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DC electrical properties of cadmium vanadate glassy semiconductors: a comparison with traditional glasses

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Abstract

The temperature and composition dependence of the electrical conductivity of cadmium vanadate semiconducting glasses formed with V_2O_5 as a unique network former has been studied in this paper. The results for these glasses have been compared with those for traditional vanadate glasses formed with different traditional network formers (phosphate, borate, etc). The variation of the conductivity and the activation energy with composition for the cadmium vanadate glasses is much stronger than that for the traditional vanadate glasses. The strong compositional variation of the conductivity and the activation energy for the present glasses has been attributed to the significant structural changes observed in the Fourier transform infrared (FT-IR) spectra due to the introduction of a CdO modifier in the glassy matrix. The experimental results have been analysed in the light of the existing theories of polaronic conduction. It has been observed that the electrical conduction at high temperatures in these glass compositions is described by Mott's phonon-assisted hopping model, while the low-temperature data in a limited temperature range are consistent with the variable-range hopping model. The parameters obtained from the fits of these models to the experimental data are reasonable.

1. Introduction

The electrical properties of transition metal oxide glasses formed with traditional glass formers such as phosphate, borate, etc have been studied extensively because of their interesting semiconducting properties [1–6]. These glasses are also interesting for their electrical switching properties [7, 8]. The semiconducting behaviour of these transition metal oxide glasses arises from the fact that the transition metal ions exist in more than one valence state so that electrical

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conduction takes place by the hopping of electrons (or polarons) from the low valence state to the high valence state of transition metal ions [3, 8, 9]. Interpretation of the conduction process in these glasses is difficult, since the conductivity is affected by numerous factors including the nature of the transition metal ions, the concentration of transition metal ions in the reduced valence state, the preparation conditions, and the existence of microscopic or macroscopic structure within the glassy matrix. In particular, vanadate glasses formed with the addition of traditional network formers or modifier oxides, where V_2O_5 acts as a network former, exhibit semiconducting properties due to the presence of both V^{4+} and V^{5+} ions. The electron–phonon interaction is strong enough to form small polarons in these glasses, and the electrical conduction occurs by the hopping of small polarons between V^{4+} and V^{5+} ions either in the adiabatic or in the non-adiabatic regime [8–10]. However, there exists a controversy over the nature of the hopping mechanism in different temperature and composition regimes [11–13]. Also, the role of different modifier oxides in the hopping process has not been clarified yet. A few structural studies of vanadate glasses have been reported [14–17]. It has been observed that the structure of these glasses depends on the nature of the network formers as well as the network modifiers.

The objective of the present paper is to study the electrical transport properties of cadmium vanadate glasses to shed some light on the role of the cadmium oxide as a modifier in this system and to compare them with those of different traditional semiconducting vanadate glasses such as V_2O_5–P_2O_5, V_2O_5–B_2O_3, and V_2O_5–TeO_2 glasses [7, 18, 19]. We have observed that the composition dependence of the electrical properties of the cadmium vanadate glasses is much stronger than that for the traditional vanadate glasses arising from the structural modification of the vanadate glass network by the cadmium oxide.

2. Experiment

Glass samples of compositions xV_2O_5–$(1 − x)CdO$ where $x = 0.6, 0.7, 0.8,$ and 0.9 mole fraction were prepared using reagent grade chemicals $CdCO_3$ and V_2O_5. Appropriate amounts of dry crystalline powders in 10 g batches of each glass composition were mixed and preheated in an alumina crucible at 450 °C for 2 h for calcination of $CdCO_3$. Then the mixtures were melted at a temperature in the range 800–900 °C depending upon the composition. The melts were kept for 2 h and stirred occasionally to enhance homogeneity. The melts were then quenched by pouring them in between twin-rollers revolving in opposite directions. Glass samples of thickness ∼0.1 mm were obtained for $x = 0.6$–0.9. The as-prepared samples were characterized by different routine studies, such as x-ray diffraction and differential thermal analysis, details of which can be found in some earlier communications [16, 17]. Density of the samples was measured by Archimedes' principle using acetone as an immersion liquid. The total vanadium ion concentration (N) was estimated from the glass composition and density, while the concentration of the reduced vanadium ions V^{4+} was obtained from magnetic susceptibility measurements (Parc model 155). We have observed that 0.2–0.8% of the vanadium ions were reduced to V^{4+} ions. Glass transition temperature (table 1) of the different glass compositions was determined from differential thermal analysis (Perkin Elmer Diamond TG/DTA). Fourier transform infrared (FT-IR) spectra of the glass samples were recorded in a Shimadzu FT-IR 8400S spectrometer at 25 °C and at relative humidity of 50–60%. For FT-IR measurements, pellets of thickness 1 mm and diameter 13 mm were obtained by pressing a mixture of 1 part of glass and 60 parts of KBr at a pressure of 200 kg cm^{-2}. For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples of diameter ∼10 mm. The dc electrical measurements of the samples were carried out in a Keithley electrometer (model 617) in the temperature range 120–423 K.

