Electrical properties of vanadium pentoxide doped with lithium and sodium in the α -phase range

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The electrical conductivity and Seebeck coefficients have been measured from room temperature to 500° C for polycrystalline V_2O_5 and V_2O_5 doped with lithium and sodium in the α-phase range. The conductivity increases with doping and the energy of activation decreases. The Seebeck coefficient indicates that electrons are the majority carriers. The results have been discussed in terms of the two-level hopping model.

1. Introduction

Vanadium pentoxide is a widely used oxidation catalyst. Alkali metal ions are often incorporated in it as promoters but the mechanism of their action is not well understood. The important role of electrical properties in selecting an oxidation catalyst is being realized more and more in the fields concerned [1–4].

It has been observed that with the addition of alkali metal ions, V_2O_5 forms a series of phases of composition $M_xV_2O_5$. For $x \leqslant 0.02$, the structure of V_2O_5 (orthorhombic) is retained for $Na_xV_2O_5$ [5–6]. In the range $0.22 \leqslant x \leqslant 0.40$, the β-phase is formed which is monoclinic [7–8]. Both the α and β-phase have distorted VO_6 octahedra as their structural unit, and have comparable V–O and near-neighbour V–V distances [9]. These common structural features are likely to show some similarities in their conduction mechanism. However, the activation energy of conduction in the β-phase is very much lower (0.05 eV) [10] than that of vanadium pentoxide (0.2 eV) [11].

The present work was undertaken to investigate the role of a small quantity of alkali metal ions incorporated in the V_2O_5 lattice on its electrical properties. This may provide basic data to elucidate the mechanism of oxidation of V_2O_5 catalysts doped with alkali metal ions. The results of catalytic oxidation reaction studies will be reported elsewhere.

2. Experimental methods

Vanadium pentoxide was prepared by heating powdered ammonium metavanadate in air at 400° C [12, 13]. Analar grade alkali metal carbonates in requisite amounts were thoroughly mixed with V_2O_5 in an agate mortar by adding benzene. No particular care was taken to control the powder size, but the mixture after drying passed easily through a 400 mesh B.S.S. sieve. The dry powder was then compressed into pellet form under 5 ton in.$^{-2}$ pressure and heated at 450° C for 24 h. The pellets were then ground in an agate mortar, thoroughly mixed under a benzene medium and the dried mass was pelletized as before using a punch and die of 2 cm i. di. and heated at 450° C for another 24 h. Pellets with thickness 2 and 0.3 cm were used for the measurement of Seebeck coefficient and electrical conductivity, respectively.

The packing density of the pellets was determined from their mass and volume as obtained by measuring the dimensions of the pellets with a micrometer screw gauge. It was found to be about 60% of the X-ray density.

X-ray powder diffraction patterns were taken on Philips PW 1051 X-ray diffractometer using Cu$K\alpha$ radiation filtered through a nickel foil.

The electrical conductivity was measured by using the four-probe technique. The four probes (of Pt/Pt–10% Rh wires; 24 SWG) were embedded collinearly at equal distances 0.25 cm into a calcia-

stabilized zirconia block. The lead wires (of pure platinum; 24 SWG) were spot-welded to these probes and taken out through a four-bore re-crystallized alumina tube. This tube, which passed through an aluminium cap, was attached to the cap by means of three tension springs. When the sample was fixed in the holder, the springs helped to provide a good pressure contact of the probes against the sample. The sample was placed in the cavity of a zirconia block. The system was kept in the constant temperature zone of a tubular furnace, whose temperature was controlled by a Philips plastomatic temperature controller. The sample temperature was measured by a chromel-alumel thermocouple.

The outer two probes were connected in series with a standard resistance and a d.c. power supply. The potential drops across the inner probes of the sample and of the standard resistance were measured by a Philips d.c. microvoltmeter (P 9004). The ohmic nature of the contact was confirmed by the linearity of the potential-current plots. The necessary correction factors for the sample diameter and thickness were obtained from the literature [14, 15].

