{0.90})O_3$ $K(Ni_{0.10}\ Fe_{0.10}\ Nb_{.80})O_3$ and $K(Ni_{0.15}\ Fe_{0.15}\ Nb_{0.70})O_3$ is shown in Fig. 5.3 to 5.7.

In order to detect the type of conduction, d.c.conductivity of test samples was measured at a constant temperature. A graph is plotted log t vs log σ. Such two typtical plots were obtained for each of the ferroelectrics $KNbO_3$ and $K(Ni_{0.15}\ Fe_{0.15}\ Nb_{0.70})O_3$ at constant temperature, below curie temperatures (T_c) and as well at a value above curie temperature. These are presented in Figs. 5.8 to 5.12.

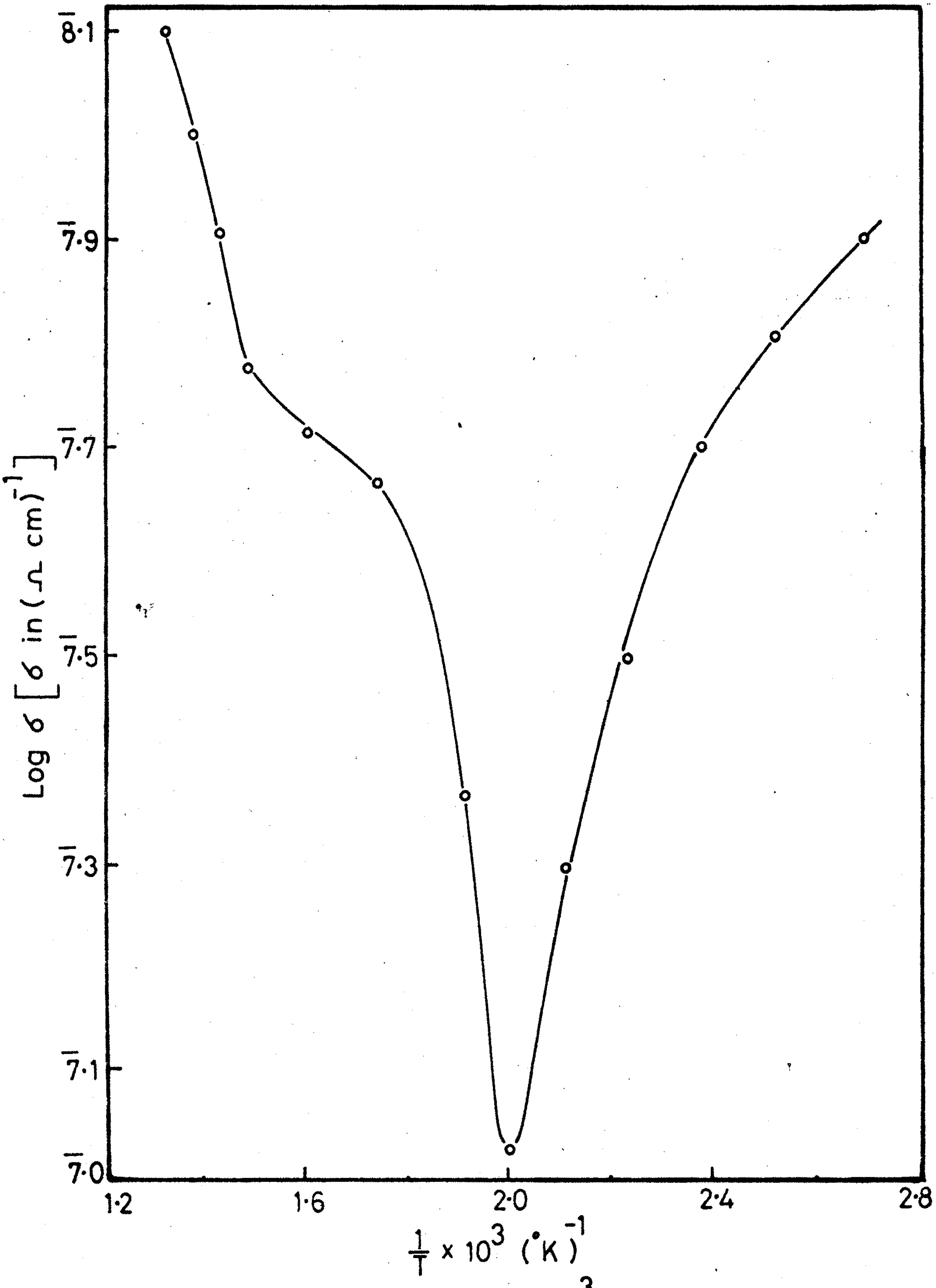


Fig. 5·3- PLOT OF LOG σ vs $1/T \times 10^3$ FOR $KNbO_3$

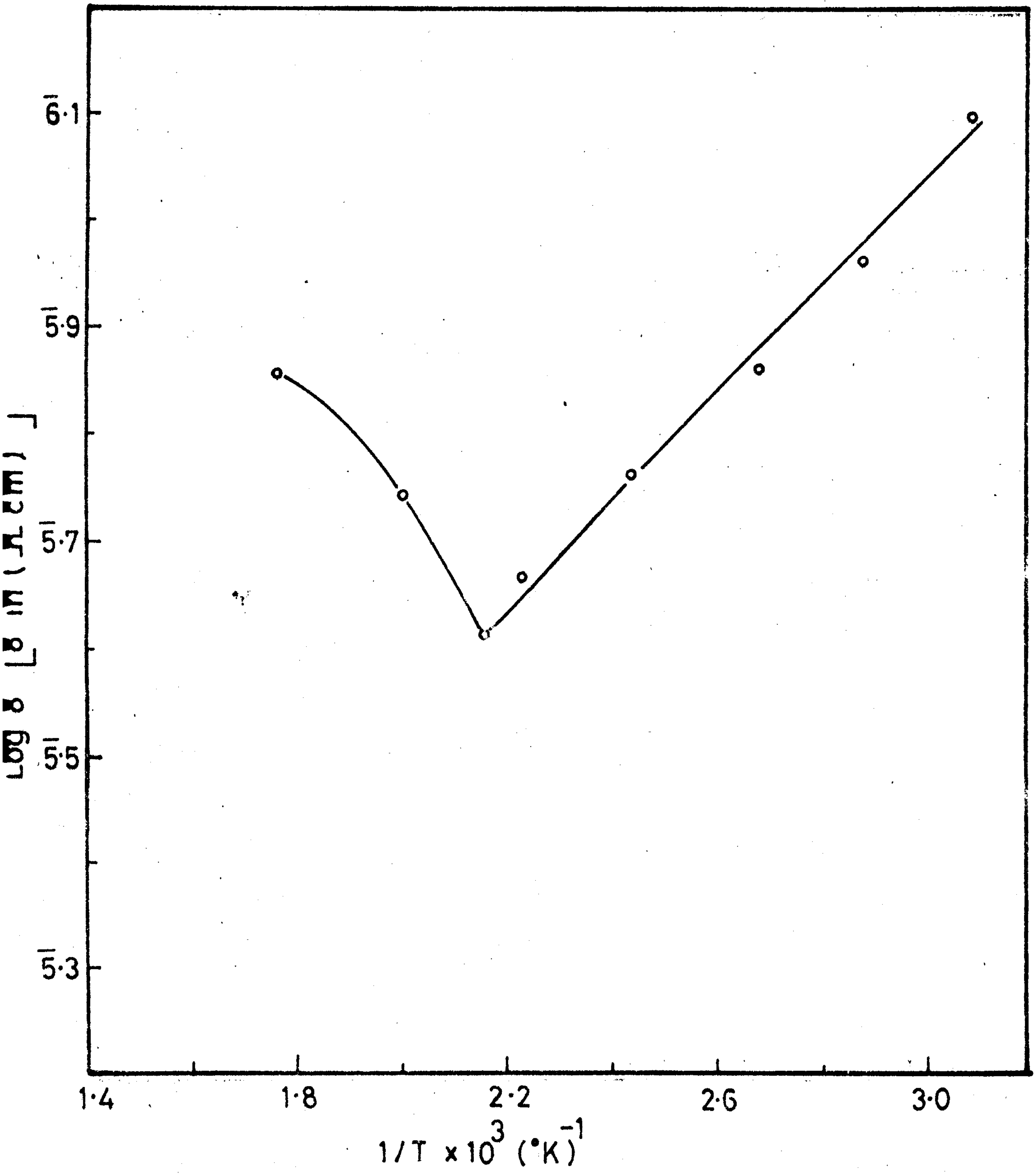


Fig. 5·4– PLOT OF LOG σ vs $1/T \times 10^3$ FOR $K(Ni_{0.02}Fe_{0.02}Nb_{0.96})O_3$

