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CHAPTER - IV

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D.C. ELECTRICAL CONDUCTIVITY

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### D. C. ELECTRICAL CONDUCTIVITY

#### 4.1 Introduction :

Electrical conductivity is intrinsic property of the materials. Some materials, and usually ferroelectrics, will exhibit conduction and semiconduction effects not usually observed in insulators. The conduction mechanism in ferroelectric materials can be ionic, electronic or mixed (partially ionic and electronic) in nature. There are several ways of determining the nature of conductivity. The simplest way is to measure d.c. conductivity as a function of time using electrodes which block ionic conduction. In the case of pure ionic conduction, d.c. conductivity decreases with time and tends to become zero after sufficiently long time, whereas for a pure electronic conductor it is independent of time. For mixed conduction it decreases with time but tends to stabilize at some finite constant value, which is the electronic contribution.

Conductivity is associated with solids although electrical conduction also occurs in liquids, electrolytes and ionised gases. Electrons are usually charge carriers in solids but ionic conduction can be important for some materials. Factors affecting the magnitude of the electrical conductivity of a material are conduction electron, or ion,

density and the nature of the interatomic forces. The conduction cannot occur unless the charge carriers are able to cross the potential well and for this purpose they need to be activated by some external agency. Activation can be affected by thermal and electrical energies. The variation of conductivity ( $\sigma$ ) with temperature (T) can be represented by the general exponential relation,

$$\sigma = \sigma_0 \exp[-\Delta E/KT]$$

where  $\Delta E$  is the activation energy,  $\sigma_0$  the constant and K the Boltzmann constant.

The ferroelectric activity of sodium vanadate below 380°C was reported by Sawada and Nomura (1951). The Raman scattering of lithium, sodium and potassium vanadates was studied by Feigelson et al (1972) and they have shown that lithium and sodium vanadates are monoclinic while potassium vanadate is orthorhombic. The electrical conductivity of rare-earth vanadates  $\text{LnVO}_3$  (Ln = La, Lu and Y) compounds was measured by Sakai et al (1976). The crystal chemistry of  $\text{M}^+ \text{VO}_3$  ( $\text{M}^+ = \text{Li}, \text{Na}, \text{K}, \text{Cs}, \text{Rb}, \text{NH}_4$  and  $\text{Tl}$ ) pyroxenes were studied by Hawthorne and Calvo (1977). Electrical transport studies on heavy rare-earth tungstates were reported by Verma and Lal (1981), wherein they have predicated that these materials are mixed (ionic-electronic) conductors.

Electrical conduction in  $\text{PrVO}_4$  single crystal was studied by Yadav et al (1985) and concluded that  $\text{PrVO}_4$  is a semiconductor with an energy gap of 1.5 eV. Kanchan Gaur et al (1985, 1986) have reported the electrical transport in light and heavy rare-earth vanadates. Electrical transport properties of iron vanadate were studied by Gupta et al (1986) wherein they have related dielectric constant variations with electrical conductivity. Hyperfine interaction in the mixed conductor  $\gamma\text{LiV}_2\text{O}_5$  was studied by Bose et al (1987).

Electrical conductivity of  $\text{BaTiO}_3$  ceramics doped with rare-earth oxides studied by Tennery and Cook (1961). Electrical conductivity of  $\text{BaTiO}_3$  ceramics doped with rare-earth oxides studied by Murakami et al (1973). Recently, Patil et al (1987) reported the temperature dependence of d.c. electrical conductivity of lithium vanadate, potassium vanadate, sodium vanadate and their solid solutions both in ferro and para electric regions.

The aim of the present work is to study the temperature dependence of d.c. electrical conductivity of undoped sodium vanadate and doped with various concentrations of Neodymium oxide. These mixtures being ferroelectric materials, possess large values of piezoelectric properties near the transition temperature make attractive in devices requiring piezoelectricity.

#### 4.2 Experimental :

The experimental set-up used for the study of d.c. electrical conductivity measurements is shown in fig.(4.1). The set-up consisted of a transistorized power supply unit to provide d.c. electrical field, a temperature controller arrangement, a Digital Dc Micro Volt Meter (VMV 15), with a picoammeter adaptor and an electrically heated furnace. The sintered pellets of the samples used were first polished and then painted on two sides with a thin layer of air-drying silver paste for good electrical contact. At constant temperature the current through the pellets of the samples was measured as a function of applied d.c. electric field and the current density (J) was plotted against the applied electric field (E). A typical plots for undoped  $\text{NaVO}_3$  and doped with different concentrations (0.025 to 1 mol%) of  $\text{Nd}_2\text{O}_3$  are shown in fig.(4.2). From this figure it is observed that the current density (J) varies linearly with the applied electric field (E) upto a critical field ( $E_m$ ) and after that variation of the current density (J) becomes non-linear. Thus the contact between electrode and pellet interface remains ohmic at about 105 v/cm d.c. electrical field which falls within critical field. Therefore, the applied d.c. voltage of 105 v/cm was selected in the study of conductivity.