For Seebeck coefficient measurement, a pellet 2 cm thick was pressed between two platinum discs fixed at the end of two ceramic blocks; one of these blocks was spring-loaded to obtain good contact. The sample was placed in the constant temperature zone of a vertical tubular furnace. In order to impose the necessary gradient in temperature, an auxiliary heater was wound over the top ceramic block. The temperatures of the ends of the sample were measured with chromel-alumel thermocouples, placed in such a way as to touch the sample ends. These junctions were insulated from the platinum discs by thin mica sheaths. During measurements, the sample was equilibrated at each temperature and then a gradient of 5 to $10°C$ was produced by the auxiliary heater. The thermoelectric voltage across the sample was measured on a d.c. microvoltmeter.

3. Results

Figure 1 shows the logarthmic plots of con-ductivity (σ) against reciprocal temperature for various samples. Table I shows the energy of activation below and above the breaks observed in the plots (between 242 and 337° C). Seebeck co-efficient (α) versus temperature plots have been shown in Fig. 2. α is negative throughout and has

TABLE I Energy of activation

Composition	Energy of activation (eV)	
	Low temperature	High temperature
V_2O_5	0.21 (300–595 K)	0.37
$Li_{0.002}V_2O_5$	0.20 (300–562 K)	0.36
$Li_{0.006}V_2O_5$	0.19 (300–515 K)	0.26
$Li_{0.02}V_2O_5$	0.18 (300–610 K)	0.10
$Li_{0.06}V_2O_5$	0.16 (300–582 K)	0.10
$Na_{0.002}V_2O_5$	0.19 (300–549 K)	0.26
$Na_{0.006}V_2O_5$	0.17	0.17
$Na_{0.02}V_2O_5$	0.15	0.15
$Na_{0.06}V_2O_5$	0.13 (300–544 K)	0.10

a value of 1130 $\mu V °C^{-1}$ at room temperature for pure V_2O_5, close to the value reported by Vinogradov and Shelykh [16]. With increased doping concentration α decreases. The con-centration of the conduction electrons has been obtained using the relation:

$$\sigma = n e \mu, \qquad (1)$$

where σ is the conductivity ($\Omega^{-1} cm^{-1}$), n is the concentration of conduction electrons/cm^3, e is the electronic charge and μ is the drift mobility in $cm^2 V^{-1} sec^{-1}$. A reliable measurement of the Hall effect in the polycrystalline materials of low con-ductivity is a difficult task. This is reflected in the reported mobility data for V_2O_5 at room tempera-ture which varies from 0.03 [17] to 2.2 $cm^2 V^{-1} sec^{-1}$ [18]. This discrepancy is obviously due to experimental difficulties. Perlstein [19] has assumed that the mobility of the charge carrier in the α- and β-phases are the same, considering the similarities in the local vanadium site symmetry in the two phases. Using a value 0.2 $cm^2 V^{-1} sec^{-1}$ for the β-phase as reported by Perlstein and Sienko [10], he calculated the charge carrier concen-tration of V_2O_5 and copper-doped V_2O_5. Since our attempts to measure the Hall coefficient of polycrystalline V_2O_5 did not yield consistent results, we have used the value 0.03 $cm^2 V^{-1} sec^{-1}$ reported for the V_2O_5 single crystal by Ioffe and Patrina [17]. The results are presented in Table II column B.

In the doped samples, the carrier concentration was also calculated from the dopant concentration assuming the reaction