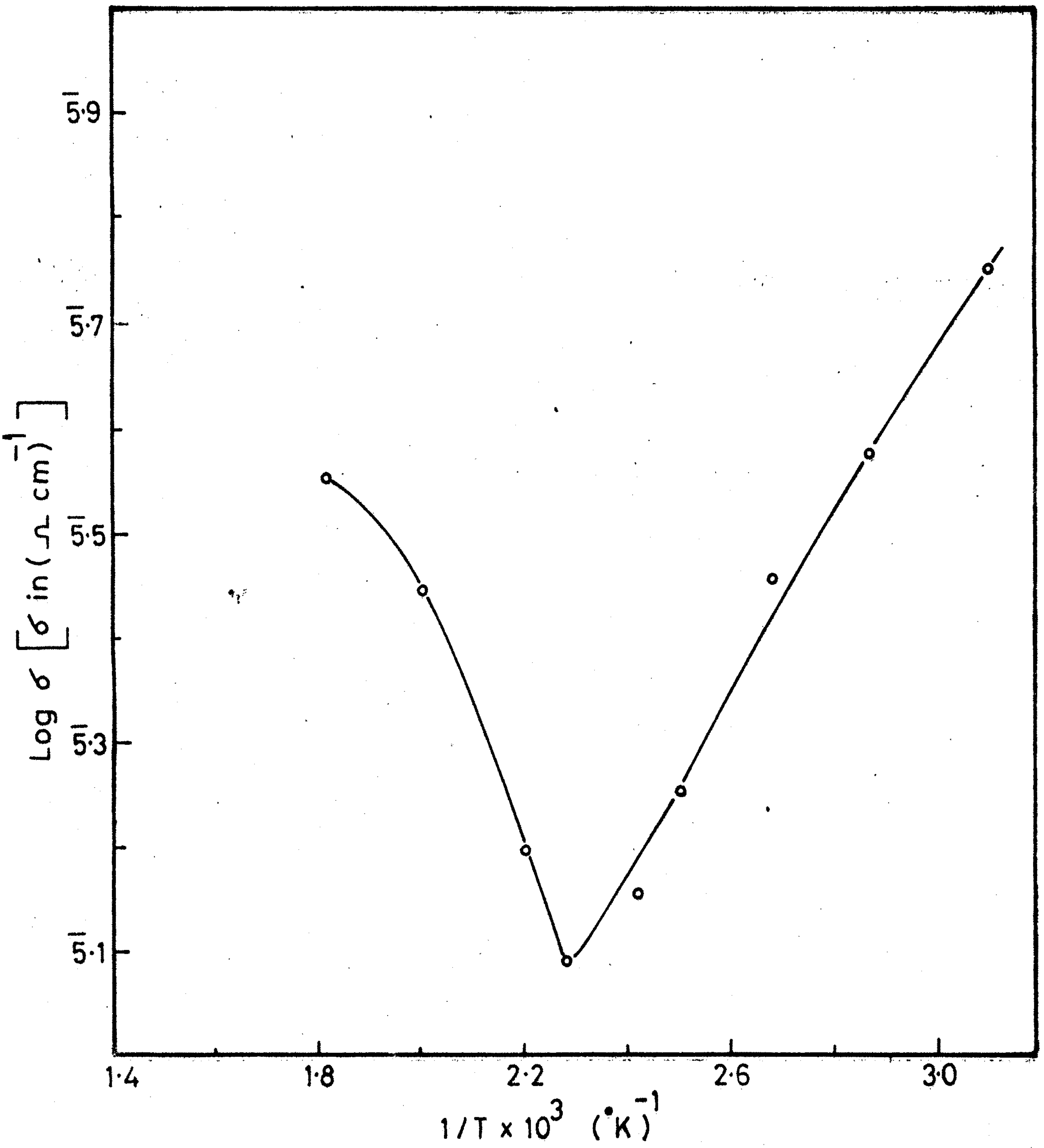


Fig. 5·5 – PLOT OF LOG σ vs 1/T x 10^3 FOR $K(Ni_{0.05}Fe_{0.05}Nb_{0.90})O_3$

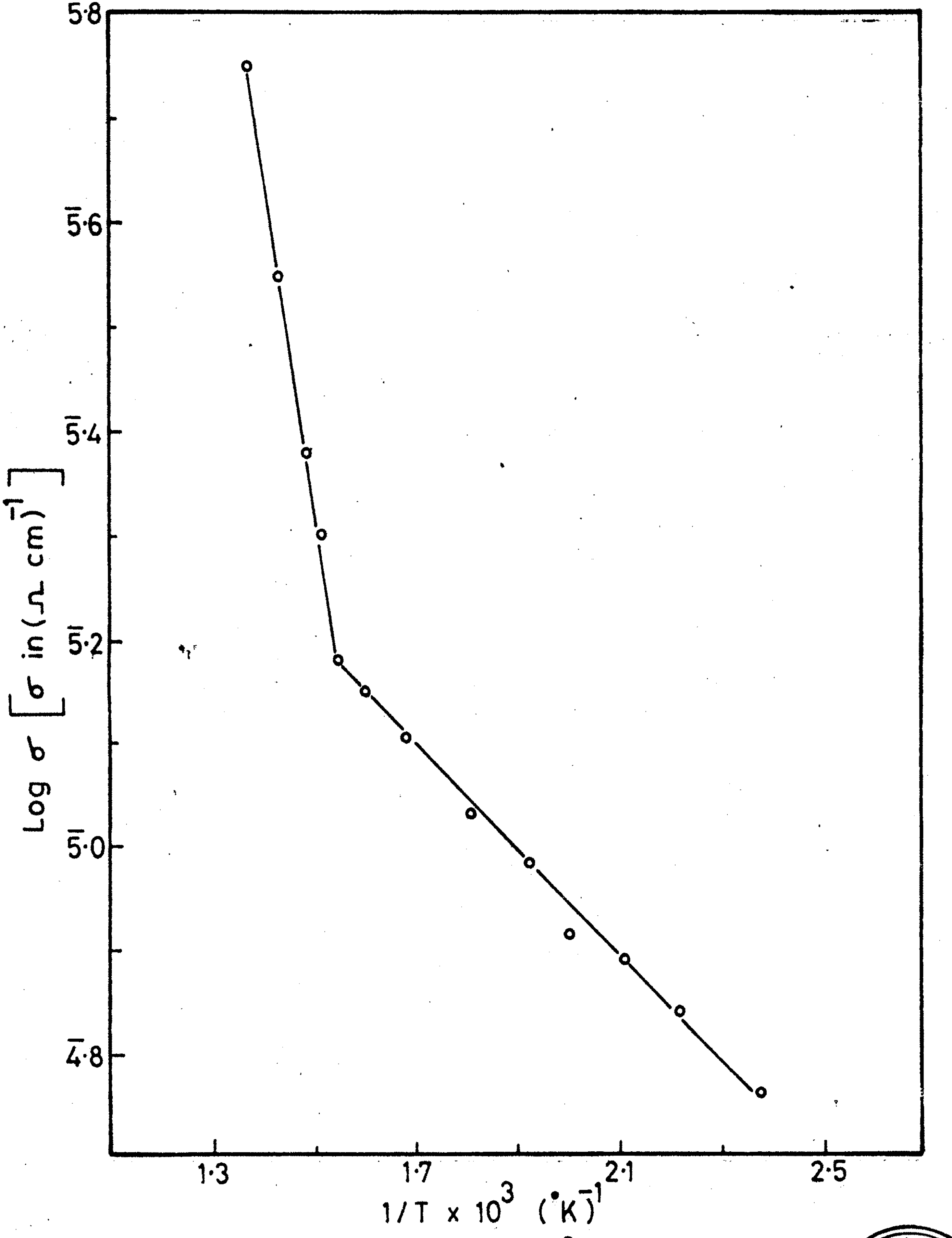