Table 1. Glass transition temperature (T_g), density, total vanadium ion concentrations, activation energies at high and low temperatures, polaron radius, density of state at the Fermi level, and the values of T_0 for different compositions of cadmium vanadate glasses.

Compositions	T_g (°C)	Density (g cm^{-3})	N (10^{22}) (cm^{-3})	W (eV) at high temperature ±(0.01)	W (eV) at low temperature ±(0.01)	r_p (Å)	$N(E_F)$ (10^{22}) (eV^{-1} cm^{-3})	T_0 (10^9) (K)	α^{-1} (Å)
$0.9V_2O_5$–$0.1CdO$	255	3.02	1.85	0.28	0.15	1.49	3.16	1.44	0.23
$0.8V_2O_5$–$0.2CdO$	266	3.24	1.82	0.35	0.17	1.51	2.68	1.80	0.23
$0.7V_2O_5$–$0.3CdO$	277	3.42	1.74	0.43	0.17	1.54	2.52	1.82	0.26
$0.6V_2O_5$–$0.4CdO$	301	3.69	1.66	0.47	0.18	1.57	2.23	1.90	0.27

The ionic contribution to the total conductivity for different glass compositions was determined using Wagner's polarization technique. We observed that the ionic contribution to the total conductivity was only ∼0.2%. Thus the measured conductivity is purely electronic in origin.

3. Results and discussion

The dc conductivity for the different glass compositions is shown in figure 1(a) as a function of reciprocal temperature. All glass compositions show a smooth variation of the conductivity with reciprocal temperature, indicating a temperature dependent activation energy characteristic of small polaron hopping conduction [10]. It is also observed that the dc conductivity for all the glass compositions increases with the increase in temperature, indicating typical semiconducting behaviour. However, for all the samples the logarithmic conductivity in the high-temperature range (310–423 K), shown in figure 1(b), exhibits a linear dependence on reciprocal temperature i.e. thermally activated behaviour. The activation energy computed from the slope of the graphs in figure 1(b) is shown in table 1. It may be noted from table 1 that the activation energy is lower for the glass compositions with higher V_2O_5 content. Figure 1(a) also indicates that the plots at low temperatures in a limited temperature range (120–160 K) is almost linear. The activation energy obtained in this temperature range is almost temperature independent (table 1).

Figures 2(a) and (b) show respectively the composition dependence of the conductivity at 373 K and the high-temperature activation energy. The data for the traditional vanadate glasses such as V_2O_5–P_2O_5, V_2O_5–B_2O_3, and V_2O_5–TeO_2 glasses [7, 18, 19] are also included in the figure for comparison. We note that the variation of the conductivity and the activation energy with composition is much stronger for the cadmium vanadate glasses than those for the traditional vanadate glasses. The difference in the transport properties between the cadmium vanadate and the traditional vanadate glasses arises from the difference in their structures, which is clarified below from the analysis of the FT-IR spectra.