$$\frac{x}{2} Li_2CO_3 + V_2O_5 \longrightarrow Li_xV_2O_5 + \frac{x}{2} CO_2 + \frac{x}{2} O_2 + 2xe \qquad (2)$$
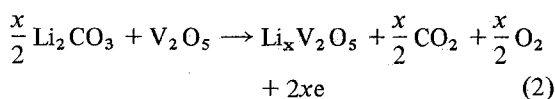
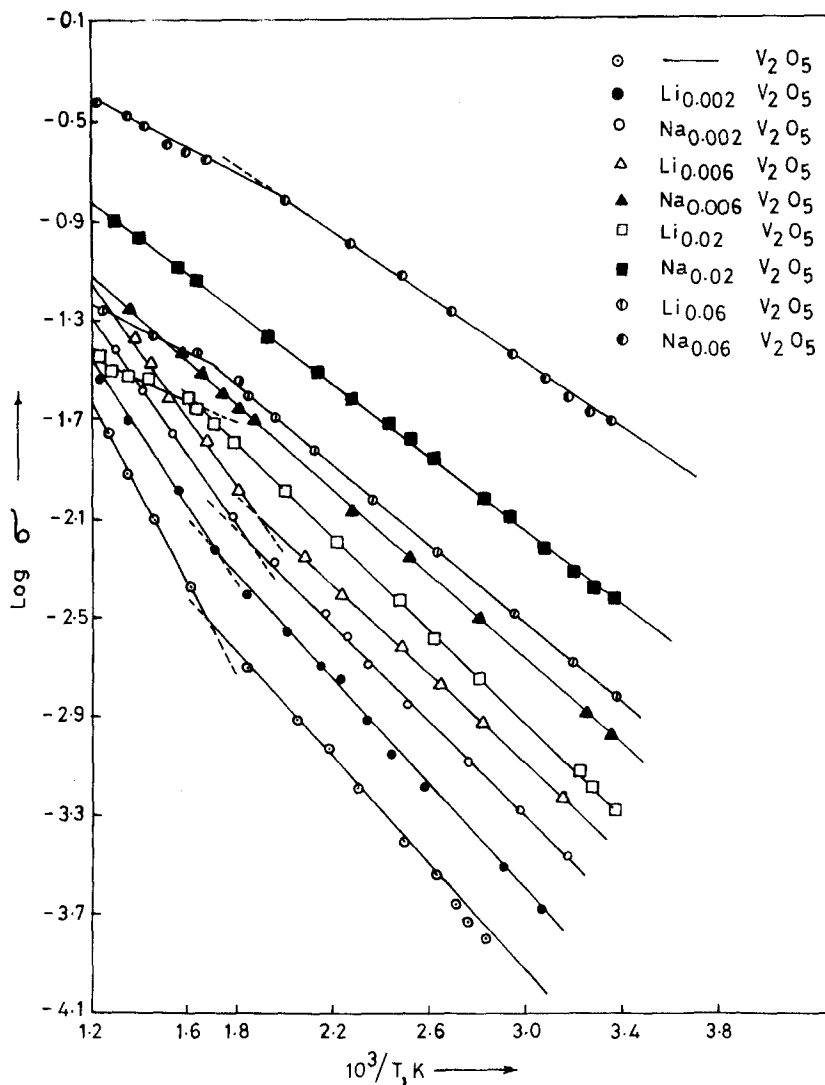The assumption that each alkali metal atom con-

Figure 1 Log σ versus $1/T$ plots for pure and doped V_2O_5.

TABLE II Electrical conductivity and charge carrier concentration at $25°C$ for V_2O_5 and doped V_2O_5 samples

	Conductivity $(\Omega^{-1}\ cm^{-1} \times 10^{-3})$	Charge carrier concentration/cm^3	
		A*	B†
V_2O_5	0.05		1.04×10^{16}
$Li_{0.002}\,V_2O_5$	0.115	1.43×10^{19}	$2.4\ \times 10^{16}$
$Li_{0.006}\,V_2O_5$	0.38	4.29×10^{19}	$7.9\ \times 10^{16}$
$Li_{0.02}\,V_2O_5$	0.525	1.43×10^{20}	1.09×10^{17}
$Li_{0.06}\,V_2O_5$	1.51	4.29×10^{20}	3.14×10^{17}
$Na_{0.002}\,V_2O_5$	0.24	1.43×10^{19}	$5.0\ \times 10^{16}$
$Na_{0.006}\,V_2O_5$	1.05	4.29×10^{19}	2.19×10^{17}
$Na_{0.02}\,V_2O_5$	3.8	1.43×10^{20}	7.92×10^{17}
$Na_{0.06}\,V_2O_5$	19.5	4.29×10^{20}	4.06×10^{18}

* Obtained from alkali metal atom concentration.
† Obtained from electrical conductivity using $\mu = 0.03\ cm^2\ V^{-1}\ sec^{-1}$.