Fig 5·6 – PLOT OF LOG σ vs 1/T x 10^3 FOR $K(Ni_{0.10}Fe_{0.10}Nb_{0.80})O_3$

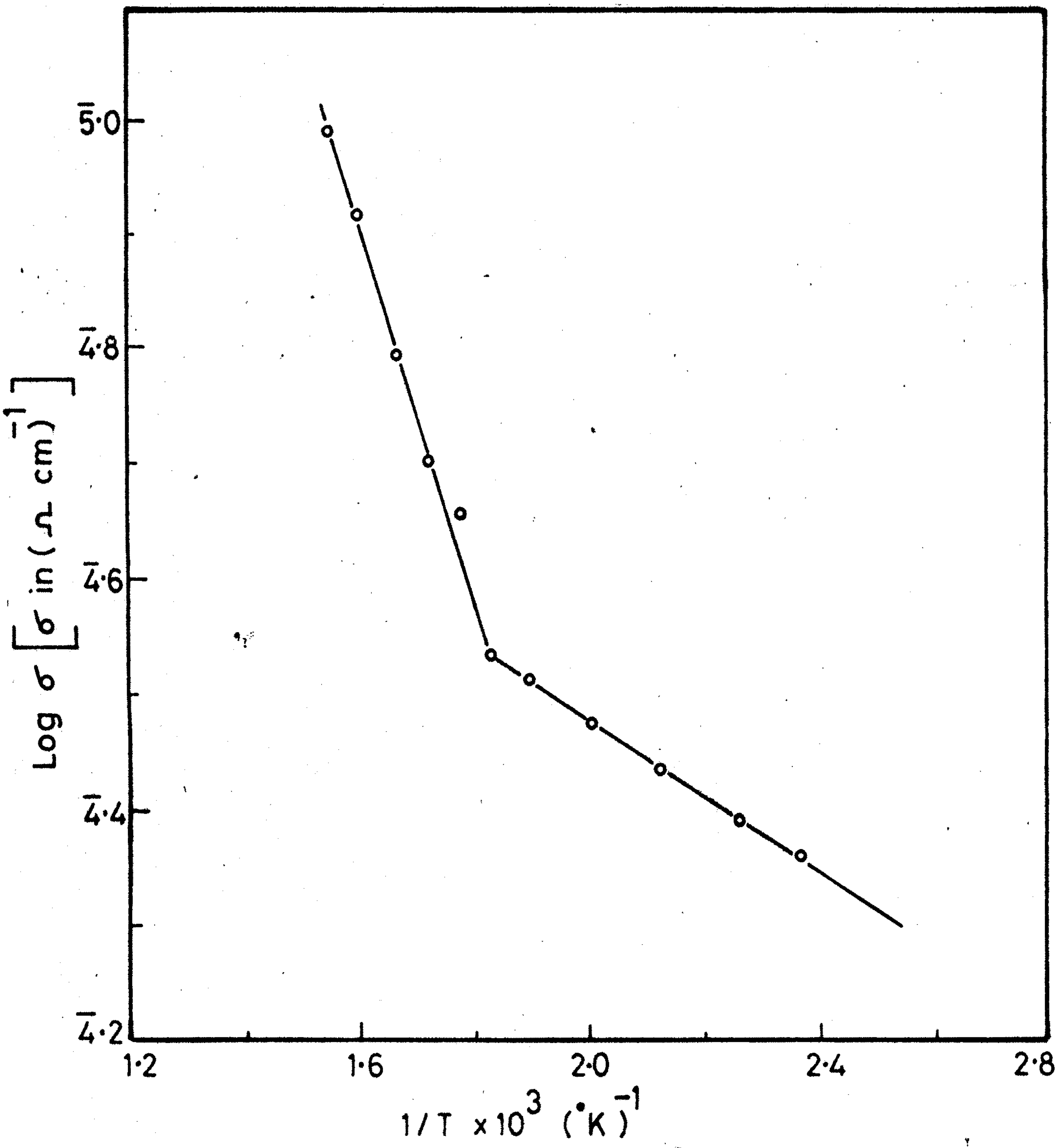


Fig. 5·7 - PLOT OF LOG σ vs 1/T x 10^3 FOR $K(Ni_{0.15}Fe_{0.15}Nb_{0.70})O_3$

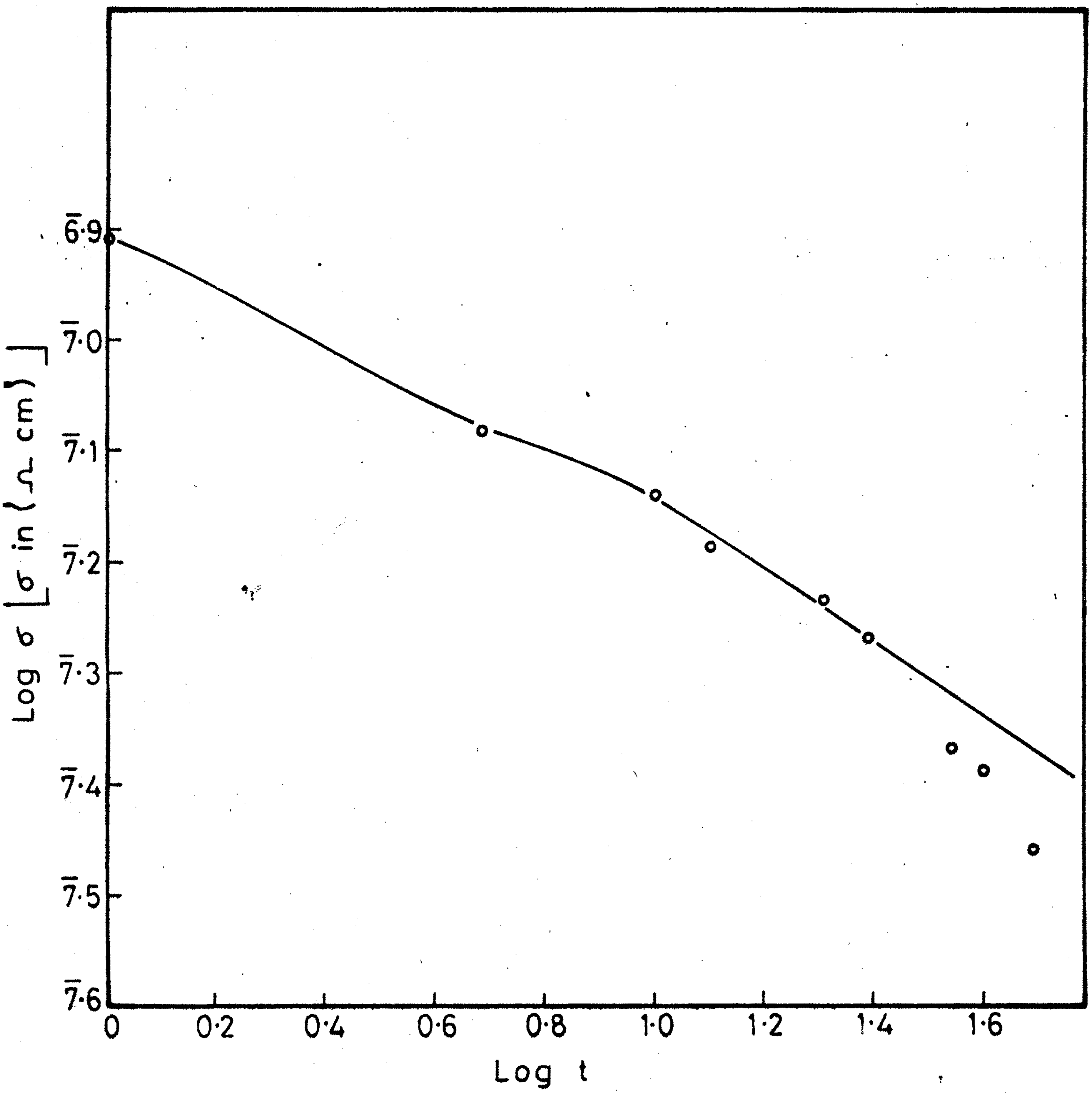


Fig. 5·8 – PLOT OF LOG σ OF $KNbO_3$ AS A FUNCTION OF LOG t AT 473 °K BELOW CURIE TEMPERATURE.

