Transport mechanism in semiconducting glassy silicon vanadates

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Measurements are reported for the electrical conductivity of the semiconducting glassy silicon vanadates in the temperature range 80–400 K. The experimental results have been analyzed with reference to the existing theoretical models of hopping conduction. The analysis shows that at high temperatures the conductivity data are consistent with Mott's model [J. Non-Cryst. Solids **1**, 1 (1968)] of phonon-assisted polaronic hopping, while Mott's variable range hopping model [Philos. Mag. **19**, 835 (1969)] is valid at low temperatures. The small polaron model of Schnakenberg [Phys. Status Solidi **28**, 623 (1968)] is also found to be consistent with the temperature dependence of the conductivity. The temperature dependence of the conductivity can also be interpreted in the framework of the percolation model proposed by Triberis and Friedman [J. Phys. C **18**, 2281 (1985)]. The analysis of the conductivity data also indicates that the hopping in these vanadate glasses occurs in the nonadiabatic regime.

I. INTRODUCTION

Recently the study of the electrical properties of amorphous transition metal (TM) oxides,[1] TM oxide gels,[2] and glasses containing TM ions[3–6] is of considerable interest, because of their various technological applications, namely electrical and optical switching devices.[2,7] These glassy materials exhibit semiconducting properties due to the presence of TM ions in multivalent states.[1–6] Electron-phonon interaction in them is strong enough that small polarons can be formed and it is generally agreed that the electrical conduction occurs by the hopping of small polarons between two different valent states of the TM ions.[8,9] The activation energy for the hopping conduction in these glasses is observed to be temperature dependent.[3–6,8,9] Glassy vanadates with different glass formers, like P_2O_5, GeO_2, etc., have been studied extensively.[3–6] However, reports on the electrical properties of the glassy vanadates with SiO_2 as a glass former are rare in the literature.[10] We have studied extensively the electrical transport properties of the glassy silicon vanadates. In this paper, the dc conduction mechanism in these vanadate glasses is reported in the temperature range 80–400 K.

II. THEORETICAL BACKGROUND

Different theories,[8,9,11–20] which have been used to interpret the results of the present work, are briefly discussed here. Mott[8] has proposed a model for electrical conduction in TM oxide glasses in which the conduction process is considered in terms of phonon-assisted hopping of small polarons between localized states. The dc conductivity in this model for the nearest neighbor hopping in the nonadiabatic regime at high temperatures ($T > \theta_D/2$) is given by

$$\sigma = \nu_0[e^2 C(1-C)/kTR]\exp(-2\alpha R)\exp(-W/kT), \tag{1}$$

where ν_0 is the longitudinal optical phonon frequency, R is the average intersite separation, α is the inverse localization length of the s-like wave function assumed to describe the localized state at each site, C is the fraction of sites occupied by an electron or polaron and is therefore the ratio of the TM ion concentration in the low valent state to the total TM ion concentration, and W is the activation energy for the hopping conduction. Assuming a strong electron-phonon interaction, Austin and Mott[9] have shown that

$$W = \begin{cases} W_H + W_D/2 & \text{for } T > \theta_D/2 \\ W_D & \text{for } T < \theta_D/4, \end{cases} \tag{2}$$

where W_H is the polaron hopping energy, W_D is the disorder energy arising from the variation in the local arrangements of ions in glasses and θ_D is the Debye temperature. In the adiabatic limit, the overlap term $\exp(-2\alpha R)$ in Eq. (1) reduces to unity. An estimate of the hopping energy is also given by[9]

$$W_H = e^2/4\epsilon_p r_p, \tag{3}$$

where r_p is the polaron radius and ϵ_p is an effective dielectric constant given by

$$\epsilon_p^{-1} = \epsilon_\alpha^{-1} - \epsilon_0^{-1}, \tag{4}$$

where ϵ_0 and ϵ_α are the static and high frequency dielectric constants, respectively.

At low temperatures, where polaron hopping energy is small and disorder energy plays dominant role in the conduction process, Mott[11,12] has proposed that hop may occur preferentially beyond nearest neighbors. The conductivity for the so-called variable range hopping is predicted to be

$$\sigma = A \exp(-B/T^{1/4}), \tag{5}$$

where A and B are constants and B is given by

$$B = 2.1[\alpha^3/kN(E_F)]^{1/4}, \tag{6}$$

where $N(E_F)$ is the density of states at the Fermi level. Similar temperature dependence of the conductivity at low

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temperatures has been also obtained by Ambegaokar and co-workers[13] on the basis of percolation model.

