

## Electrical properties of some alkaline earth vanadate glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 7567

(<http://iopscience.iop.org/0953-8984/10/34/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 16:42

Please note that [terms and conditions apply](#).

# Electrical properties of some alkaline earth vanadate glasses

A Ghosh†, M Sural and S Sen

Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

Received 11 February 1998, in final form 7 April 1998

**Abstract.** Electrical conductivity of some alkaline earth vanadate glasses has been reported in the temperature range 80–500 K. It has been observed that the conductivity and the activation energy for different glass compositions did not differ markedly. The general behaviour of the temperature dependence of the conductivity is similar for all the glass compositions studied. At high temperatures, Mott's nearest neighbour hopping is applicable, while at low temperatures, variable range hopping is valid. The polaron hopping models of Schnakenberg and of Emin and coworkers are consistent with the experimental data in the entire temperature range of measurements. However, the polaron hopping model of Emin and coworkers is the most suitable to explain the observed behaviour. The effect of the different alkaline earth oxide modifiers on the electrical properties of the vanadate glasses is similar.

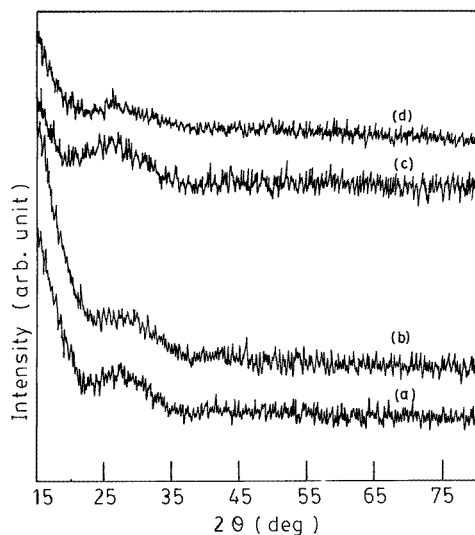
## 1. Introduction

Electrical properties of the semiconducting transition metal (TM) oxide glasses with formers of traditional networks such as  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$  etc have been studied extensively [1–4]. However, there are few reports on the electrical properties of glasses containing TM oxides as forming unique networks [5]. Although it has been accepted that the electrical conduction in TM oxide glasses occurs by the hopping of small polarons, between TM ions of different valence states (e.g.  $\text{V}^{4+}$  and  $\text{V}^{5+}$  in vanadate glasses) [6, 7], the nature of the hopping mechanism in different temperature and composition regions has not been resolved. The effect of glass former and modifier oxides on the electrical properties of these glasses is also a subject of controversy [8–10]. Several authors [8] have suggested that glass former oxides act as noninteracting solvents in the conduction process in vanadium phosphate glasses, while Flynn *et al* [9] have suggested that the glass former oxides affect the activation energy of the hopping conduction in vanadium tellurite glasses. Recently, we have reported [10] the electrical properties of vanadium tellurite glasses containing different glass formers and have observed that the glass former oxides affect significantly the electrical properties of these glasses. However, the role of different modifier oxides in the hopping process in vanadate glasses has not been reported so far. The objective of the present work is to study the electrical properties of alkaline earth vanadate glasses in order to observe the effect of glass modifiers on the electrical properties. In these glasses, the vanadium oxide acts as a unique glass network former and alkaline earth oxides as modifiers.

† Author for correspondence.

## 2. Experiment

Glass samples of compositions 80 V<sub>2</sub>O<sub>5</sub>-20 MO (mol%), where M = Mg, Ca, Sr and Ba, were prepared from reagent grade V<sub>2</sub>O<sub>5</sub>, MgO, CaCO<sub>3</sub>, SrCO<sub>3</sub> and BaCO<sub>3</sub>. The mixtures of these chemicals were melted in covered alumina crucibles at 1000 °C. After homogenization for 2 h, the melts were quenched between two brass plates. The amorphous nature of the samples was confirmed from x-ray diffraction (figure 1). The concentrations of the total (*N*) and reduced (V<sup>4+</sup>) vanadium ions were estimated from the glass compositions and magnetic measurements respectively. The density of the samples was determined from Archimedes' principle. The average intersite separation between vanadium ions was obtained from the glass composition and density. The various physical parameters of the prepared glasses are displayed in table 1.