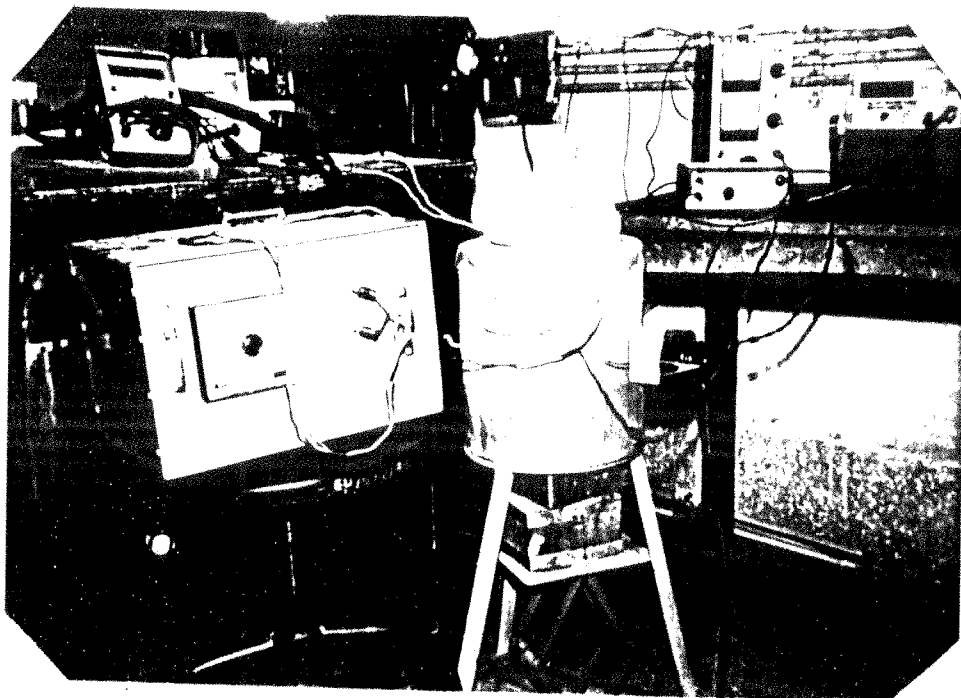
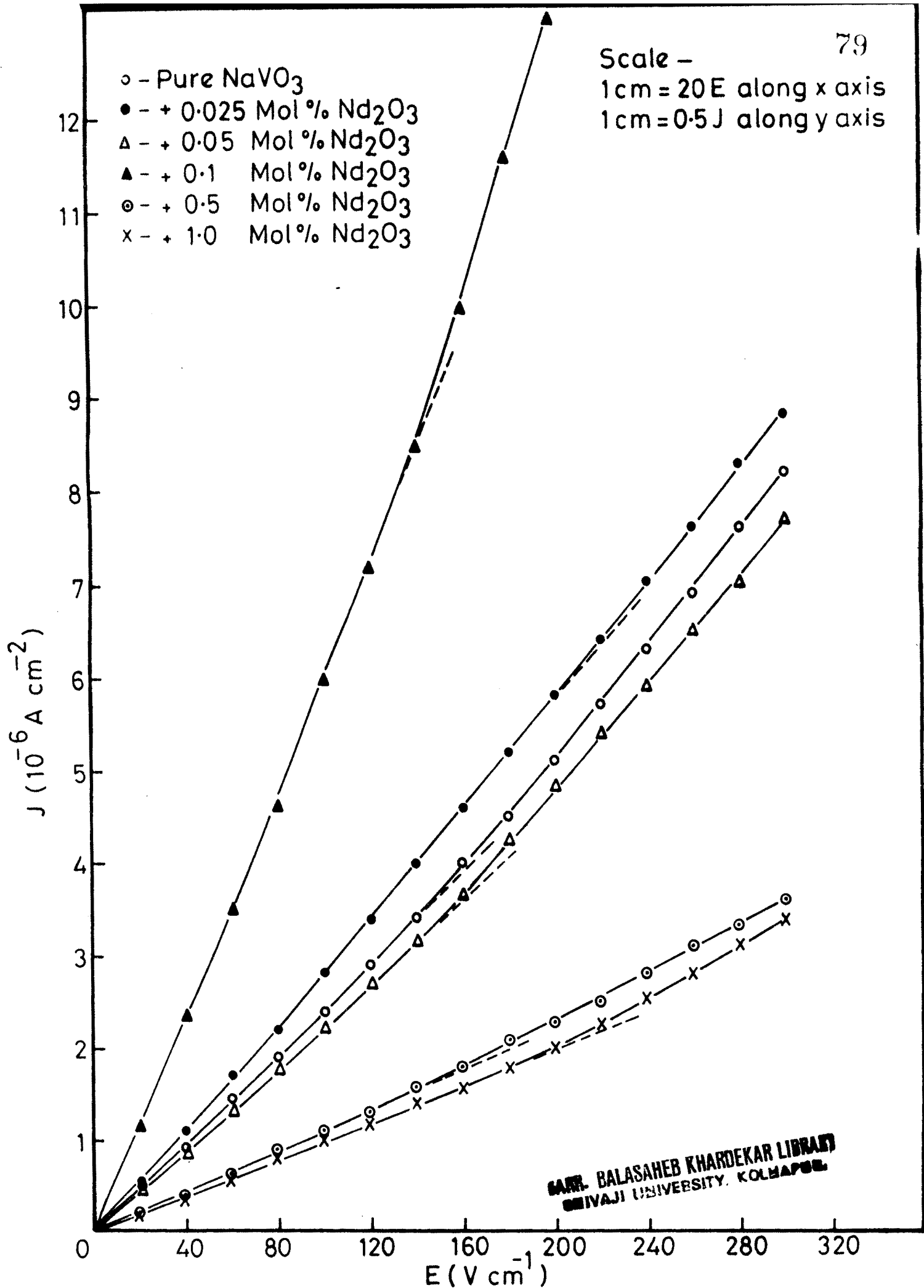


Fig. 4.1 — Experimental set-up for measurement of d. c. conductivity.

Scale -  
1cm = 20E along x axis  
1cm = 0.5J along y axis

- - Pure NaVO<sub>3</sub>
- - + 0.025 Mol % Nd<sub>2</sub>O<sub>3</sub>
- △ - + 0.05 Mol % Nd<sub>2</sub>O<sub>3</sub>
- ▲ - + 0.1 Mol % Nd<sub>2</sub>O<sub>3</sub>
- ⊙ - + 0.5 Mol % Nd<sub>2</sub>O<sub>3</sub>
- x - + 1.0 Mol % Nd<sub>2</sub>O<sub>3</sub>



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Fig. 4.2 - VARIATION OF CURRENT DENSITY (J) WITH D.C. ELECTRIC FIELD (E)

#### 4.3 Electrical Conductivity Of Undoped $\text{NaVO}_3$ And Doped With Different Concentrations (0.025 to 1 mol%) of $\text{Nd}_2\text{O}_3$ :

The sintered pellet placed in a pellet holder with stainless steel electrodes was slowly heated in a furnace by applying a d.c. voltage of 105 v/cm in series with picoammeter, and d.c. resistivity measurements were taken in the temperature range covering the transition points of the samples. The measurement of d.c. conductivity were based on the d.c. resistivity data obtained by the two-probe method. The resistivity data thus obtained was used to calculate d.c. conductivity. The graphs of  $\log\sigma$  against  $T^{-1}$  for ferroelectric undoped  $\text{NaVO}_3$  and doped with different concentrations (0.025 to 1 mol%) of  $\text{Nd}_2\text{O}_3$  are shown in fig. [(4.3) to (4.8)] respectively.