Holstein and co-workers[14-16] have investigated a generalized polaron hopping model in the absence of disorder energy, covering both adiabatic and nonadiabatic hopping processes. On the basis of molecular crystal model, the dc conductivity has been deduced as[16]

$$\sigma = (3e^2NR^2J^2/2kT)(\pi/kTW_H)^{1/2}\exp(-W_H/kT) \quad (7)$$

for nonadiabatic hopping, while for adiabatic hopping it has been shown[15] that

$$\sigma = (8\pi Ne^2R^2\nu_0/3kT)\exp[-(W_H-J)/kT], \quad (8)$$

where N is the site concentration and J is the polaron band width related to the electron wave function overlap on adjacent sites. The condition for the nature of hopping is also given, in this model, by[14]

$$J \begin{array}{c} > \\ < \end{array} \left| (2kTW_H/\pi)^{1/4}(h\nu_0/\pi)^{1/2} \right| \begin{array}{l} \text{for adiabatic hopping} \\ \text{for nonadiabatic hopping,} \end{array} \quad (9)$$

with the condition for the formation of a small polaron being $J < W_H/3$.

A more general polaron hopping model has been proposed by Schnakenberg[17] considering disorder energy. In this model, optical multiphonon process determines the conductivity at high temperatures, while at low temperatures charge carrier transport is an acoustical one phonon-assisted hopping process. The conductivity in the Schnakenberg model has the form

$$\sigma \sim T^{-1}[\sinh(h\nu_0/kT)]^{1/2}\exp[-(4W_H/h\nu_0)$$
$$\times \tanh(h\nu_0/4kT)]\exp(-W_D/kT). \quad (10a)$$

It may be noted that the Eq. (10a) predicts a temperature dependent hopping energy given by

$$W_H' = W_H[\tanh(h\nu_0/4kT)]/(h\nu_0/4kT), \quad (10b)$$

which decreases with decreasing temperature.

Killias[18] has proposed a polaron hopping model in which the variation of the activation energy with temperature is considered to be due to thermally activated hopping in a system which has a distribution of hopping distances. Assuming a Gaussian distribution of hopping distances centered around a median value R_0, Killias has obtained the following expression for the conductivity:

$$\sigma = A\exp[-W(R_0)/kT - (a/2\beta kT)^2]$$
$$\times[1 - \tfrac{1}{2}\text{erfc}(\beta R_0 - a/2\beta kT)], \quad (11)$$

where A is a constant, $a = dW/dR$, and β^{-1} is proportional to the width of the Gaussian distribution. Equation (11) predicts a nonlinear variation of the conductivity which may be described conveniently by a temperature dependent activation energy given by[18]

$$W(T) = W_0(1 - \theta_R/T), \quad (12a)$$

where W_0 and θ_R are constants and the latter is given by

$$\theta_R = a^2/4\beta kW_0. \quad (12b)$$

Recently Triberis and Friedman[19] have applied percolation theory to the small polaron hopping regime in the disordered systems. Considering correlation due to the energy of a common site in a percolation cluster, they have obtained

$$\sigma = \sigma_0\exp[-(T_0/T)^{1/4}], \quad (13)$$

where the constant T_0 has different forms at high and low temperatures:

$$T_0 = \begin{cases} 12.5\alpha^3/kN_0 & \text{for high temperatures} \quad (13a) \\ 17.8\alpha^3/kN_0 & \text{for low temperatures,} \quad (13b) \end{cases}$$

where N_0 is the density of states assumed constant. It may be noted that Eq. (13) is similar to Eqs. (5) and (6) predicted by Mott's model with different values of T_0.

III. EXPERIMENTAL PROCEDURE

Glassy samples (Table I) were prepared from reagent grade V_2O_5 and SiO_2. The mixtures of these chemicals were melted in alumina crucibles at 1373 K for 2 h in air. The melts were quenched by pouring between twin rollers revolving in opposite directions. The glassy nature of the samples was confirmed by x-ray diffraction, electron microscopy, differential thermal analysis, and infrared (IR) spectroscopy. The concentrations of the total (N) and reduced (V^{4+}) vanadium ions were estimated from glass compositions and magnetic measurements, respectively. The density of the samples was determined by Archimedes' principle. The average intersite separation (R) was obtained from glass composition and density. The various physical parameters of the prepared glasses are shown in Table I.