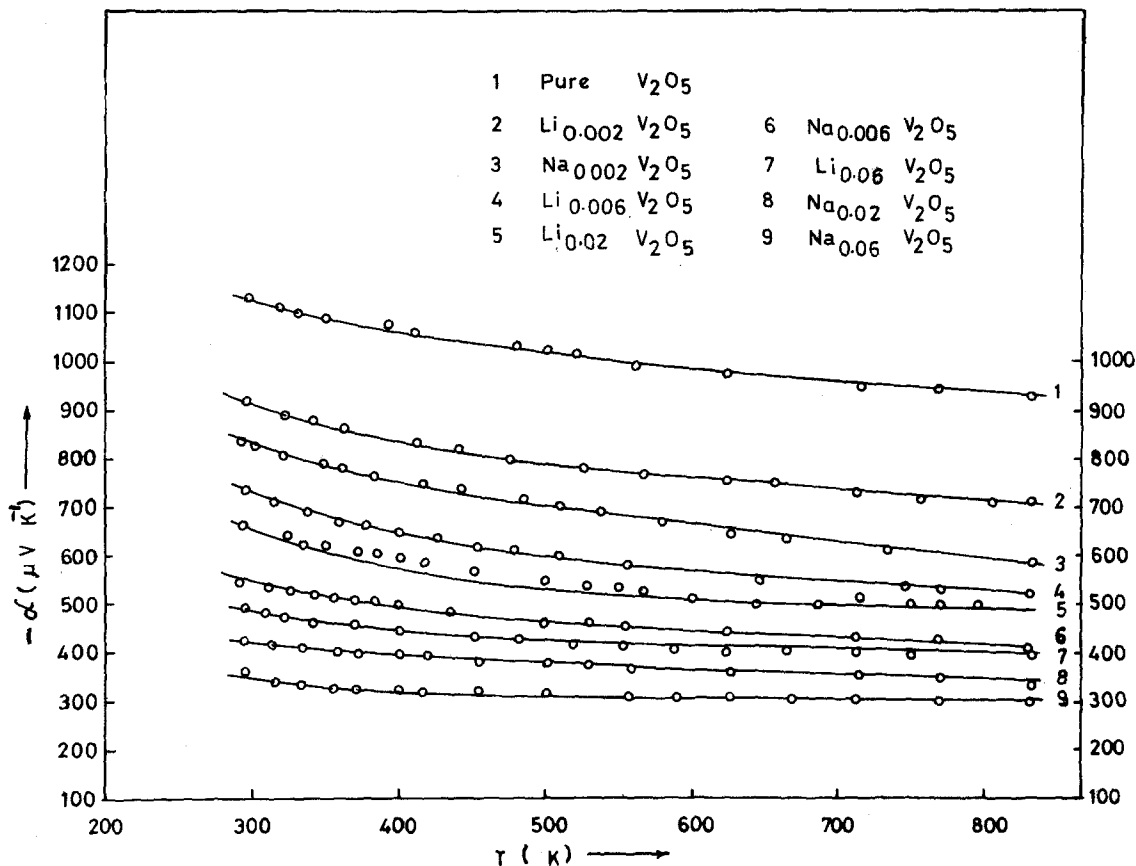| 1 | Pure | V_2O_5 | | |
2	$Li_{0.002}$	V_2O_5	6	$Na_{0.006}$ V_2O_5
3	$Na_{0.002}$	V_2O_5	7	$Li_{0.06}$ V_2O_5
4	$Li_{0.006}$	V_2O_5	8	$Na_{0.02}$ V_2O_5
5	$Li_{0.02}$	V_2O_5	9	$Na_{0.06}$ V_2O_5

Figure 2 Seebeck coefficient (α) versus temperatures plots for pure and doped V_2O_5.

tributes one electron to the V_2O_5 lattice seems justified by the esr studies of $Li_{0.33}V_2O_5$ by Gendell *et al.* [20] and the Hall voltage measurements of $Na_{0.33}V_2O_5$ by Perlstein and Sienko [10]. Furthermore, the absense of a Knight shift in the nmr of Li^7 in $L_{0.33}V_2O_5$ indicates that the Li^+ ions are completely ionized [20]. Compared to the β-phase, the α-phase contains a much smaller percentage of the alkali metals and it is natural to assume that they will be completely ionized, donating one electron per alkali metal atom.