The room temperature FT-IR spectra in the region 400–4000 cm^{-1} of all glass compositions are shown in figure 3. All the spectra show a water band at 1620–1630 cm^{-1} and a broad band around 3400 cm^{-1} due to adsorbed water in the powdered samples required for making pellets. The band near 1020 cm^{-1}, assigned to the stretching vibration of the isolated V=O vanadyl groups in VO_5 trigonal bipyramid [14], is observed only in the spectra for the glass compositions with higher V_2O_5 content ($x = 0.9$ and 0.8). This band becomes weaker with the decrease of V_2O_5 content in the glass compositions, as shown in the spectra for $x = 0.7$, and then almost vanishes for the glass composition with $x = 0.6$. The second high-frequency band in the 915–920 cm^{-1} range is assigned to the vibrations of the free VO_2-groups of the VO_4-polyhedra [12]. They become the dominant high-frequency vibrations for
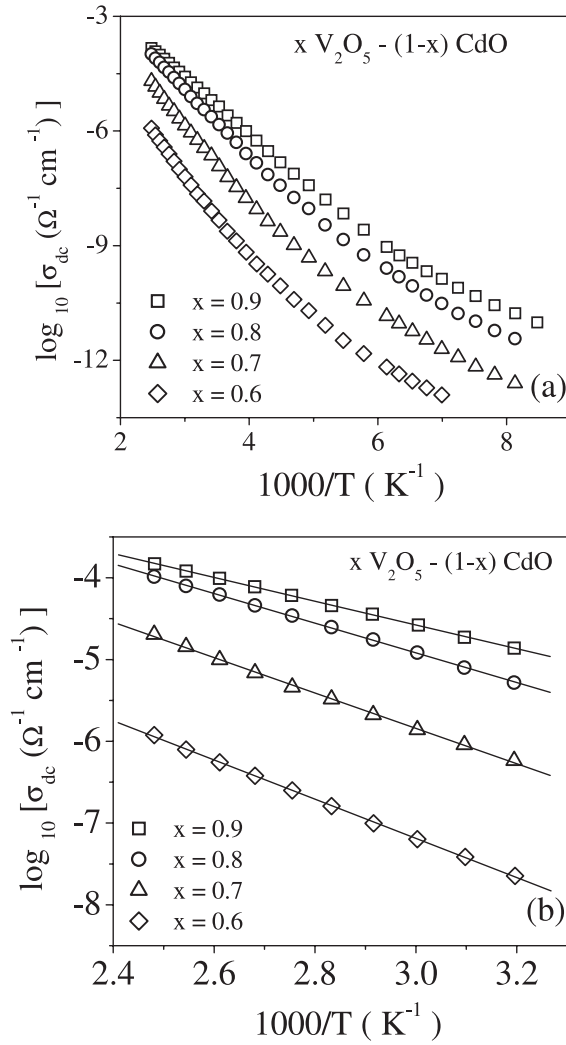
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Figure 1. (a) Temperature dependence of the dc conductivity as a function of T^{-1} for different compositions of the cadmium vanadate glasses. (b) The high-temperature dc conductivity data for different compositions. Solid lines are the least square straight line fits to the data.

$x = 0.7$ and 0.6 compositions. In this case, the VO_5-groups are gradually destroyed and the main structural units become VO_4 polyhedra [14]. It may be noted that the network structure of the traditional vanadium phosphate, borate, etc [18] glasses is built up of VO_5 trigonal bipyramid only, and the band at 1020 cm^{-1} for these glasses [14] remains unaltered for different compositions in contrast with the present glass compositions. Thus, this structural change for the cadmium vanadate glasses is responsible for the strong composition dependence of the conductivity.

We note in figure 1 that the magnitude of the conductivity tends to be higher for those compositions having lower activation energy. The result is consistent with the small polaron hopping theory proposed by Mott [6]. In Mott's model [6] the conduction process at high temperatures is considered in terms of optical phonon-assisted hopping of small polarons between localized states. The dc conductivity in the non-adiabatic regime at high temperatures ($T > \theta_D/2$, θ_D being the Debye temperature) is given by