For electrical measurements gold electrodes were deposited on both surfaces of the samples. The conductivity of the samples was measured using a Keithley (model 614) electrometer. Ohmic behavior at the contacts was ascertained from the linearity of the I-V characteristics. Low temperature measurements were carried out in a cryostat (Oxford). Measurements were made in the temperature range 80–400 K with a stability of ±0.5 K.

IV. RESULTS AND DISCUSSION

The logarithmic dc conductivity of the different glass compositions is shown in Fig. 1 as a function of reciprocal temperature. It is observed from the figure that the conductivity shows an activated behavior above ~200 K and

TABLE I. Glass compositions and physical parameters of glassy silicon vanadates.

Glass compositions		Density (g cm^{-3})	N (10^{-22} cm^{-3})	[V^{4+}] (10^{-20} cm^{-3})	C	R (Å)
V_2O_5	SiO_2					
80	20	2.46	1.50	6.98	0.039	4.05
90	10	2.77	1.77	8.21	0.055	3.84
95	05	2.90	1.89	11.70	0.062	3.76

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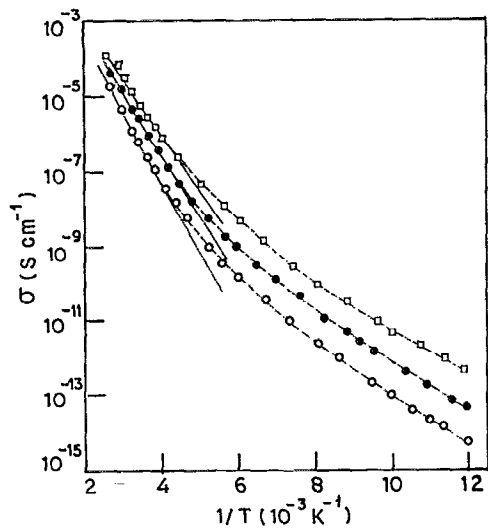
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FIG. 1. The dc conductivity shown as a function of reciprocal temperature for three sample compositions: O, 80 mol % V_2O_5; ●, 90 mol % V_2O_5; □, 95 mol % V_2O_5. The solid lines are fits to Eq. (1) predicted by Mott's model. The dashed curves are drawn through the data.

below this temperature the conductivity exhibits a nonlinear characteristic, indicating a temperature dependent activation energy which decreases with decreasing temperature.

Equation (1) predicted by the phonon-assisted hopping model of Mott can be fitted to the data in Fig. 1 at high temperatures. The best fits are observed above 200 K for the values of the parameters W, v_0, and α shown in Table II. It is noted in Table II that the activation energy W increases with decreasing vanadium content in the glass compositions similar to other vanadate glasses.[3–6] The values of v_0 do not differ appreciably for different compositions and are consistent with their estimates from the IR studies.[21] This observation suggests that the optical phonon distribution does not differ between different compositions. The values of α are reasonable for localized states and indicate strong localization[12] in glassy silicon vanadates.

An estimate of the polaron radius r_p may be obtained from Eq. (3), assuming $W \approx W_H$ and $W_H > J$. The calculated values of r_p are shown in Table III. The values of ϵ_p were estimated from Eq. (4), where ϵ_0 and ϵ_α were obtained from the Cole–Cole plot of the complex dielectric constants. Bogomolov and co-workers[22] have shown theoretically that for the case of nondispersive system the polaron radius is given by

TABLE II. Parameters obtained from the fits of the high temperature data to the Mott model.

Compositions mol % V_2O_5	W (eV)	v_0 (10^{-13} s^{-1})	α (Å^{-1})
80	0.37	1.01	0.37
90	0.33	1.08	0.52
95	0.29	1.21	0.62

TABLE III. Effective dielectric constants and polaron radii calculated from Eqs. (3) and (14).