In calculating the charge carrier concentration, appropriate corrections were introduced for the bulk density of the pellets ($2.16 \, g \, cm^{-3}$ for a typical V_2O_5 pellet) as against X-ray density ($3.36 \, g \, cm^{-3}$). Since doping did not change the lattice parameters of V_2O_5 as shown by their X-ray diffraction patterns (Fig. 3), the same X-ray density was assumed for the doped samples as the quantity of the dopant was small. The carrier concentration obtained from the alkali metal atom concentration

(Table II column A) was found to be much greater than that obtained from conductivity.

4. Discussion

The exponential dependence of mobility on temperature in V_2O_5 single crystals as reported by Volzhenskii *et al.* [21] as well as the constancy of the Seebeck coefficient over a wide temperature range as observed here is inconsistent with the band model suggested by Clark and Berets [12] to explain the conductivity in V_2O_5. It has been suggested by others [21, 22] that the conduction in V_2O_5 is due to its non-stoichiometry, leading to the hopping of electrons from V^{4+} to V^{5+} sites. Hence an increase in the density of V^{4+} states as affected by incorporating alkali metals into the lattice, should increase the conductivity. An increase in conductivity with doping has been observed in all our samples. However, the energy of activation for mobility in the hopping model should remain constant as long as the closest V—V distance is not changed. Our results, on the other
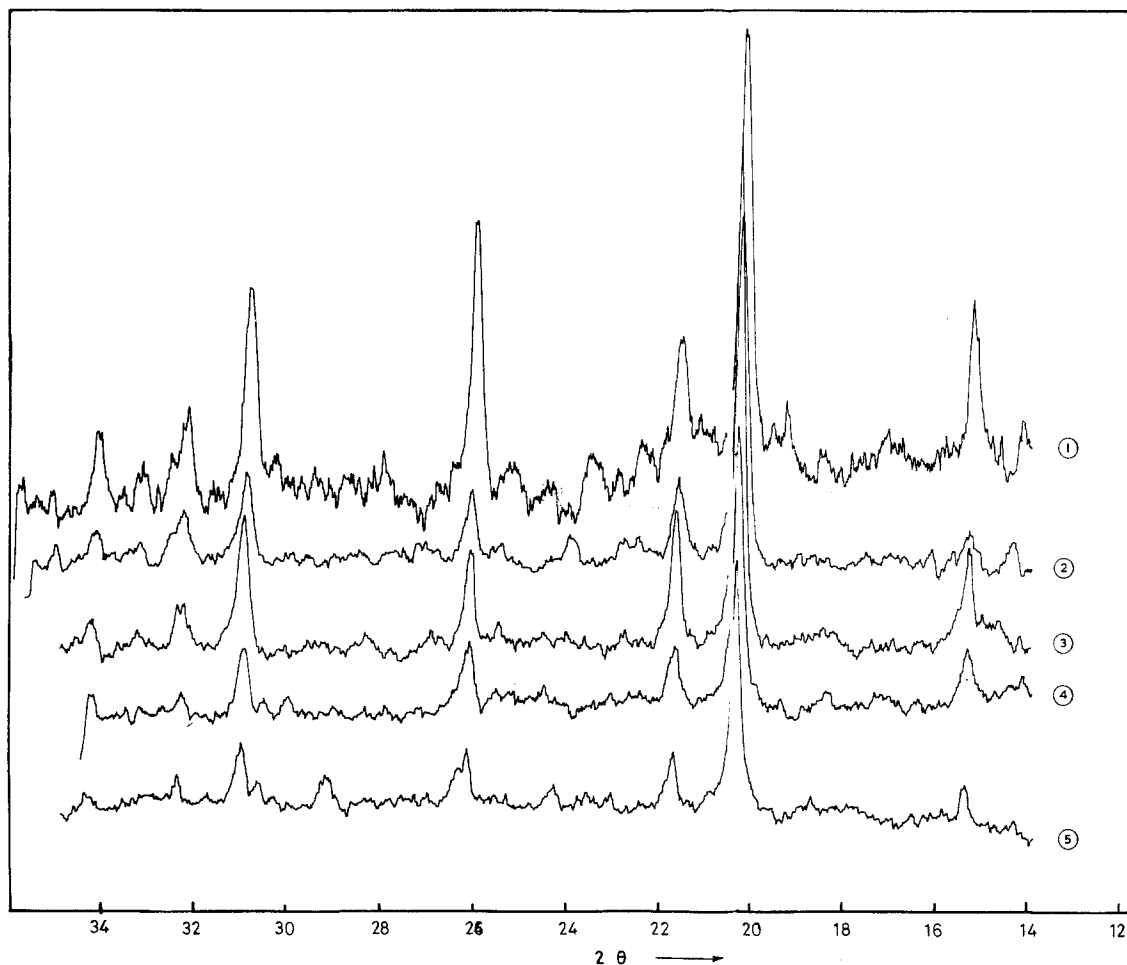
Figure 3 X-ray diffraction patterns: (1) V_2O_5; (2) $Na_{0.002}V_2O_5$; (3) $Na_{0.006}V_2O_5$; (4) $Na_{0.02}V_2O_5$; (5) $Na_{0.06}V_2O_5$.