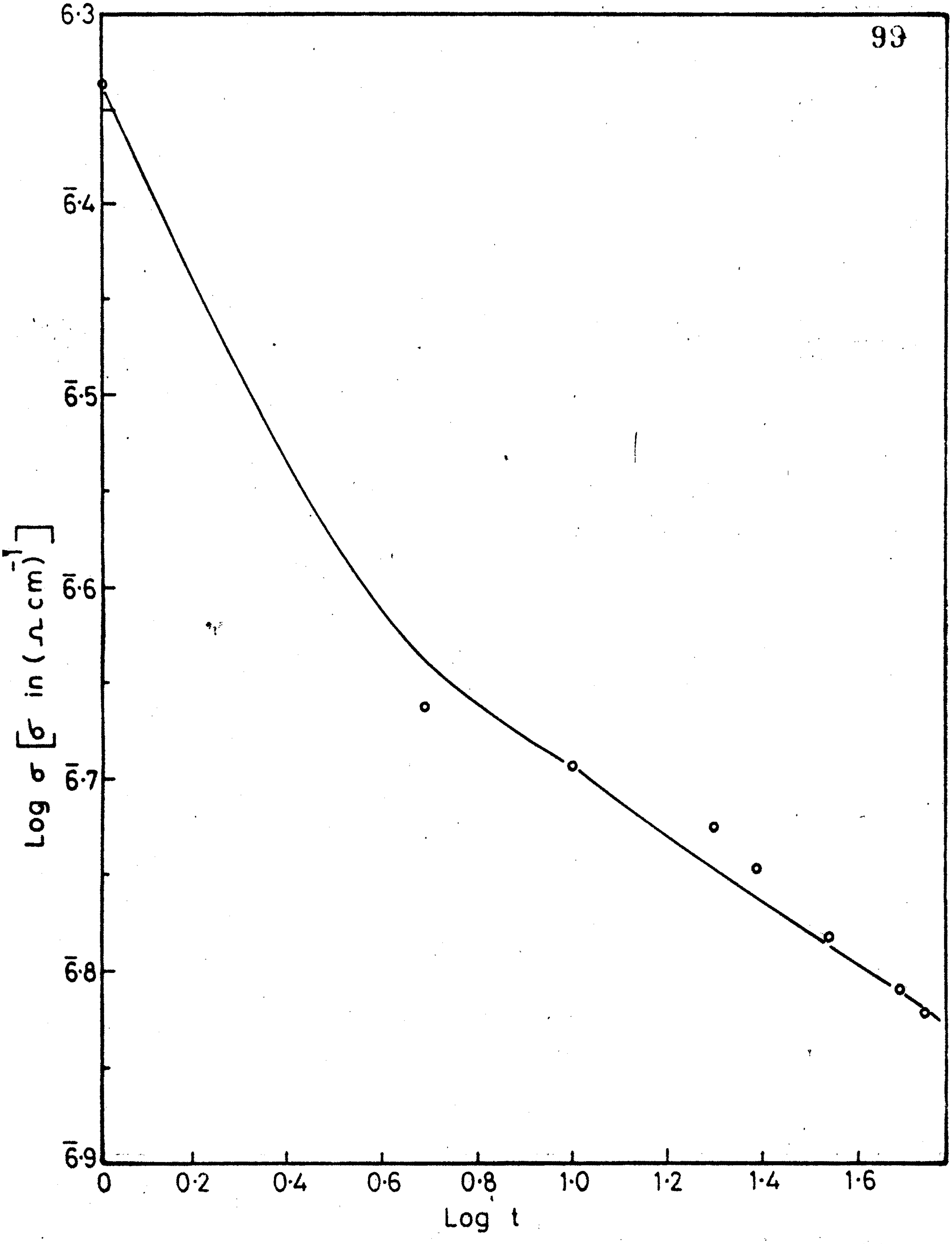


Fig. 5·9 - PLOT OF LOG σ OF $KNbO_3$ AS A FUNCTION OF LOG t AT 523 °K ABOVE CURIE TEMPERATURE.

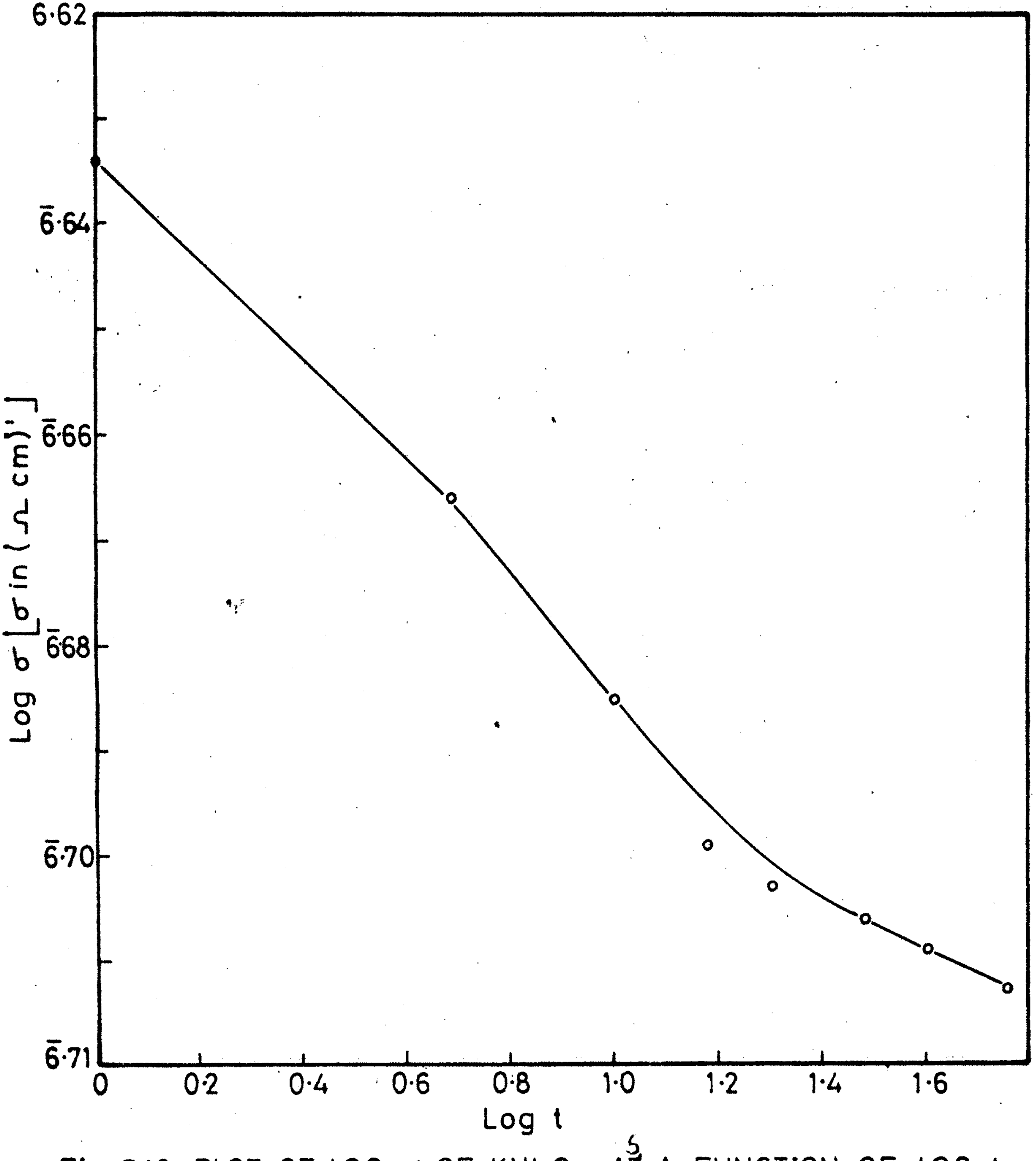


Fig. 5·10 - PLOT OF LOG σ OF $KNbO_3$ AS A FUNCTION OF LOG t AT 710°K ABOVE CURIE TEMPERATURE.