**Figure 1.** X-ray diffractograms of different glass samples: (a) 80 V<sub>2</sub>O<sub>5</sub>-20 BaO, (b) 80 V<sub>2</sub>O<sub>5</sub>-20 SrO, (c) 80 V<sub>2</sub>O<sub>5</sub>-20 CaO, (d) 80 V<sub>2</sub>O<sub>5</sub>-20 MgO.

**Table 1.** Density, concentrations of total and reduced vanadium ions and their ratio and the average intersite separation for different alkaline earth vanadate glass compositions.

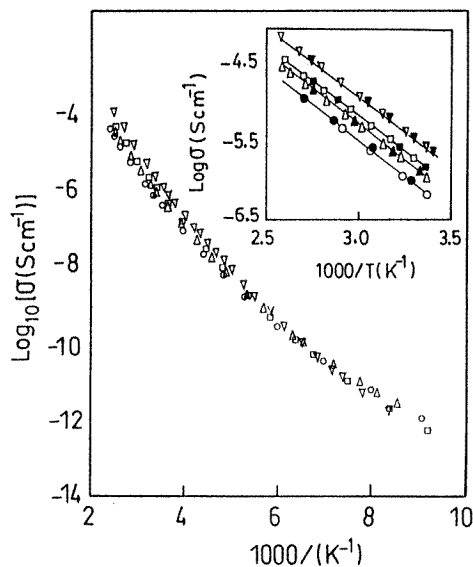
Sample compositions (mol%)	Density (g cm <sup>-3</sup> )	<i>N</i> (cm <sup>-3</sup> )	[V <sup>4+</sup> ] (cm <sup>-3</sup> )	<i>C</i>	<i>R</i> (Å)
80 V <sub>2</sub> O <sub>5</sub> -20 MgO	2.95	1.16 × 10 <sup>22</sup>	1.70 × 10 <sup>21</sup>	0.147	4.42
80 V <sub>2</sub> O <sub>5</sub> -20 CaO	2.98	1.14 × 10 <sup>22</sup>	1.55 × 10 <sup>21</sup>	0.135	4.44
80 V <sub>2</sub> O <sub>5</sub> -20 SrO	3.12	1.13 × 10 <sup>22</sup>	1.52 × 10 <sup>21</sup>	0.135	4.46
80 V <sub>2</sub> O <sub>5</sub> -20 BaO	3.33	1.14 × 10 <sup>22</sup>	1.56 × 10 <sup>21</sup>	0.137	4.45

Gold electrodes were deposited on both surfaces of the samples for electrical measurements. Dc electrical conductivity measurements of the samples were carried out in a Keithley electrometer (model 617). The absence of barrier layers at the contacts was confirmed from the linear *I*-*V* characteristics. The dc conductivity of the samples was also

obtained from the complex impedance plot of the ac data measured in a wide frequency range (10 Hz–1 MHz) using a Quad-Tech RLC meter. The dc conductivity data obtained by these two methods agreed perfectly (see the inset of figure 2). For low temperature measurements the sample cell was inserted into a cryogenic unit. Measurements were made in the temperature range 80–500 K.