To ensure whether the conductivity is ionic, electronic or mixed (ionic-electronic), the variation of the d.c. conductivity with time at a constant temperature was studied both in ferroelectric and paraelectric states, with electrodes which block ionic conduction. Such plots of  $\log\sigma$  against  $\log t$  for undoped  $\text{NaVO}_3$  and doped with 0.05 mol% of  $\text{Nd}_2\text{O}_3$  at constant temperature, below curie temperature ( $T_C$ ) and above curie temperature ( $T_C$ ) are shown in figs. [(4.9) to (4.10)] respectively.





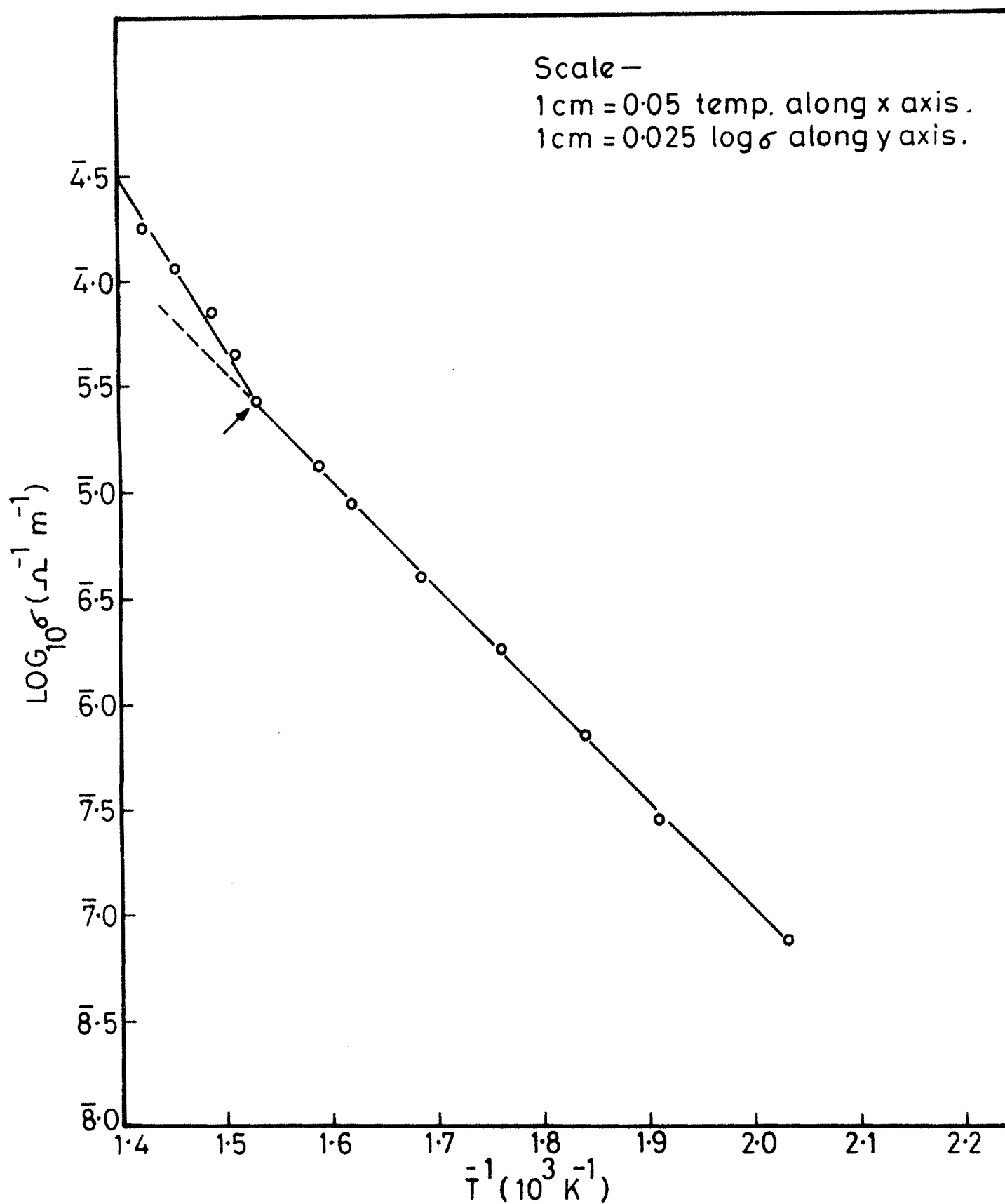


Fig.4.3 — VARIATION OF LOGARITHMIC CONDUCTIVITY WITH  $1/T$  FOR  $\text{NaVO}_3$ .