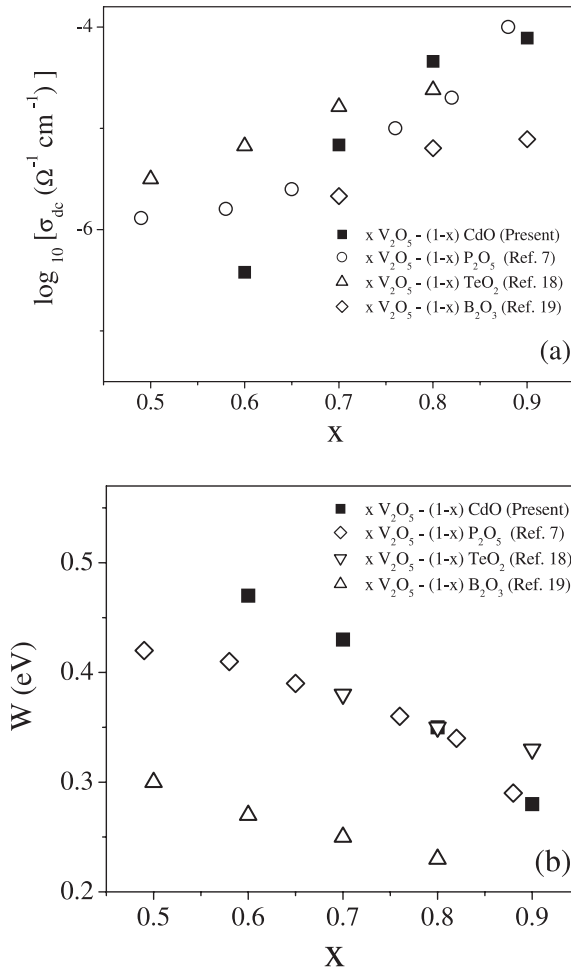$$\sigma = \nu_0[e^2 C(1 - C)/kTR]\exp(-2\alpha R)\exp(-W/kT) \tag{1}$$

Figure 2. (a) Composition dependence of the dc conductivity at 373 K for cadmium vanadate glasses. (b) Composition dependence of the activation energy computed at high temperature. The data for traditional vanadate glasses such as V_2O_5–P_2O_5, V_2O_5–B_2O_3, and V_2O_5–TeO_2 are included for comparison.

where ν_0 is the phonon frequency which is also the hopping frequency of electrons or polarons, R is the average site separation, α is the inverse localization length, C is the fraction of sites occupied by an electron (or polaron) and W is the activation energy given by [6, 10]

$$W = W_H + W_D/2 \qquad \text{for} \quad T > \theta_D/2$$
$$\approx W_D \qquad \text{for} \quad T < \theta_D/4 \qquad\qquad (2)$$

where W_H is the polaron hopping energy and W_D is the disorder energy arising from the energy difference between two sites due to variation in the local arrangement of ions. An estimate of the polaron radius r_p can be obtained from the following formula [20] derived for the case of the non-dispersive system of frequency ν_0:

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

where R is the average distance between the vanadium ions, which was estimated from the glass composition and density. It may be noted that although V_2O_5 acts as a network former in the present glass compositions, the hopping of polarons occurs between V^{4+} and V^{5+} ions and therefore the average distance between vanadium ions is taken as the hopping distance as in traditional vanadate glasses. The values of the polaron radius calculated from equation (3)
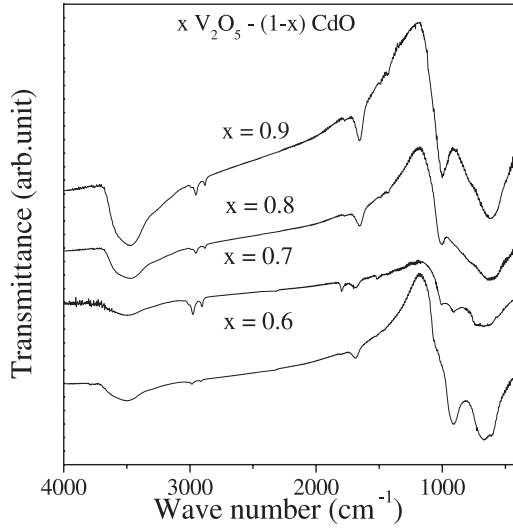
Figure 3. Room-temperature FT-IR spectra in the transmittance mode for different cadmium vanadate glasses.

are shown in table 1 for the present glasses. Although the possible effects of disorder have been neglected in the above calculation, the small values of the polaron radius suggest that the polarons are highly localized. In this model the density of state at the Fermi level can be estimated from the following expression [10]

$$N(E_F) = 3/4\pi R^3 W_D. \tag{4}$$

The values of $N(E_F)$ for the present glasses were calculated from equation (4) assuming the values of W at low temperatures (table 1) as the values of W_D and the results are displayed in table 1. It may be noted that the values of $N(E_F)$ are reasonable for localized states [6].