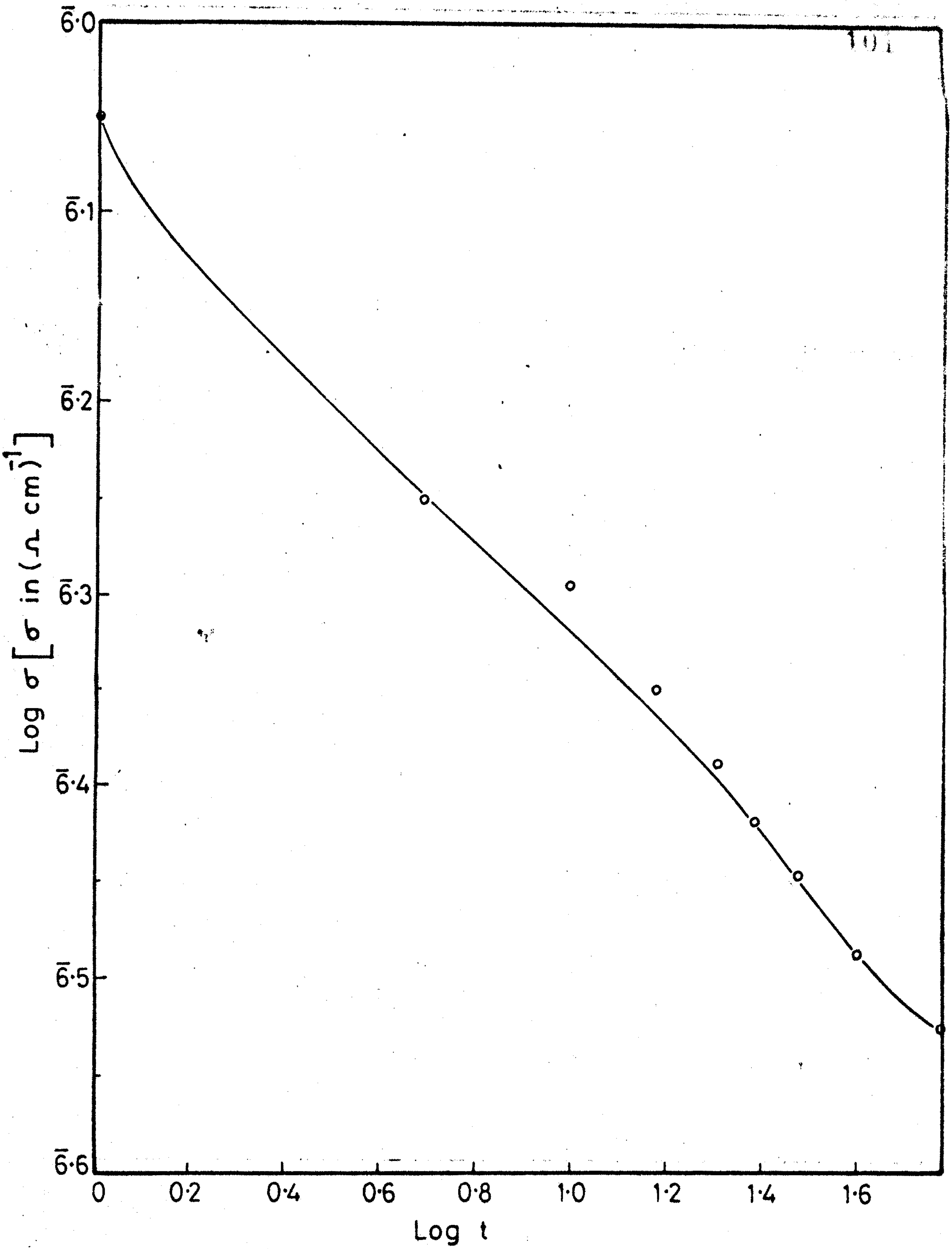


Fig. 5·11 – PLOT OF LOG σ OF $(Ni_{0\cdot15}Fe_{0\cdot15}Nb_{0\cdot70})O_3$ AS A FUNCTION OF LOG t AT 523 °K BELOW CURIE TEMPERATURE.

