Frequency dependent conductivity of cadmium vanadate glassy semiconductor

2008 J. Phys.: Condens. Matter 20 035203

(http://iopscience.iop.org/0953-8984/20/3/035203)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 035203 (5pp) doi:10.1088/0953-8984/20/03/035203

Frequency dependent conductivity of cadmium vanadate glassy semiconductor

Aloka Ghosh[1], S Bhattacharya[2], D P Bhattacharya[1] and A Ghosh[2,3]

[1] Department of Physics, Jadavpur University, Jadavpur, Kolkata 700 032, India
[2] Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

E-mail: sspag@iacs.res.in

Received 29 October 2007, in final form 14 November 2007
Published 10 December 2007
Online at stacks.iop.org/JPhysCM/20/035203

Abstract

We have studied the frequency dependent conductivity of the semiconducting cadmium vanadate glasses of compositions $x\mathrm{V_2O_5}$–$(1-x)\mathrm{CdO}$ where $x = 0.6, 0.7, 0.8$ and 0.9 in the temperature range 93–423 K and in the frequency range 10 Hz–2 MHz. We have observed sub-linear frequency dependence and weak temperature dependence of the ac conductivity. We have analyzed the experimental results in the framework of various theoretical models based on quantum mechanical tunneling and classical hopping over barriers. It has been observed that the temperature and frequency dependence of the ac conductivity is consistent with the overlapping large polaron tunneling model, while the classical barrier hopping models fail to interpret the data.

1. Introduction

Transition metal oxide glasses show semiconducting properties which arise from the presence of more than one valence state of the transition metal ions [1–3]. These glasses have drawn much attention due to their possible application as optical and memory switching devices, etc [4–7]. The dc electrical conduction in these semiconductors was observed to be due to the hopping of either electrons or polarons with strong temperature dependence of the corresponding activation energy [8–14]. The frequency dependent loss in amorphous semiconductor containing transition metal ions has also been studied [15–21]. However, it becomes the subject of much controversy depending on the materials studied and the temperature range considered [15–17]. It was observed in most studies [15–21] that the frequency dependent ac conductivity in amorphous semiconductor shows an approximately sub-linear frequency dependence at low frequencies and temperatures. Several models [1, 3, 22–24] based on the relaxation caused by the hopping or tunneling of electrons (polarons) or atoms between equilibrium sites have been developed to explain the frequency and temperature dependence of the ac conductivity in different limited temperature ranges. However, it still needs more insight on hopping mechanisms in these materials. The objective of the present work is to study comprehensively the frequency dependent ac conductivity of a glass series prepared using $\mathrm{V_2O_5}$ as network former and CdO as network modifier, in the frequency range 10 Hz–2 MHz and in the temperature range 93–423 K, and to determine the mechanism for the ac conductivity by examining the observed experimental results in terms of the existing theoretical models. We have observed that the tunneling of the overlapping large polarons is the dominant mechanism for the ac conductivity in these glasses.

2. Experiment

Glass samples of compositions $x\mathrm{V_2O_5}$–$(1-x)\mathrm{CdO}$ where $x = 0.6, 0.7, 0.8$ and 0.9 were prepared using the chemicals $\mathrm{CdCO_3}$ (Loba Chemie 99.9% pure) and $\mathrm{V_2O_5}$ (Loba Chemie 99% pure). The appropriate amounts of these chemicals were thoroughly mixed and preheated in an alumina crucible at 450 °C for 2 h for calcination of $\mathrm{CdCO_3}$. The mixtures were then melted in the temperature range from 800 to 900 °C depending upon the composition. The melts were equilibrated for 30 min and quenched between twin rollers rotating in opposite directions. Black colored glass samples of thickness ~0.1 mm were obtained for $x = 0.6$–0.9. The amorphous nature of the prepared samples was confirmed from the x-ray diffraction (Seifert, model 3000P) studies of the powdered samples. For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples of diameter

[3] Author to whom any correspondence should be addressed.