hand, showed a regular decrease in the activation energy with increased doping, although the structure apparently remained unchanged. The carrier concentration obtained from the alkali metal concentration was found to be considerably greater than that obtained from conductivity, and was also found to increase with temperature. These observations cannot be explained by the conventional hopping model.

In order to explain the electrical properties of copper-doped V_2O_5, Perlstein [19] proposed a dislocation model based on the crystal structure of V_2O_5 reported by Bystrom *et al.* [23] and Bachmann *et al.* [24]. Its essential features are: a dislocation structure is formed by the slippage of *a-c* planes by 0.2 lattice spacings along the *a*-axis and 0.5 lattice spacings along the *c*-axis. Such dislocation gives rise to one oxygen interstitial per V_4O_{10} unit cell. This will bring two vanadium atoms of adjacent planes in the same line along the

b-axis forming a vanadium pair per unit cell. The electrons from the oxygen interstitials or from interstitial impurities may be trapped in the molecular orbital of the V−V pair. Conduction at higher temperature will involve breaking of the molecular orbital forming the V−V pair with the electron left at one vanadium site. This electron then hops from one vanadium site to another which forms a zig-zag chain along the *c*-axis with a V−V distance 3.08 Å. Perlstein postulates that the energy of hopping is 0.05 eV, the same as in the β-phase, and the energy necessary to break the V−V pair is 0.15 eV. The activation energy of conduction is the sum of these two quantities, which agrees well with the experimental activation energy of conduction, 0.2 eV, for V_2O_5. The pairs are separated by 3.55 Å along the *c*-axis. Below 170 K, conductivity is due to hopping between these pair states with an activation energy of 0.077 eV.

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The above model can satisfactorily explain the conductivity at low temperature (below 170 K) but it needs the energy of activation to remain constant with varying dopant concentration. Although this was found to be true for conductivity below 170 K, above this temperature the results obtained by Perlstein [19] were not consistent. However, the measurements were not extended above room temperature.

Our measurements up to 500° C and a limited number of measurements reported in [25] showed a regular decrease in activation energy with increasing doping. This is inconsistent with the dislocation model. The simple hopping model cannot be applied either, due to reasons already stated. The difference between the carrier concentration obtained from conductivity and dopant concentration can be explained by assuming that the electrons are initially trapped at the trapping centres and hence are not available for conduction unless thermally excited. However, the trapping centres are possibly oxygen defects and not the V—V pairs. The decrease in activation energy with increase in dopant concentration then can be explained as due to increased population in the trapping levels, thus reducing the energy gap between the conduction states and the trapping levels. The electrons are first raised to a vanadium

site from the trapping level and these then hop from V^{4+} to V^{5+} sites.