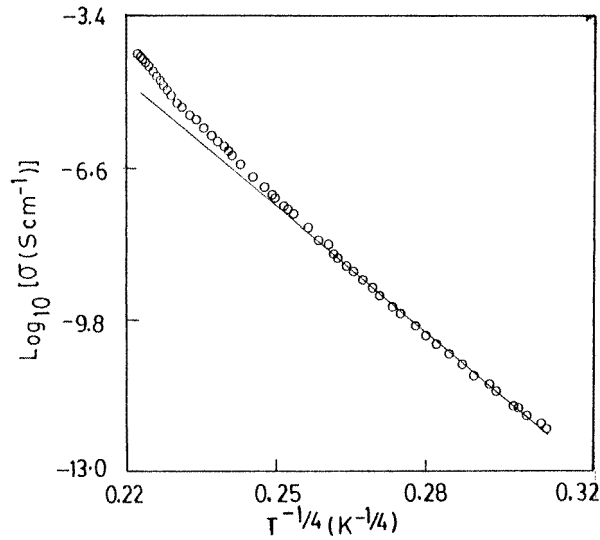
### 3. Results and discussion

The temperature dependence of the dc conductivity of all the glass compositions is shown in figure 2 as a function of inverse temperature. It is clear from the figure that the conductivity is nonlinear showing a decrease of the activation energy with the decreasing temperature. However, at higher temperatures (above  $\sim 290$  K), the conductivity exhibits an activated behaviour for all glass compositions (inset of figure 2). It is also observed in figure 2 that the conductivity does not differ significantly for glasses with different alkaline earth modifiers. The result is significant because the conductivity of glasses with different conventional glass formers such as  $P_2O_5$  and  $TeO_2$  [1, 2, 10] is markedly different for the same  $V_2O_5$  content. The probable origin of the different conductivity behaviour of conventional and alkaline earth vanadate glasses might be the difference in their structures. The conductivity is shown in figure 3, as a function of  $T^{-1/4}$  for one glass composition. Figure 3 shows linearity in the plot below 250 K, indicating variable range hopping [11]. The above results are analysed below in view of small polaron hopping theories [6, 7, 11–15].



**Figure 2.** Temperature dependence of the dc conductivity shown as a function of inverse temperature for different glass compositions:  $\nabla$ , 80  $V_2O_5$ –20 BaO;  $\square$ , 80  $V_2O_5$ –20 SrO;  $\triangle$ , 80  $V_2O_5$ –20 CaO and  $\circ$ , 80  $V_2O_5$ –20 MgO. The inset shows the same for the data above 290 K. The data represented by the solid symbols in the inset were obtained from the ac measurements.

Mott [6, 7] theoretically investigated the hopping conductivity of TM oxide glasses. The conduction process in TM oxide glasses has been described in terms of phonon assisted hopping of small polarons between localized states and the following expression has been



**Figure 3.** The dc conductivity shown as a function of  $T^{-1/4}$  for the 80 V<sub>2</sub>O<sub>5</sub>–20 MgO glass composition. The solid line is the least squares straight line fit to the data below 250 K.

obtained for the nearest neighbour hopping conductivity in the nonadiabatic regime at higher temperatures ( $T > \theta_{D/2}$ ):

$$\sigma = v_0 [e^2 C (1 - C) / kTR] \exp(-2\alpha R) \exp(-W/kT) \quad (1)$$

where  $v_0$  is the optical phonon frequency,  $\alpha^{-1}$  is the localized length of the s-like wave function assumed to describe the localized state at each TM ion site,  $R$  is the average intersite separation,  $C$  is the fraction of sites occupied by an electron or a polaron and is, therefore, the ratio of the concentration of the reduced TM ions to the concentration of the total TM ions and  $W$  is the activation energy for the hopping conduction. Assuming a strong electron–phonon interaction, Austin and Mott [7] showed that

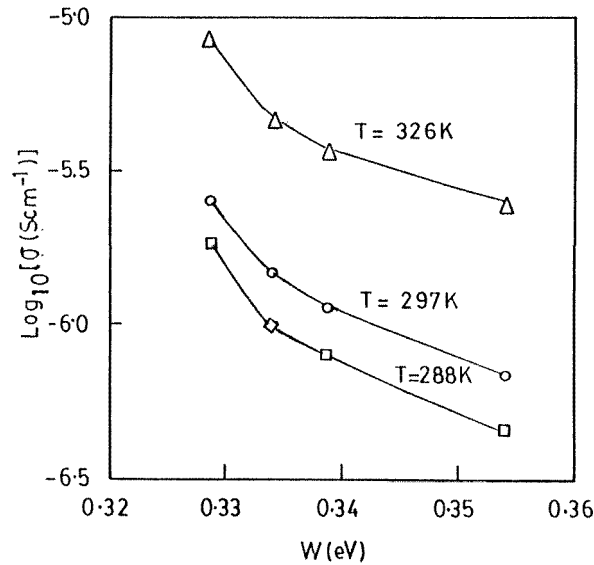
$$\begin{aligned} W &\approx W_H + W_D/2 && \text{for } T < \theta_{D/2} \\ &\approx W_D && \text{for } T < \theta_{D/4} \end{aligned} \quad (2)$$

where  $W_H$  is the hopping energy,  $W_D$  is the disorder energy arising from the variation of the local arrangements of ions and  $\theta_D$  is the Debye temperature.