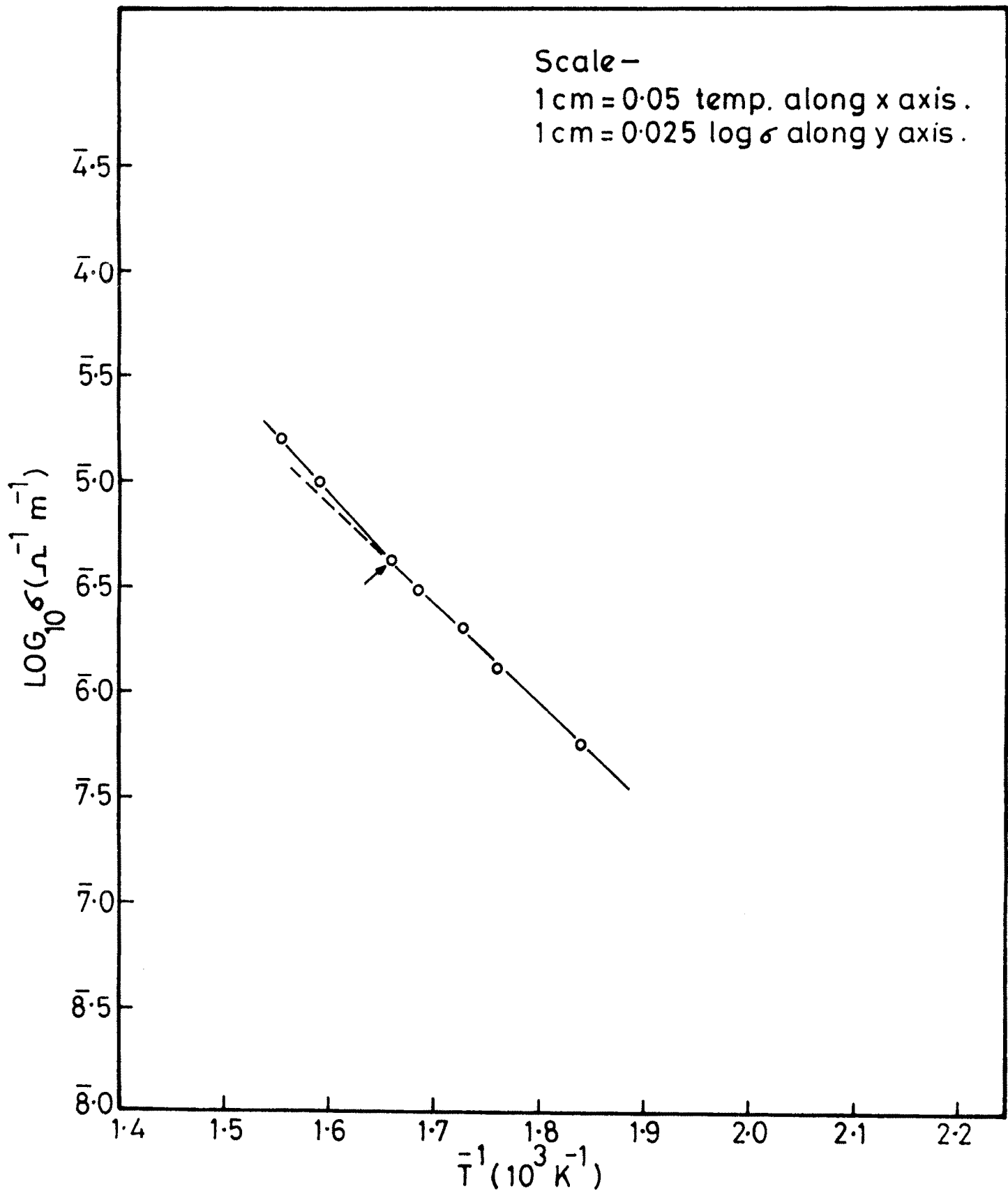


Fig. 4.4 - VARIATION OF LOGARITHMIC CONDUCTIVITY WITH  $1/T$  FOR  $\text{NaVO}_3 + 0.025 \text{ Mol \% Nd}_2\text{O}_3$ .

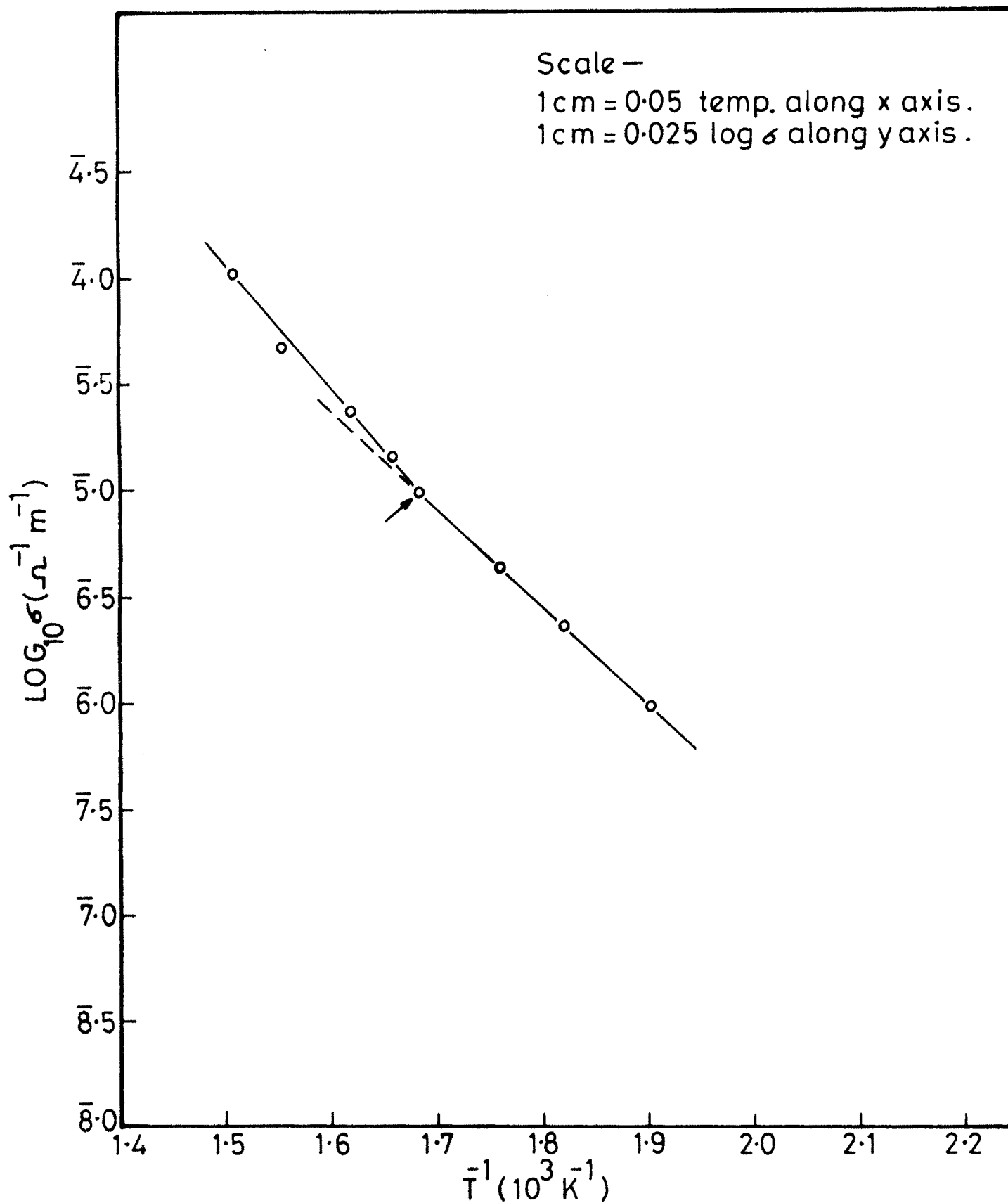


Fig. 4.5 - VARIATION OF LOGARITHMIC CONDUCTIVITY WITH  $1/T$  FOR  $\text{NaVO}_3 + 0.05 \text{ Mol \% Nd}_2\text{O}_3$ .