Compositions mol % V_2O_5	ϵ_p^a	r_p^b (Å)	r_p^c (Å)
80	5.95	1.63	1.60
90	7.00	1.55	1.53
95	7.80	1.52	1.51

[a]From Ref. 21.
[b]Calculated from Eq. (3).
[c]Calculated from Eq. (14).

$$r_p = (\pi/6)^{1/3}(R/2). \qquad (14)$$

Equation (14) is obviously oversimplified for a complex system. However, the IR spectra of the present vanadate glasses[21] suggest that this approximation is valid for them fairly well. The values of polaron radius calculated from Eq. (14), using the values of R from Table I, are included in Table III which indicates that the experimental and theoretical values of r_p are comparable.

At low temperatures, the conductivity data can be fitted to Eq. (5) predicted by the variable range hopping model. A semilogarithmic plot of the conductivity vs $T^{-1/4}$ is shown in Fig. 2 for the silicon vanadate glasses. The plot shows two distinct linear regions one above and other below about 155 K. The data below 155 K are fitted to Eqs. (5) and (6) in Fig. 2 by the least square fitting procedure. It may be noted that the fits are fairly well. The values of α and $N(E_F)$ obtained from the fits are shown in Table IV. The values of α are consistent with the estimates (Table II) from the analysis of the high temperature data. The values of $N(E_F)$ are also reasonable for localized states.[12] However, the data above 155 K, where mul-
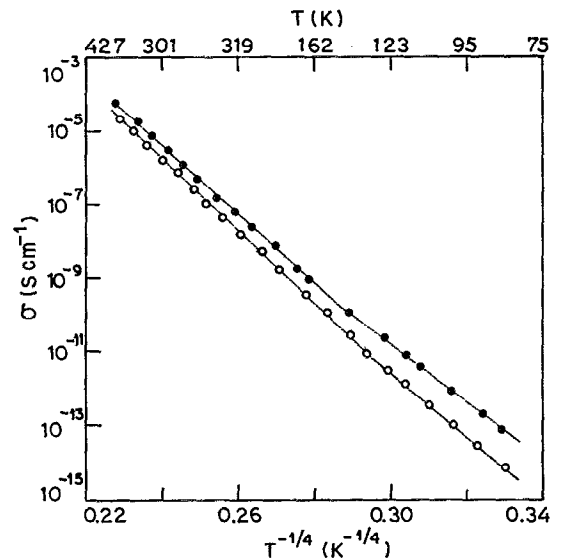

FIG. 2. The dc conductivity shown as a function of $T^{-1/4}$ for two sample compositions: O, 80 mol % V_2O_5 and ●, 90 mol % V_2O_5. The solid lines below 155 K are fits to the variable range hopping model [Eq. (5)] and the solid lines above 155 K are fits to the percolation model of Triberis and Friedman [Eq. (13)].

TABLE IV. Parameters obtained from Mott's variable range hopping model below 155 K.

| Compositions mol % V_2O_5	$N(E_F)$ $(10^{-19}\,eV^{-1}\,cm^{-3})$	α (Å^{-1})
80	1.0	0.41
90	4.2	0.58
95	9.7	0.63

FIG. 3. Plot of $\log_{10}(\sigma T)$ as a function of reciprocal temperature for the same glass compositions as in Fig. 1. The solid curves are fits to Eq. (10) predicted by Schnakenberg's model.

tiphonon processes are dominant,[8,9] are not fitted to the variable range hopping model and are discussed later in the text.

The temperature dependence of the conductivity at high temperatures, similar to the Mott model, is also predicted by the Holstein model [Eq. (8)] in the nonadiabatic limit. This model also provides an independent check for the nature of hopping process. The limiting values of J estimated from the right-hand side of Eq. (6) at 300 K, using the values of v_0 and $W_H \approx W$ from Table II, are in the range 0.030–0.032 eV for all compositions. An estimate of J can be made from the following expression:[12]

$$J \approx e^3 [N(E_F)/\epsilon_p^3]^{1/2}, \tag{15}$$

which gives $J \approx 0.012$–0.024 eV, using $N(E_F)$ from Table IV and thus $J < W_H/3 \approx W/3$, confirming the formation of small polaron. The nonadiabatic hopping theory is therefore most appropriate to describe the polaronic conduction in glassy silicon vanadates.