The conductivity data at higher temperatures presented in figure 2 are consistent with (1). The activation energy and the inverse localization length were obtained from the least squares straight line fits of the high temperature data and are shown in table 2 for all glass compositions. It is noted in table 2 that the activation energy for the different compositions does not differ markedly. Values of  $\alpha$  suggest strong localization in these glass compositions [6]. However, (1) cannot predict the temperature dependence of the activation energy observed below 250 K. A semilogarithmic plot of the conductivity measured at three arbitrarily chosen temperatures (above 250 K) versus the activation energy estimated above for all glass compositions is shown in figure 4. It is observed that the plot is not linear and thus, as suggested earlier [2], the preexponential term in (1) inclusive of  $\exp(-2\alpha R)$  depends on glass compositions and the thermal activation energy alone cannot determine the conductivity. The tunnelling term  $\exp(-2\alpha R)$  needs to vary with glass composition to account for the variation of the conductivity with compositions.

**Table 2.** Parameters obtained from Mott's model for different glass compositions.

Sample compositions (mol%)	$W$ (eV)	$\alpha$ ( $\text{\AA}^{-1}$ )	$N(E_F)$ ( $\text{eV}^{-1} \text{cm}^{-3}$ )
80 $\text{V}_2\text{O}_5$ -20 MgO	0.354	0.31	$1.64 \times 10^{18}$
80 $\text{V}_2\text{O}_5$ -20 CaO	0.339	0.57	$1.79 \times 10^{19}$
80 $\text{V}_2\text{O}_5$ -20 SrO	0.334	0.41	$5.32 \times 10^{18}$
80 $\text{V}_2\text{O}_5$ -20 BaO	0.329	0.33	$2.26 \times 10^{18}$

**Figure 4.** The plot of the conductivity at different temperatures (shown) versus the activation energy for different glass compositions. The solid curves are drawn to guide the eye.

At lower temperatures ( $T < \theta_D/4$ ) Mott [11] proposed that hops may occur preferentially beyond nearest neighbours. The conductivity for the variable range hopping is given by

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \quad (3)$$

where  $\sigma_0$  and  $T_0$  are constants and  $T_0$  is given by

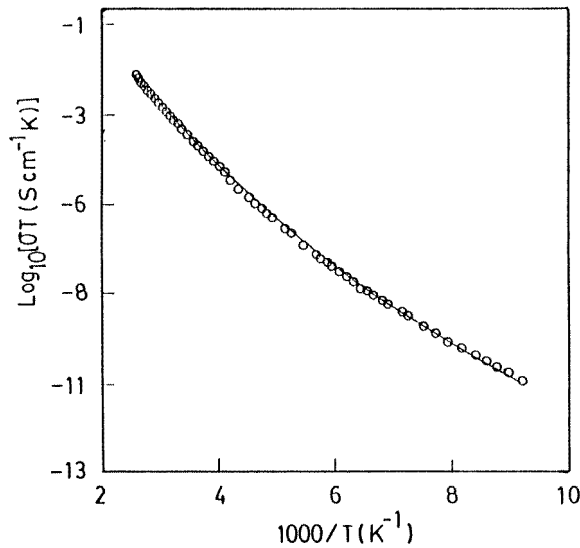
$$T_0 = 16\alpha^3/kN(E_F) \quad (4)$$

where  $N(E_F)$  is the density of states at the Fermi level. The value of  $T_0$  was obtained from the least squares straight line fit of the data in figure 3. The value of  $N(E_F)$  obtained from (4), employing the value of  $\alpha$  from table 2 are also shown in table 2. It may be noted that these values are within the limits of values of  $N(E_F)$  observed for amorphous semiconductors [16].

Schnakenberg [13] developed a polaron hopping model which predicts a decrease of the activation energy with the increase of temperature in consistence with our experimental data (figure 2). The temperature dependence of the conductivity in this model is described by

$$\sigma \propto T^{-1} [\sinh(h\nu_0/kT)]^{1/2} \exp[-(4W_H/h\nu_0) \tanh(h\nu_0/4kT)] \exp(-W_D/kT). \quad (5)$$

The experimental data were fitted to (5) by the best fit method using  $W_H$ ,  $W_D$  and  $\nu_0$  as variable parameters. Such a best fit is shown in figure 5 for one glass composition. It is observed that the fit is very good. Other glass compositions also showed similar fits. The values of  $\nu_0$ ,  $W_H$  and  $W_D$  obtained from the fits are shown in table 3 for different glass compositions. It may be mentioned that the value of  $\nu_0$  obtained from the fits does not agree well with the value obtained from infrared spectra [17]. However, the hopping energies obtained from the fits are consistent with the activation energy and the values of the disorder energy are in agreement with the values obtained from other vanadate glasses [1].