In the framework of Mott's model [6, 10], the nature of the hopping mechanism in the high-temperature range, where a nearly activated behaviour of the conductivity is observed, can be ascertained from the plot of the logarithmic conductivity versus the activation energy at an arbitrarily chosen temperature in this range. It has been suggested [7] that the hopping would be in the adiabatic regime if the temperature estimated from the slope of such a plot is close to the experimental temperature. Otherwise, the hopping would be in the non-adiabatic regime. A semi-logarithmic plot of the conductivity measured at an arbitrarily chosen temperature versus the activation energy computed at high temperatures is shown in figure 4. The data for the traditional vanadate glasses such as V_2O_5–P_2O_5, V_2O_5–B_2O_3, and V_2O_5–TeO_2 glasses [7, 18, 19] are also included in this figure for comparison. We note that the data for the different traditional vanadate glasses fall on straight lines for the entire interval of W. However, it is evident from the figure that the variation is not linear for the cadmium vanadate glasses unlike traditional vanadate glasses and thus an estimation of temperature is not possible from the plot as was done for the traditional vanadate glasses [7, 18, 19]. However, the results suggest that the pre-exponential term including $\exp(-2\alpha R)$ in equation (1) depends on glass composition for the present cadmium vanadate glasses in sharp contrast to the traditional vanadate glasses [7, 18, 19]. Thus, the thermal activation energy alone cannot dominate the factors that determine the conductivity for the present glass compositions in contrast to the traditional vanadate glasses.

At low temperatures, Mott [21] assumed that the localized states are randomly distributed in energy and that the density of states $N(E_F)$ at the Fermi level is uniform. Below a particular temperature, however, the phonon factor (i.e. $\exp(-W/k_B T)$) predominates the conduction
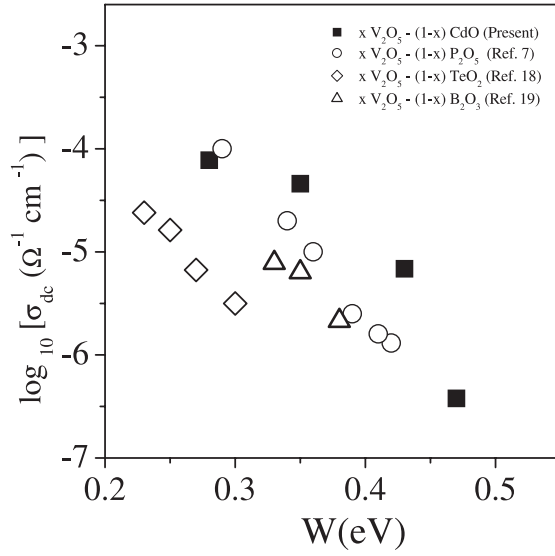
Figure 4. A plot of $\log_{10}\sigma$ versus W for different glass compositions at 373 K. The data for traditional vanadate glasses like V_2O_5–P_2O_5, V_2O_5–B_2O_3, and V_2O_5–TeO_2 are included for comparison.
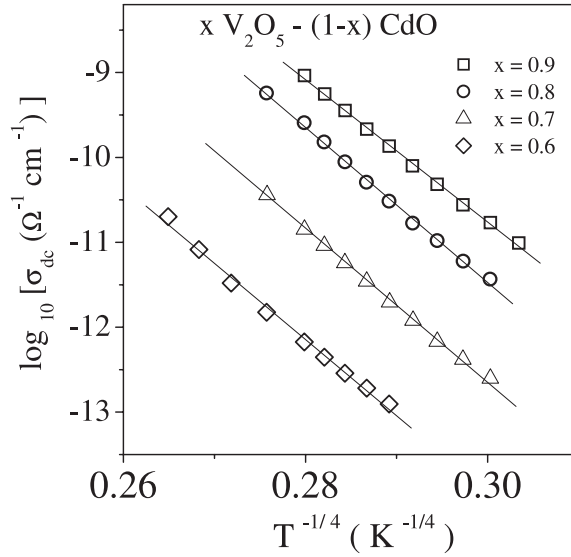

Figure 5. A plot of $\log_{10}\sigma$ versus $T^{-1/4}$ for different glass compositions of the cadmium vanadate glasses. The solid lines are the least-square straight-line fits to equation (5).

over the overlap factor (i.e. $\exp(-2\alpha R)$) so that with the lowering of temperature, a smaller W is preferred by the electrons and hence the hopping distance continuously changes, resulting in variable range hopping of polarons. The variable range hopping conductivity is given by Mott [21]:

$$\sigma = A \exp[-(T_0/T)^{1/4}] \tag{5}$$

where A and T_0 are constants and T_0 is given by

$$T_0 = 16\alpha^3/kN(E_F) \tag{6}$$

where $N(E_F)$ is the density of states at the Fermi level.