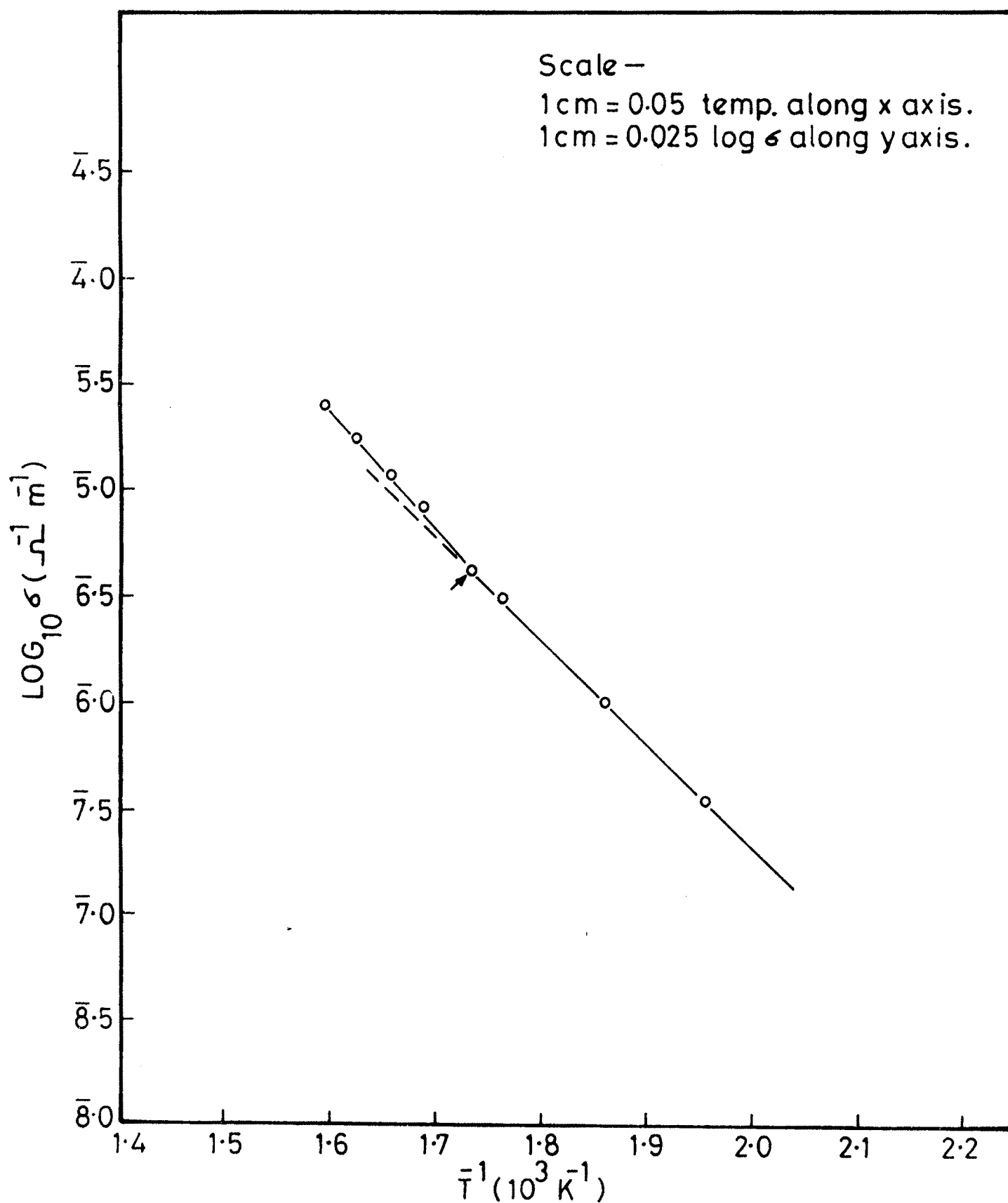


Fig. 4.6 – VARIATION OF LOGARITHMIC CONDUCTIVITY WITH  $1/T$  FOR  $\text{NaVO}_3 + 0.1 \text{ Mol \% Nd}_2\text{O}_3$ .