**Figure 5.** The plot of  $\log_{10}(\sigma T)$  versus  $10^3/T$  for the 80  $V_2O_5$ -20 SrO glass. The solid curve is the best fit to (5).

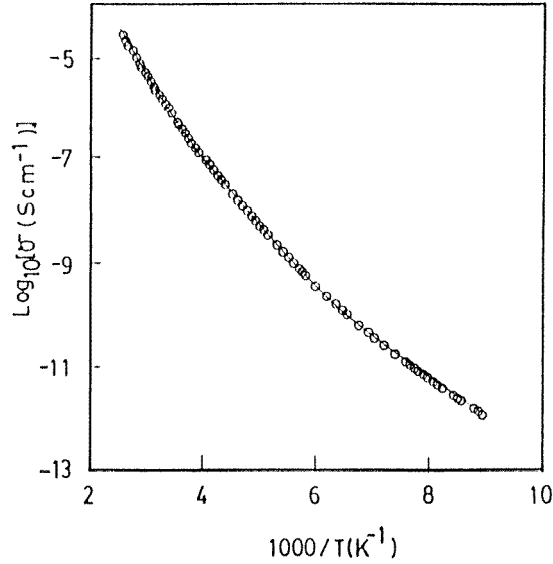
**Table 3.** Parameters obtained from Schnakenberg's model for different glasses.

Sample compositions (mol%)	$W_H$ (eV)	$W_D$ (eV)	$\nu_0$ ( $s^{-1}$ )	$\nu_0^a$ ( $s^{-1}$ )
80 $V_2O_5$ -20 MgO	0.443	0.037	$3.70 \times 10^{13}$	$3.0 \times 10^{13}$
80 $V_2O_5$ -20 CaO	0.386	0.052	$1.18 \times 10^{13}$	$2.1 \times 10^{13}$
80 $V_2O_5$ -20 SrO	0.379	0.030	$1.01 \times 10^{13}$	$1.9 \times 10^{13}$
80 $V_2O_5$ -20 BaO	0.369	0.039	$0.94 \times 10^{13}$	$1.5 \times 10^{13}$

<sup>a</sup> From infrared spectra [17].

A phonon assisted hopping model, in which electrons could couple with either optical or acoustical phonons or both, was discussed by Emin and coworkers [14, 15]. Considering interactions of electrons with both acoustical and optical phonons, the dc conductivity for the nonadiabatic multiphonon hopping of small polarons has been calculated as [15]

$$\sigma = (Ne^2 R^2 / 6kT)(J/h)^2 [\pi \hbar^2 / 2(E_c^{op} + E_c^{ac})kT]^{1/2} \exp[-W_D^2 / 8(E_c^{op} + E_c^{ac})kT] \times \exp(-W_D / 2kT) \exp(-E_A^{op} / kT - E_A^{ac} / kT) \quad (6)$$



**Figure 6.** The plot of  $\log_{10} \sigma$  versus  $10^3/T$  for the 80  $V_2O_5$ -20 CaO glass composition. The solid curve is the best fit to (6) and (7).

**Table 4.** Parameters obtained from Emin's model for different glasses.

Sample compositions (mol%)	$W_D$ (eV)	$\nu_0$ ( $s^{-1}$ )	$J$ (eV)	$E_b^{op}$ (eV)	$E_b^{ac}$ (eV)
80 $V_2O_5$ -20 MgO	0.028	$2.86 \times 10^{13}$	0.042	0.614	0.610
80 $V_2O_5$ -20 CaO	0.026	$2.64 \times 10^{13}$	0.033	0.550	0.580
80 $V_2O_5$ -20 SrO	0.026	$2.494 \times 10^{13}$	0.032	0.550	0.580
80 $V_2O_5$ -20 BaO	0.026	$2.351 \times 10^{13}$	0.032	0.544	0.583

where  $J$  is the transfer integral between two sites, and  $E_c^{op}$ ,  $E_c^{ac}$ ,  $E_A^{op}$  and  $E_A^{ac}$  are defined by