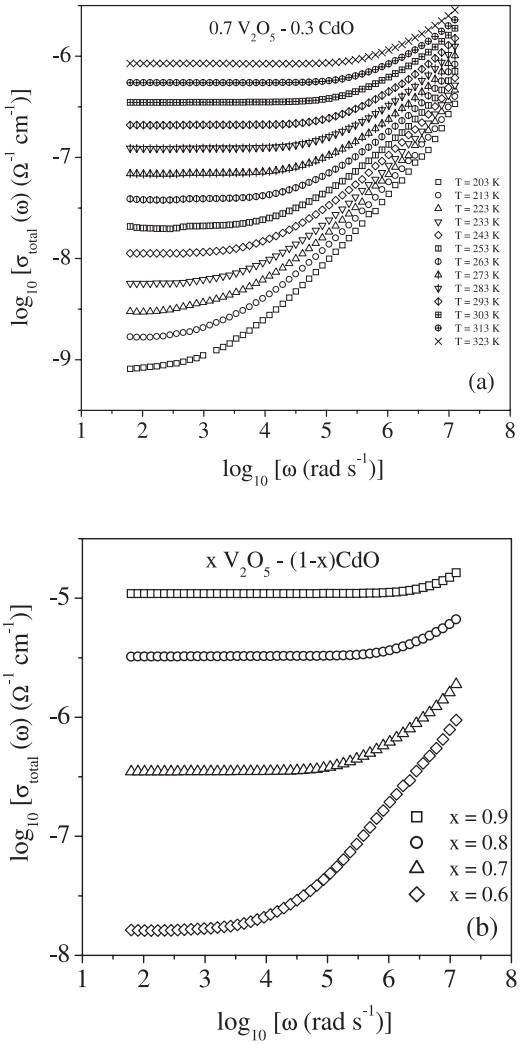

Figure 1. (a) Frequency dependence of the measured total conductivity at different temperatures (shown in the inset) for $0.7V_2O_5$–0.3CdO glass composition. (b) A comparison of the total conductivity for different cadmium vanadate glasses at 303 K.

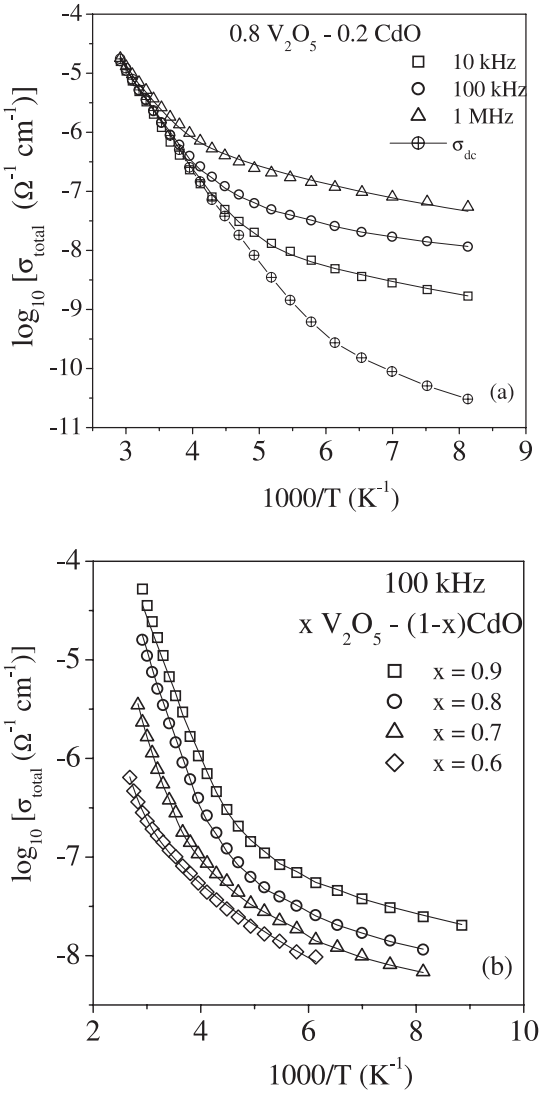

Figure 2. (a) Measured total conductivity for $0.7V_2O_5$–0.3CdO glass composition, shown as a function of inverse temperature at three different frequencies shown. The measured dc conductivity for the glass composition is also shown [10] in the figure. (b) A comparison of total conductivity at 100 kHz for different cadmium vanadate glasses shown as a function of inverse temperature. The solid lines in both figures are the best fits obtained from the overlapping large polaron model (equation (7)).

∼10 mm. Electrical measurements such as ones of the capacitance and conductance of the samples were carried out in the frequency range 10 Hz–2 MHz using an RLC meter (QuadTech, model 7600) interfaced with a computer and in the temperature range 93–423 K. The ionic contribution to the total conductivity for different glass compositions was determined using Wagner's polarization technique [25] and was found negligibly small.

3. Results and discussion

The frequency dependence of the measured total conductivity $\sigma_{\text{total}}(\omega)$ of a glass sample $0.7V_2O_5$–0.3CdO at different temperatures is shown in figure 1(a). It is observed that at low frequencies the conductivity is independent of the frequency and corresponds to the dc conductivity σ_{dc} [10]. The frequency dispersion starts at a higher frequency as the temperature is increased. Other glass compositions also show similar behavior. In figure 1(b) a comparison of the frequency dependence of the measured conductivity at room temperature ($T = 303$ K) is shown for different glass compositions. It is observed that the conductivity decreases with the increase of CdO content in the glasses.