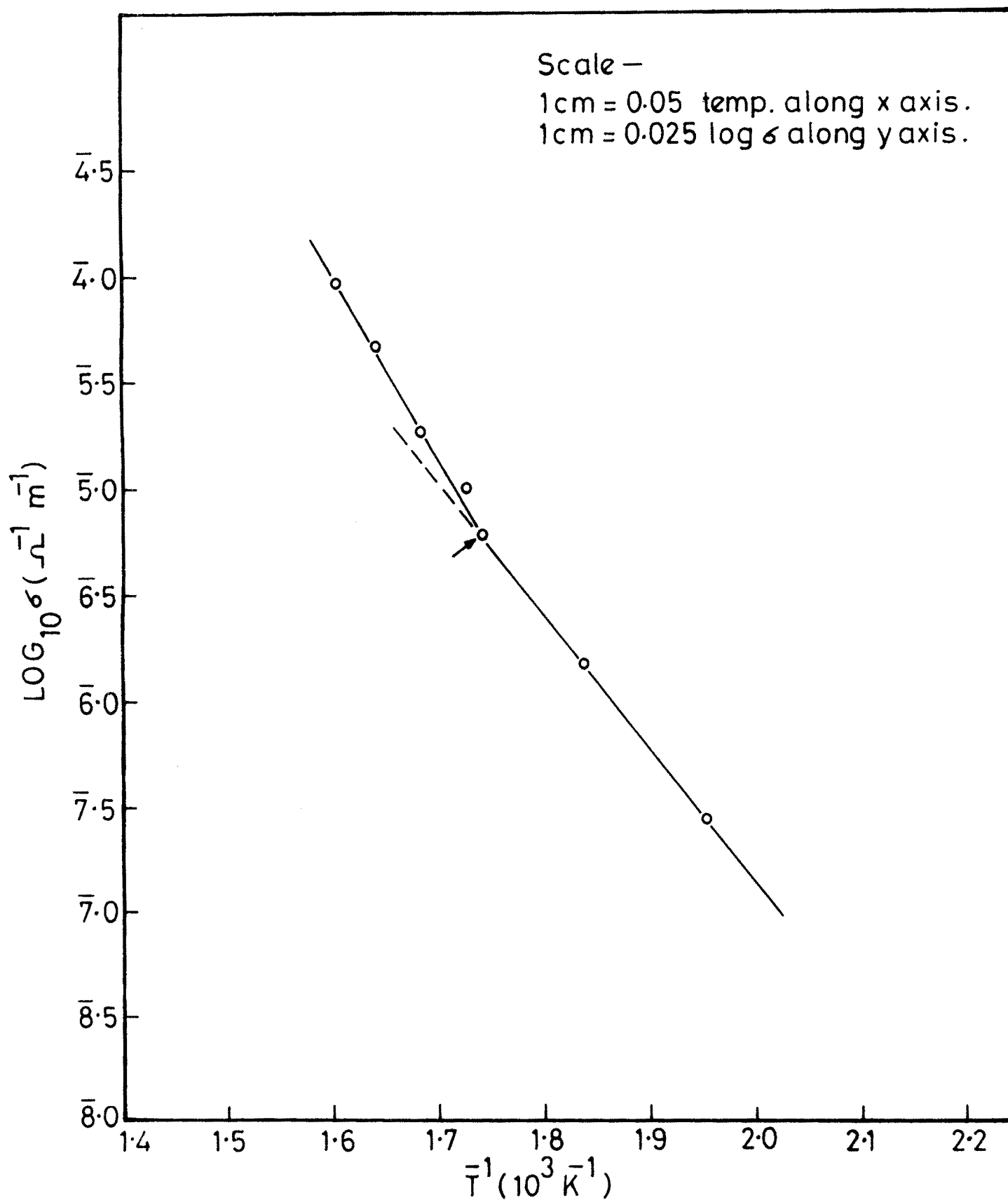


Fig. 4.7— VARIATION OF LOGARITHMIC CONDUCTIVITY WITH  $1/T$  FOR  $\text{NaVO}_3 + 0.5 \text{ Mol } \% \text{Nd}_2\text{O}_3$ .

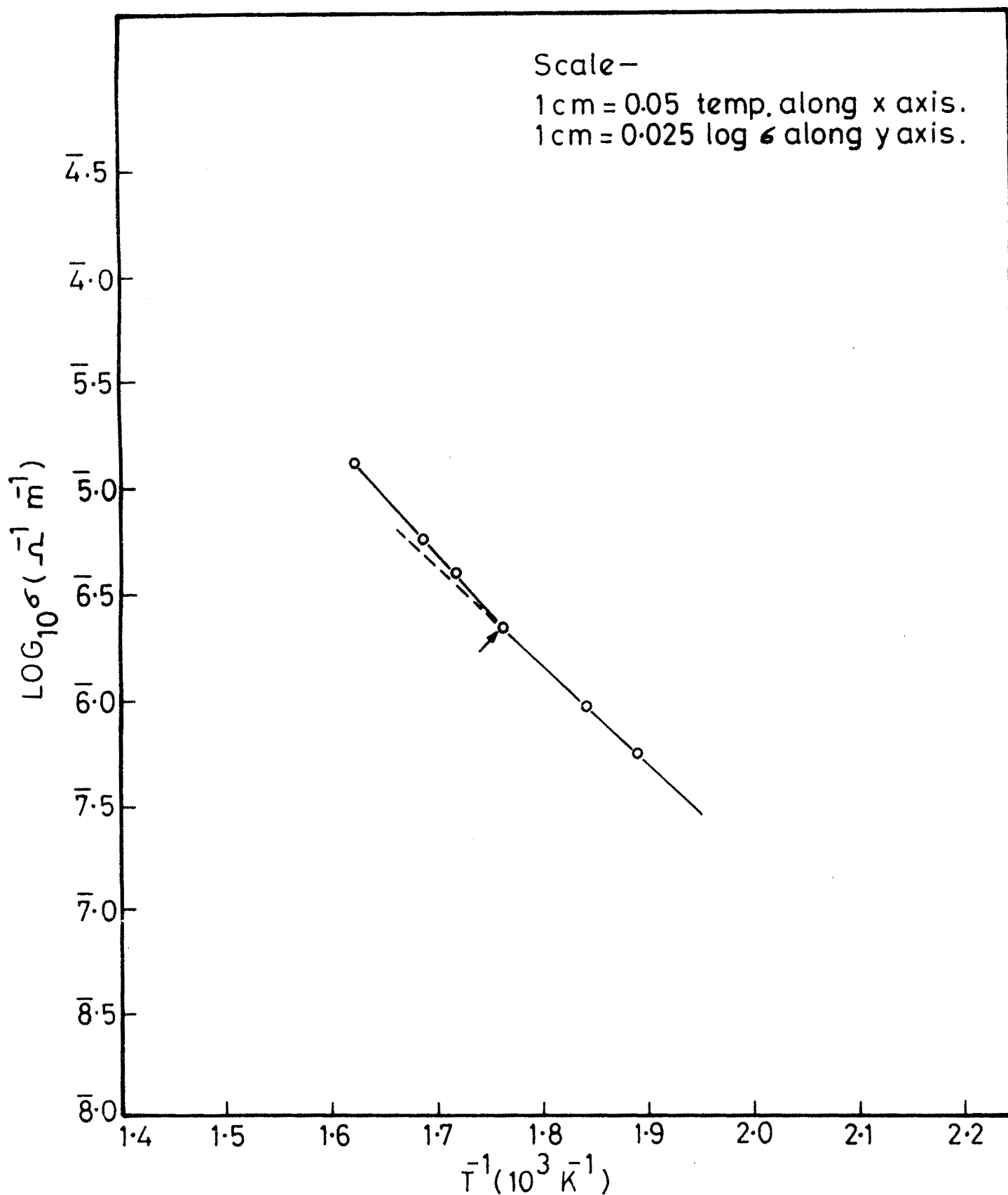


Fig.4.8— VARIATION OF LOGARITHMIC CONDUCTIVITY WITH  $1/T$  FOR  $\text{NaVO}_3 + 1.0 \text{ Mol } \% \text{Nd}_2\text{O}_3$ .