$$\begin{aligned}
 E_c^{op} &= E_b^{op} (1/N_p) \sum [h\nu_{0,q}/2kT] \text{cosech}(h\nu_{0,q}/2kT) \\
 E_c^{ac} &= E_b^{ac} (1/N_p) \sum [h\nu_{a,q}/2kT] \text{cosech}(h\nu_{a,q}/2kT) \\
 E_A^{op} &= E_b^{op} (1/N_p) \sum [h\nu_{0,q}/2kT]^{-1} \tanh(h\nu_{0,q}/2kT) \\
 E_A^{ac} &= E_b^{ac} (1/N_p) \sum [h\nu_{a,q}/2kT]^{-1} \tanh(h\nu_{a,q}/2kT)
 \end{aligned} \tag{7}$$

where  $\nu_{0,q}$  and  $\nu_{a,q}$  are the optical and acoustical phonon frequencies respectively at wave vector  $q$ ,  $N_p$  is the number of phonon modes,  $E_b^{op}$  and  $E_b^{ac}$  are the polaron binding energies related to acoustical and optical phonons respectively. The experimental data for the dc conductivity were fitted to (6) and (7) by the best fit method. In the calculation, it was assumed that the acoustic phonon density of states is approximately given by  $g(\nu) \propto \nu^2$  and that the mean optical phonon frequency  $\nu_0$  is constant. A best fit to the experimental data is shown in figure 6 for one glass composition. It is observed in figure 6 that the agreement between theory and experiment is very good. Other glass compositions also showed similar fits. Values of the parameters  $E_b^{op}$ ,  $E_b^{ac}$ ,  $W_D$ ,  $J$  and  $\nu_0$  corresponding to best



fits are shown in table 4. It may be noted that these values do not differ significantly for different glass compositions. It is to be noted that values of  $J$  are reasonable for hopping in the nonadiabatic regime. Values of other parameters are also reasonable for small polaron hopping.

#### 4. Conclusion

The temperature dependence of the electrical conductivity of alkaline earth vanadate glasses can be described by the hopping models of Mott, Schnakenberg and Emin. However, the hopping model of Emin and coworkers is the most likely to explain the observed behaviour. The difference in the conductivity behaviour of the conventional and the alkaline earth vanadate glasses has been attributed to the differences of their structures. The alkaline earth oxide modifiers have similar effects on the electrical properties of the different glass compositions.

#### Acknowledgment

Financial assistance for the work by the CSIR (India) (vide grant No 3(772)/95-EMR-II) is gratefully acknowledged.

#### References

- [1] Ghosh A 1990 *Phys. Rev. B* **42** 5665
- [2] Sayer M and Mansingh A 1972 *Phys. Rev. B* **6** 4629
- [3] Chung L H, Mackenzie J D and Murawski L 1979 *Rev. Chim. Miner.* **16** 308
- [4] Murawski L, Chuns C H and Mackenzie J D 1979 *J. Non-Cryst. Solids* **32** 91
- [5] Mandal S and Ghosh A 1994 *Phys. Rev. B* **49** 3131
- [6] Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
- [7] Austin I G and Mott N F 1969 *Adv. Phys.* **18** 41
- [8] Loffe V A, Patrino J B and Poberovshya I S 1960 *Sov. Phys.-Solid State* **2** 609
- [9] Flynn B W, Owen A E and Robertson J M 1977 *Proc. 7th Int. Conf. on Amorphous and Liquid Semiconductors* ed W E Spear (Edinburgh: CIGL) p 678
- [10] Ghosh A 1995 *J. Chem. Phys.* **102** 1386
- [11] Mott N F 1969 *Phil. Mag.* **19** 835
- [12] Emin D and Holstein T 1969 *Ann. Phys., NY* **35** 439
- [13] Schnakenberg J 1968 *Phys. Status Solidi* **28** 623
- [14] Emin D 1974 *Phys. Rev. Lett.* **32** 303  
Emin D 1975 *Adv. Phys.* **24** 305
- [15] Gorham-Bergeron E and Emin D 1977 *Phys. Rev. B* **15** 3667
- [16] Mott N F and Davis E A 1979 *Electronic Processes in Noncrystalline Materials* 2nd edn (Oxford: Clarendon)
- [17] Ghosh A, unpublished