The Schnakenberg model, which predicts a temperature dependent activation energy [Eq. (10)], can be fitted to the experimental data. The fits are shown in Fig. 3, using v_0, W_H, and W_D as variable parameters. The best fits are obtained for those values of the parameters as shown in Table V. It may be noted that the values of v_0 are close to their earlier estimates (Table II). As expected the values of W_H are less than W. The values of W_D are close to the values of W_D estimated using Miller–Abrahams theory.[23] It might be noted that the value of $W_H + W_D/2$ is approximately equal to W in accordance with Eq. (2) predicted by Mott's model.

Killias' model also predicts a decrease of activation energy with decreasing temperature. Equation (12) predicted by this model indicates that the activation energy is linearly dependent on the inverse temperature. However, the experimental data estimated from Fig. 1 do not show any inverse temperature dependent, rather follow Eq. (10) predicted by the Schnakenberg model (Fig. 3).

The percolation model [Eq. (13)] of Triberis and Friedman predicts a $T^{-1/4}$ dependence of the logarithmic conductivity in the high and low temperature regions in consistence with the experimental data shown in Fig. 2. However, it has been observed earlier in the text that data below 155 K is consistent with the variable range hopping model. When the model of Triberis and Friedman is fitted to the data below 155 K, the values of α and N_0 obtained are close to the values of α and $N(E_F)$ respectively obtained from the Mott model. In Fig. 2 the data above 155 K are fitted to Eq. (13). The best fits yield the values of α
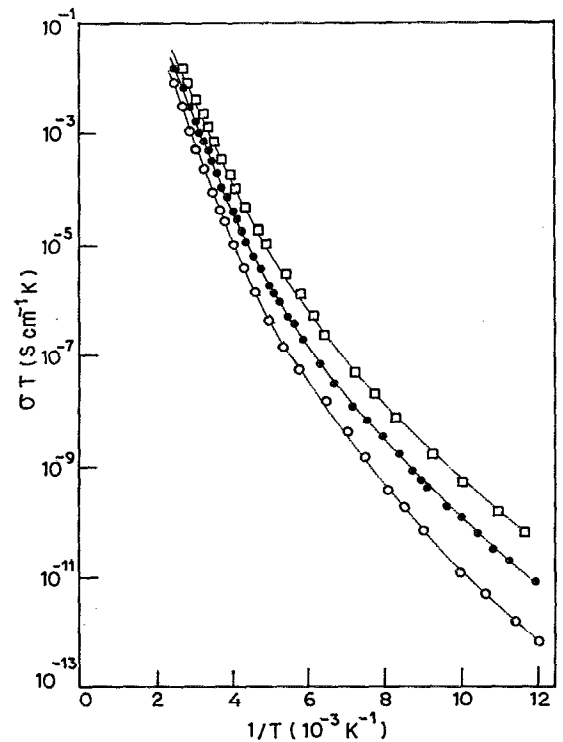
and N_0 displayed in Table VI. The values of α are reasonable for localized states,[12] although they are slightly higher than the estimates from the Mott model. The values of N_0 are also close to $N(E_F)$ obtained from the Mott model.

V. CONCLUSIONS

The dc conductivity of the semiconducting glassy silicon vanadates has been presented for the first time in the temperature range 80–400 K. Analysis of the experimental data shows that at high temperatures the conductivity is consistent with the predictions of the phonon-assisted hopping model of Mott, while the variable range hopping model is valid at low temperatures. The Holetein model indicates that the nonadiabatic hopping theory is appropriate to describe the conduction process in the silicon vanadate glasses. The Schnakenberg model is also consistent with the temperature dependence of the conductivity. The data can also be interpreted in the framework of the Triberis and Friedman model. Reasonable values of the various

TABLE V. Parameters obtained by fitting the Schnakenberg model to the experimental data.

Compositions mol % V_2O_5	v_0 $(10^{-13}\,s^{-1})$	W_H (eV)	W_D (eV)
80	1.20	0.32	0.156
90	1.23	0.28	0.160
95	1.28	0.25	0.170

TABLE VI. Parameters obtained by fitting the data above 155 K to the Triberis and Friedman model.

Compositions mol % V_2O_5	N_0 (10^{-19} eV^{-1} cm^{-3})	α (Å^{-1})
80	2.4	0.69
90	4.0	0.75
95	6.2	0.78

physical parameters, namely localization lengths, phonon frequency, density of states at the Fermi level, etc., have been obtained by the fits of these models to the experimental results.

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