Scale -

1 cm = 0.2 log t along x axis

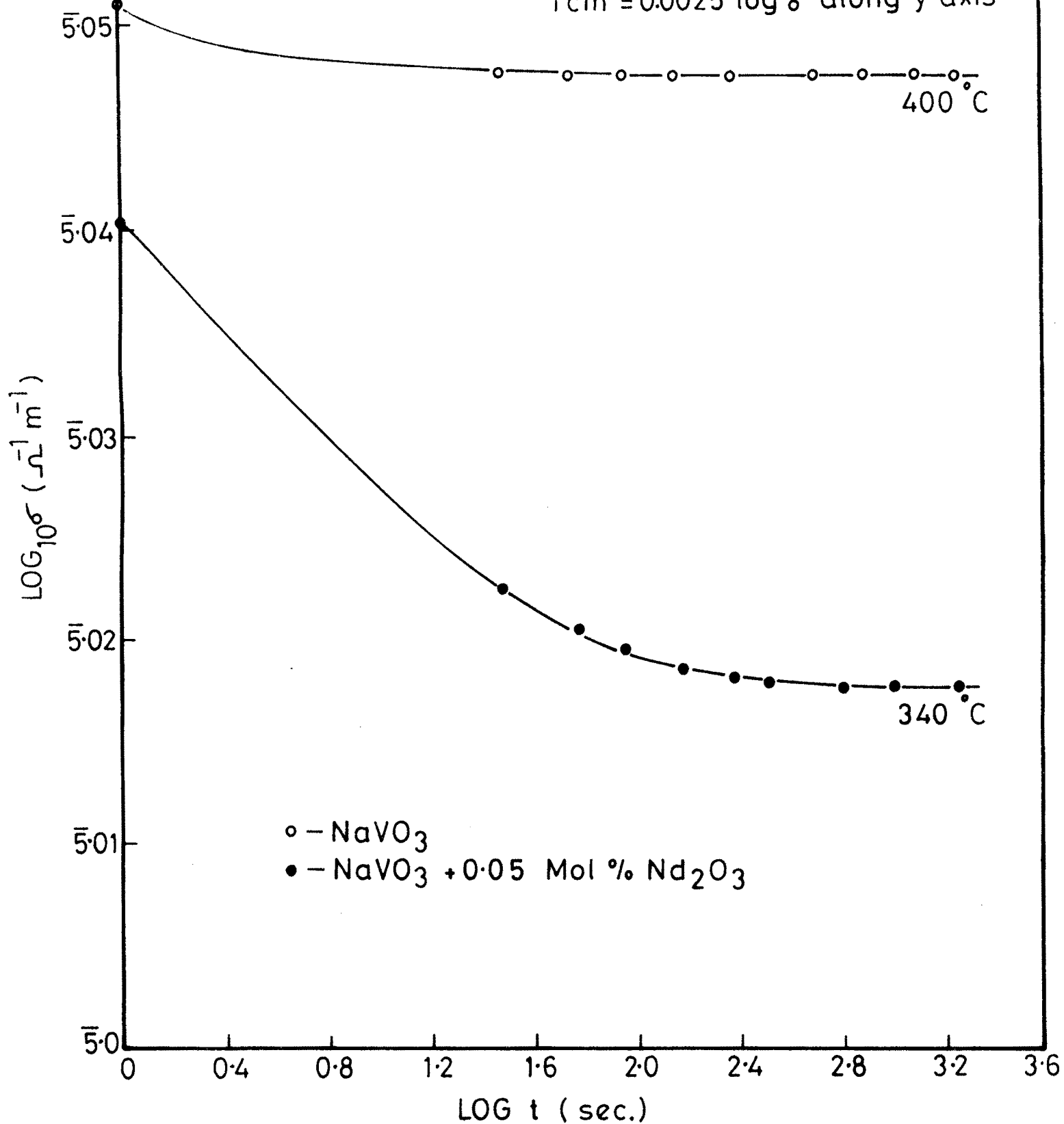
1 cm = 0.0025 log  $\sigma$  along y axis

Fig. 4.9 - VARIATION OF LOG  $\sigma$  WITH LOG t FOR NaVO<sub>3</sub> AND NaVO<sub>3</sub> + 0.05 Mol % Nd<sub>2</sub>O<sub>3</sub> ABOVE T<sub>c</sub>.

Scale -

1cm = 0.2 log t along x axis.

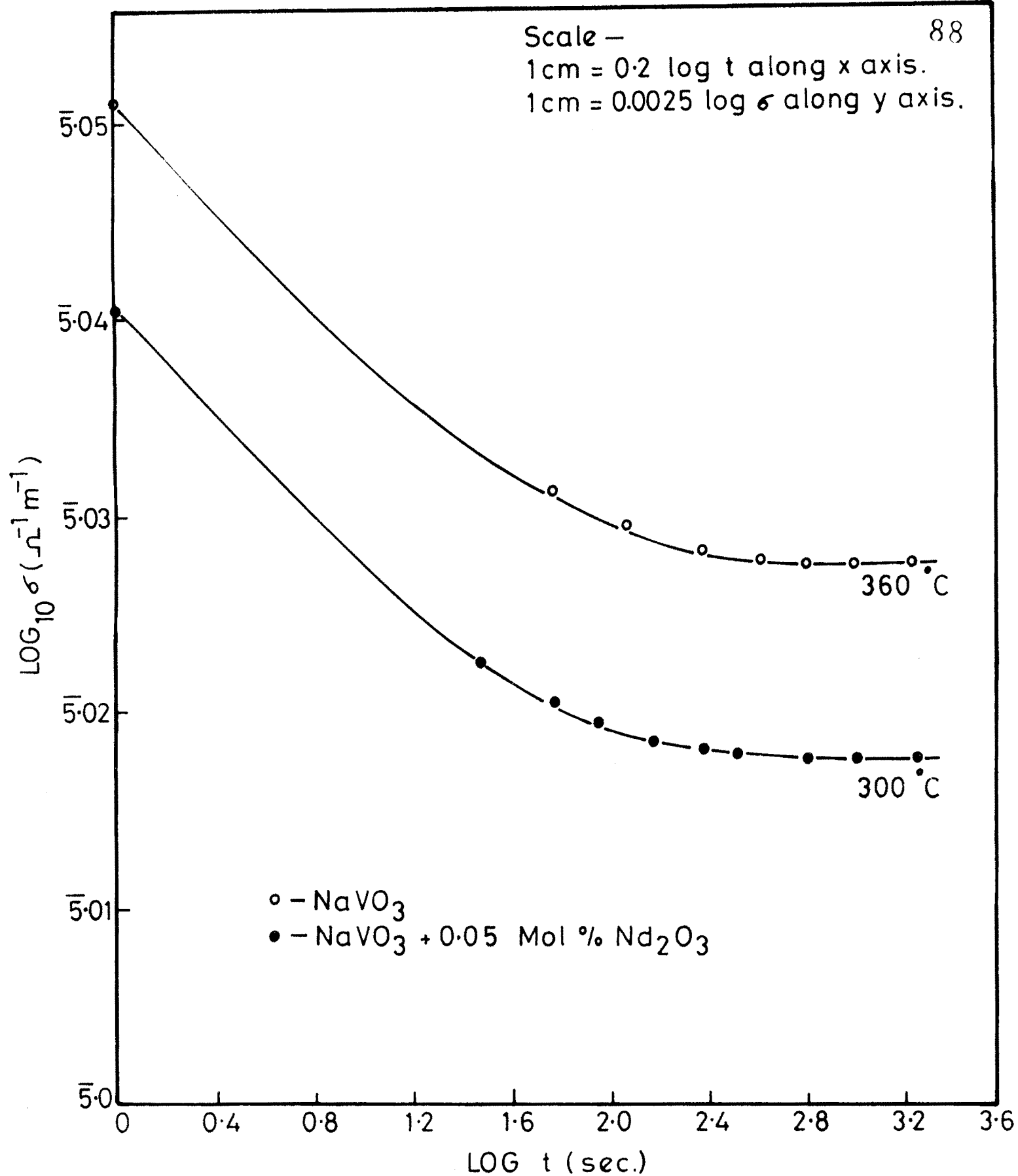
1cm = 0.0025 log  $\sigma$  along y axis.