In figure 5, the dc conductivity at low temperatures is plotted against $T^{-1/4}$. We note that the plot is approximately linear over a limited temperature range 120–160 K in accordance with

the variable range hopping model. It may be noted that the variable range hopping was also observed in a limited temperature range in other vanadate glasses [13]. The experimental data are fitted to equation (5) in figure 5. The values of T_0 obtained are shown in table 1. These values are comparable to those for other vanadate glasses [13, 18]. Using the value of $N(E_F)$ from table 1, the localization length α^{-1} is estimated from equation (6) and is shown in table 1 for different glass compositions. It may be noted that these values appear reasonable for the localized states [6, 10].

4. Conclusions

The composition dependence of the conductivity and the activation energy for the cadmium vanadate glasses is much stronger than that for the traditional vanadate glasses, indicating a significant influence of the CdO modifier on the electrical properties of the vanadate glasses. The difference in the electrical behaviour has been attributed to the difference in their structures using FT-IR spectroscopy. In the high-temperature region (310–423 K) Mott's model of small polaron hopping between the nearest neighbours is consistent with the conductivity data, while in a limited low-temperature range (120–160 K) the experimental data are consistent with the variable range hopping models of Mott. The values of the localization length and the density of states at the Fermi level obtained from the analysis are quite reasonable for localized states for all the glass compositions.

References

[1] Peng B, Fan Z, Qui X, Jiang L, Tang G H, Ford H D and Huang W 2005 *Adv. Mater.* **17** 857
[2] Mekki A, Khattak G D and Wenger L E 2003 *J. Non-Cryst. Solids* **330** 156
[3] Cheng C H and Mackenzie J D 1980 *J. Non-Cryst. Solids* **42** 151
[4] Chinkhota M, Fodor P S, Khattak G D and Wenger L E 2002 *J. Appl. Phys.* **91** 8269
[5] Rao C B, Ramesh K V and Sastry D L 2006 *Physica* B **382** 81
[6] Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
[7] Sayer M and Mansingh A 1972 *Phys. Rev.* B **6** 4629
[8] Livage J, Jollivet J P and Tronc E 1990 *J. Non-Cryst. Solids* **121** 35
[9] Ghosh A 1988 *J. Appl. Phys.* **64** 2652
[10] Mott N F and Davis E A 1979 *Electronic Processes in Non-Crystalline Materials* (Oxford: Clarendon)
[11] Sen S and Ghosh A 2000 *J. Appl. Phys.* **87** 3355
[12] Sindhu S, Sanghi S, Agarwal A, Sonam, Seth V P and Kishore N 2005 *Physica* B **365** 65
[13] Bhattacharya S and Ghosh A 2002 *Phys. Rev.* B **66** 132203
[14] Dimitrov V, Dimitiev Y, Arnaudov M and Topalov D 1983 *J. Non-Cryst. Solids* **57** 147
[15] Khattak G D, Tabet N and Wenger L E 2005 *Phys. Rev.* B **72** 104203
[16] Sen S and Ghosh A 2000 *J. Mater. Res.* **15** 995
[17] Sen S and Ghosh A 1999 *J. Non-Cryst. Solids* **258** 29
[18] Dhawan V K, Mansingh A and Sayer M 1982 *J. Non-Cryst. Solids* **51** 87
[19] Sharma B K, Dube D C and Mansingh A 1984 *J. Non-Cryst. Solids* **65** 39
[20] Bogomolov V N, Kudinov E K and Firsov A 1968 *Fiz. Tverd. Tela* **9** 3175
     Bogomolov V N, Kudinov E K and Firsov A 1968 *Sov. Phys.—Solid State* **9** 2502 (Engl. Transl.)
[21] Mott N F 1969 *Phil. Mag.* **19** 853