For two-level hopping conduction, the following equation was obtained for the Seebeck coefficient [19]

$$\alpha = -\frac{k}{e}\left\{\frac{\Delta E}{kT}(1 - \sigma_t/\sigma) + \ln \frac{N_t}{[M]}\right\} \quad (3)$$

where k is Boltzmann's constant, ΔE is the energy difference between the trapping level and the conduction states, σ_t is the contribution to conductivity due to electron hopping between trapping sites, N_t is the density of trapping sites and $[M]$ is the concentration of the impurity metal. At higher temperature $\sigma_t/\sigma = 0$, and Equation 3 becomes

$$\alpha = -\frac{k}{e}\left[\frac{\Delta E}{kT} + \ln \frac{N_t}{[M]}\right]. \quad (4)$$

From the dislocation model [19], $N_t = 5.7 \times 10^{21}$. This equation predicts that α should almost remain constant in the high temperature region, which is in agreement with our results. In the low temperature region, the contribution from σ_t/σ will be considerable and α should fall with decrease in temperature, which has been observed by Patrina and Ioffe [11].
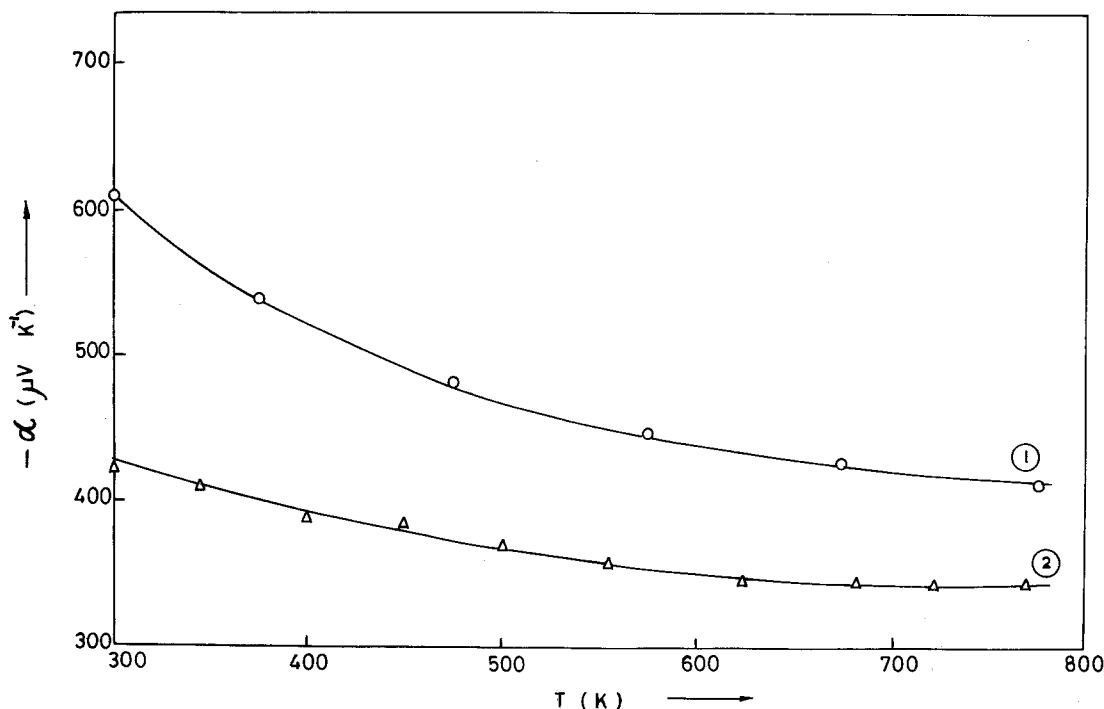
Fig. 4 shows α versus T plots for the sample

Figure 4 Variation of Seebeck coefficient with temperature for the sample $Na_{0.02}V_2O_5$: (1) calculated from Equation 4; (2) experimental.

$Na_{0.02}V_2O_5$ as calculated from Equation 4. The experimental plot is also given for comparison. In the high temperature region the two lines are parallel. However, the experimental results are consistently lower than the predicted value. This raises further doubt about the correctness of the N_t value and hence about the dislocation model.

The reason for break in the log σ versus $1/T$ plots for the samples $Li_{0.02}V_2O_5$, $Li_{0.06}V_2O_5$ and $Na_{0.06}V_2O_5$ (Fig. 1) is not clear. The results of differential scanning calorimetry do not show any phase transitions in this range.

5. Conclusions

The results on the electrical conductivity and Seebeck coefficient measurements of vanadium pentoxide doped with lithium and sodium can be explained in terms of a model in which the con-duction electrons are initially trapped as suggested by Perlstein [19]. However, the trapping centres may not be due to dislocations as suggested by him, and may be due to other reasons, such as oxygen defects.

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