Fig. 4.10 - VARIATION OF LOG  $\sigma$  WITH LOG t FOR  $\text{NaVO}_3$  AND  $\text{NaVO}_3 + 0.05 \text{ Mol } \% \text{ Nd}_2\text{O}_3$  BELOW  $T_c$ .



#### 4.4 Results and discussion :

The variation of  $\log\sigma$  with  $T^{-1}$  for undoped sodium vanadate and doped with different concentrations of Neodymium oxide (0.025, 0.05, 0.1, 0.5 and 1 mol%) are shown in figs [(4.3) to (4.8)] respectively. From these figures, it reveals that for undoped sodium vanadate and doped with different concentrations of Neodymium oxide the d.c. conductivity increases exponentially and sharp change in conductivity is observed at the transition temperature ( $T_C$ ). These transition temperatures are ferroelectric curie temperatures of respective samples, 380°C for sodium vanadate which we have confirmed by hysteresis loop method. It is in good agreement with those reported by Sawada and Nomura (1951), Chavan and Suryawanshi (1985) and Patil et al (1988). It is observed from the figs [(4.3) to (4.8)] that there is change in curie temperatures of  $\text{NaVO}_3$  doped with  $\text{Nd}_2\text{O}_3$ . It is also observed that the conductivity increases with increase of dopant content at low  $\text{Nd}_2\text{O}_3$  concentrations (0.025, 0.05, 0.1, 0.5 mol%) and exhibits a maximum at a specific content (0.5 mol%) and it begins to decrease for higher dopant content (1 mol%) of  $\text{Nd}_2\text{O}_3$ . The activation energies both in ferroelectric and paraelectric states are evaluated from the slope of  $\log\sigma$  against  $T^{-1}$  plots and their values are summarized in

table(4.1) for undoped  $\text{NaVO}_3$  and doped with  $\text{Nd}_2\text{O}_3$ .

Table(4.1) : Activation energies, Curie temperatures and Densities of material  $\text{NaVO}_3$ .

Nd <sub>2</sub> O <sub>3</sub> content (Mole %)	Activation energy (ev)		Curie Temp. (°C)	Density (g/cm <sup>3</sup> )
	Ferro-state	Para-state		
0	0.390	0.660	380	2.78
0.025	0.369	0.396	330	2.61
0.05	0.372	0.476	320	2.65
0.1	0.378	0.478	310	2.69
0.5	0.502	0.678	300	2.75
1	0.380	0.476	290	2.68

From table(4.1), it is observed that the activation energy in ferroelectric state is smaller than in paraelectric state, and it depends upon the concentrations of Neodymium oxide ( $\text{Nd}_2\text{O}_3$ ). Activation energy is maximum at a particular content (0.5 mol%).

Electrical conductivity is due to migration of ions or electrons or both. To investigate the nature of electrical conductivity, one has to distinguish which are the principal charge carriers. It is well known that the d.c. conductivity in a pure ionic conductor decreases with time. In the case of pure electronic conductor, the conductivity is independent of time, while in mixed (ionic- electronic) conduction, the d.c.

conductivity first decreases with time and then acquires a constant value after a long time. For undoped  $\text{NaVO}_3$  doped with 0.05 mol% of  $\text{Nd}_2\text{O}_3$ , the graphical variation of  $\log \sigma$  with  $\log t$  at constant temperature is shown in fig(4.9) and (4.10), indicate that the d.c. conductivity below and above transition temperature ( $T_C$ ) is mixed type (ionic-electronic). For undoped  $\text{NaVO}_3$  the d.c. conductivity below transition temperature ( $T_C$ ) is mixed type (ionic-electronic) while above transition temperature ( $T_C$ ), it is electronic. The effect of  $\text{Nd}_2\text{O}_3$  doping on the d.c. electrical conductivity of  $\text{NaVO}_3$  ceramic indicates that the high activation energy of  $\text{NaVO}_3$  containing 0.5 mol%  $\text{Nd}_2\text{O}_3$  was attributed to a rather more solid state interaction that takes place in the materials. This can be studied from the pronounced increase of density with addition of  $\text{Nd}_2\text{O}_3$ . The maximum densification is observed at 0.5 mol% doping of  $\text{Nd}_2\text{O}_3$ . Thus in this investigation the dielectric saturation states are attained at 0.5 mol%  $\text{Nd}_2\text{O}_3$  addition, which may represent the solubility limit of  $\text{Nd}_2\text{O}_3$  in  $\text{NaVO}_3$  lattices.

From the experimental observations the following conclusions could be noted.

(1) The d.c. electrical conductivity for undoped  $\text{NaVO}_3$  below

curie temperature ( $T_c$ ) is mixed type (ionic-electronic), while above the curie temperature ( $T_c$ ), it is electronic. In the case of all doping mixtures the d.c. electrical conductivity below and above the curie temperature is mixed type (ionic-electronic).

- (2) The d.c. electrical conductivity of all the materials increases with increase of temperature exponentially, both in ferroelectric and paraelectric regions.
- (3) A sharp change in electrical conductivity is observed at phase transition temperature, indicating the ferroelectric curie temperatures of the respective materials.
- (4) The curie temperatures of doping mixtures are changed with respect to undoped sodium vanadate.
- (5) The activation energy of all the materials is higher in the paraelectric state than in ferroelectric state and it depends upon doping concentrations of  $Nd_2O_3$ .
- (6) The activation energy is maximum at specific content (0.5 mol%) of  $Nd_2O_3$ .
- (7) The curie temperature decreases with increase of doping concentration.

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