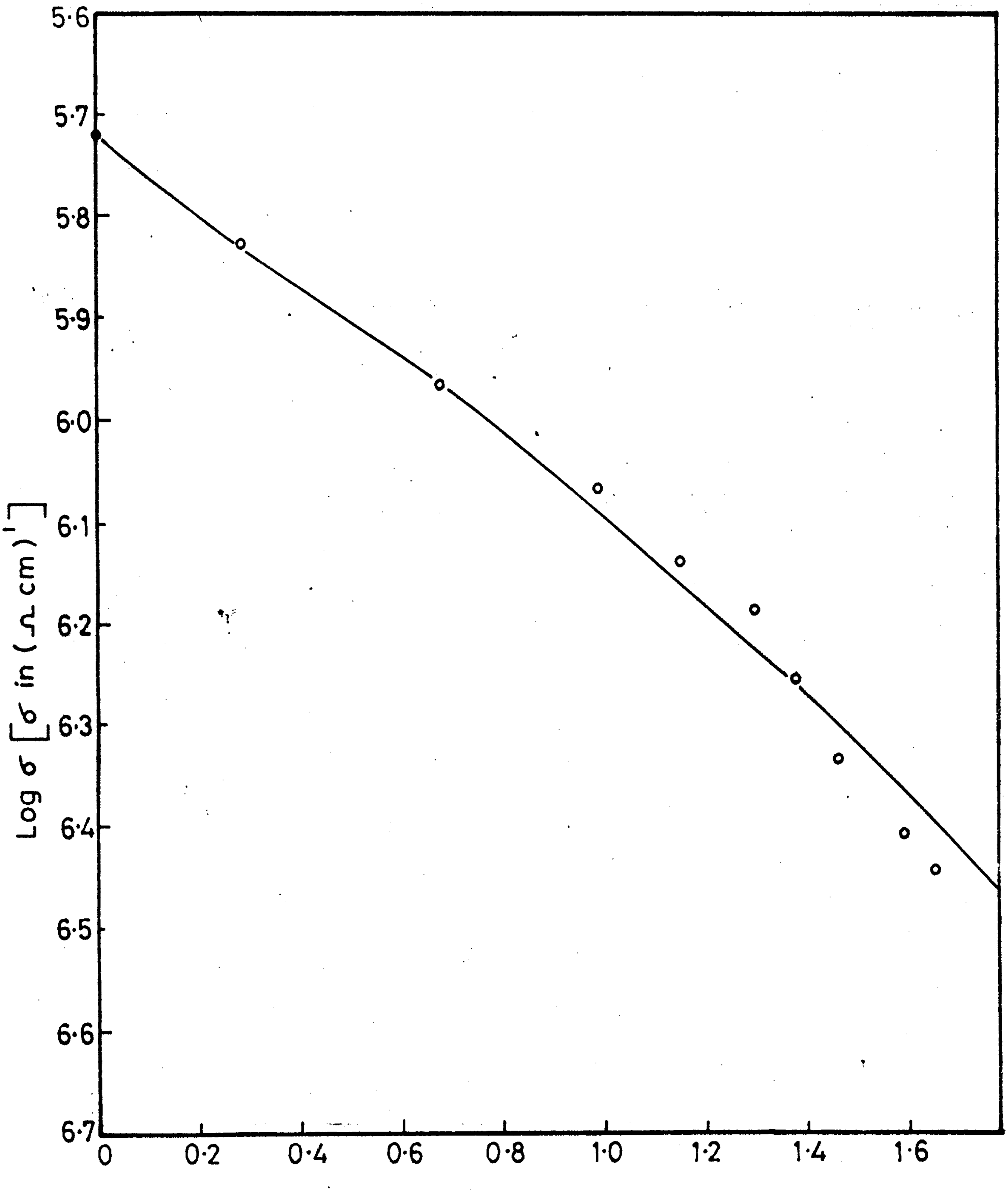


Fig. 5·12 – PLOT OF LOG σ OF $K(Ni_{0.15}Fe_{0.15}Nb_{0.70})O_3$ AS A FUNCTION OF LOG t AT 573 °K ABOVE CURIE TEMPERATURE.

5.4 Results and discussion

The variation of conductivity is governed by the relation (11)

$$\sigma = \sigma_0 \exp\left[- \frac{\Delta E}{KT}\right], \qquad (5.1)$$

where K = Boltzmann constant,

T = Absolute temperature,

σ_0 = Electrical conductivity of material at 0°k,

and σ = Electrical conductivity of the composition at temperature T°k.

It is clear from the Figures 5.3 to 5.7 that d.c. electrical conductivity of above compositions depends considerably on the temperature. It is also observed that d.c.conductivity of above compositions changes with the nature of changes in impurities, such as Ni and Fe. The change in d.c.electrical conductivity is observed at 498°k, 685°k, 460°k, 435°k, 598°k and 548°k for respectively, $KNbO_3$, $K(Ni_{0.02}\ Fe_{0.02}\ Nb_{.90})O_3$, $K(Ni_{0.05}\ Fe_{0.05}\ Nb_{0.90})O_3$ $K(Ni_{0.10}\ Fe_{0.10}\ Nb_{.80})O_3$ and $K(Ni_{0.15}\ Fe_{0.15}\ Nb_{0.70})O_3$. These tempoeratures indicate the transition temperature of respective composition samples. Such data is in good agreement with ferroelectric curie temperatures investigated by us by hysteresis loop method, dielectric constant measurements and is listed in the Table No.5.1.

The following observations are noted to be very significant :

(1) The electrical conductivity shows a change at the phase transition temperature, indicating curie temperatures of the respective compositions.

(2) The activation energy of the above compositions changes with the concentration of the impurities Ni and Fe.

(3) The activation energy of the compositions is higher in paraelectric state than the activation energy in the ferroelectric state.

(4) The electrical conductivity of the above composition is of ionic nature both in the ferroelectric phase and in the paraelectric phase.

TABLE NO.5.1

Activation energies for $K(Ni_x Fe_y Nb_z)O_3$ with different molar proportions.

Composition	Activation energy ev.			
	Ferro	Ferro	Ferro	Para
$KNbO_3$	0.2483	0.3476	0.1235	0.6290
$K(Ni_{0.02} Fe_{0.02} Nb_{.96})O_3$	0.1986	0.2597		
$K(Ni_{0.05} Fe_{0.05} Nb_{0.90})O_3$	0.1441	0.1986		
$K(Ni_{0.10} Fe_{0.10} Nb_{.80})O_3$			0.1095	0.5959
$K(Ni_{0.15} Fe_{0.15} Nb_{0.70})O_3$			0.0993	0.2483

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