The measured conductivity of the glass composition $0.8V_2O_5$–0.2CdO at three fixed frequencies is shown in figure 2(a) as a function of reciprocal temperature. The dc conductivity σ_{dc} from the earlier report [10] is also included for comparison. At low temperatures the temperature dependence of $\sigma_{\text{total}}(\omega)$ is much less than that of σ_{dc} and is not activated in nature. The value of $\sigma_{\text{total}}(\omega)$ is also substantially higher than that of the dc conductivity. However, at higher temperatures the temperature dependence of $\sigma_{\text{total}}(\omega)$ becomes strong and its frequency dependence becomes small and they almost

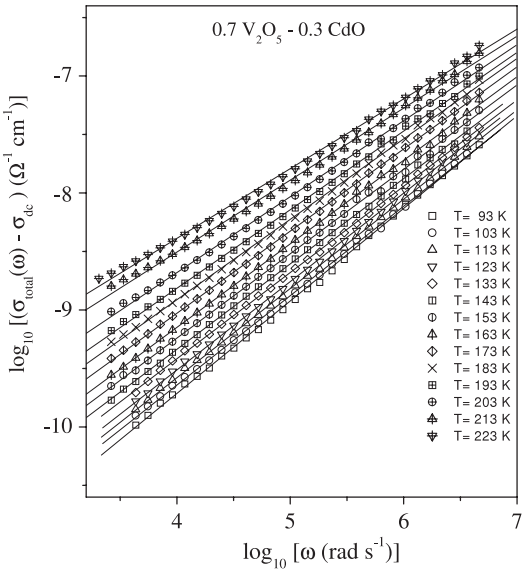

Figure 3. The frequency dependent ac conductivity for the composition $0.7V_2O_5$–0.3CdO, obtained by subtracting the dc conductivity from the measured total conductivity, are shown at different temperatures. The solid lines are the least squares straight line fits of the data.

coincide with σ_{dc}. Similar behavior is observed for the other glass compositions with only difference in the temperature at which the measured conductivity becomes equal to the dc conductivity [10]. In figure 2(b) the variation of the measured conductivity at 100 kHz is shown for different compositions. The detailed analysis of the conductivity is discussed later in the framework of the appropriate theoretical models.

In general, it has been observed that the measured total conductivity within a fixed frequency window can be expressed as [3, 22]

$$\sigma_{\text{total}}(\omega) = \sigma'(\omega) + \sigma_{\text{dc}} \tag{1}$$

where $\sigma'(\omega)$ is the ac conductivity and σ_{dc} corresponds to the frequency independent dc conductivity. A frequency dependent ac conductivity $\sigma'(\omega)$ has been observed in semiconducting glasses containing transition metal ions similar to many amorphous semiconductors [22] and invariably has the form [26]

$$\sigma'(\omega) = A\omega^s \tag{2}$$

where A is a constant dependent on temperature and the exponent s is generally equal to or less than unity.

Figure 3 shows the frequency dependent (ac) conductivity $\sigma'(\omega)$ (real part) for different temperatures, obtained by subtracting the dc conductivity from the measured total conductivity, for the same composition as is shown in figure 1(a). The solid lines are the least squares fits of the ac conductivity data, which according to the equation (2) give the value of frequency exponent s. The variation of s with temperature is shown in figure 4, which indicates that s decreases with increasing temperature. However, no frequency dependence of s was observed in the investigated frequency window. It is also observed that the frequency exponent does not show any systematic variation with the CdO content.

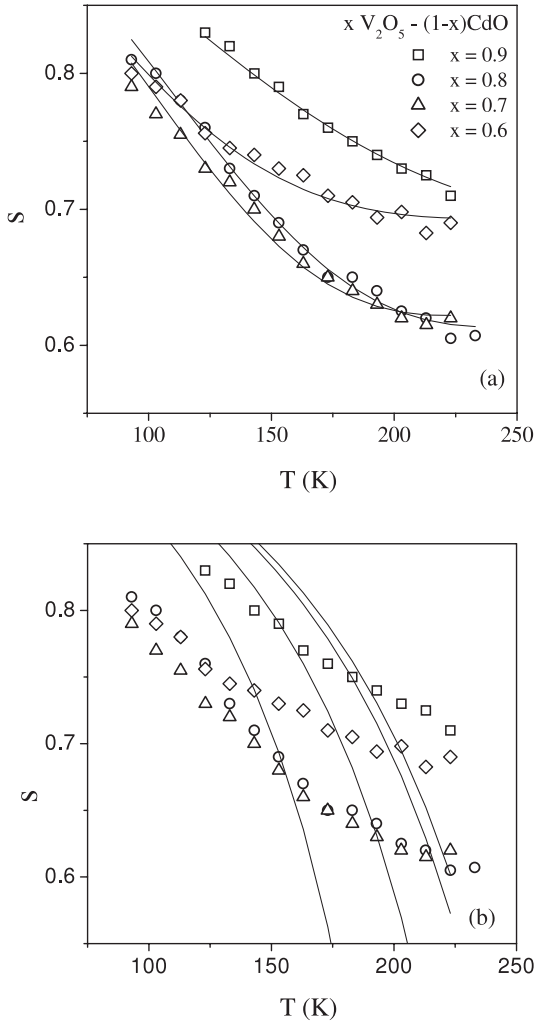

Figure 4. (a) The frequency exponents s for different cadmium vanadate glasses are shown as functions of temperature. The solid curves are the best fits obtained from the overlapping large polaron model (equation (9)). (b) The fits of the frequency exponent data to the classical barrier hopping model (equation (13)).

Now, the specific mechanism for the ac conductivity operating in the present system can be obtained by analyzing the predictions of the temperature dependence of the ac conductivity and its frequency exponent in the framework of various existing models based on quantum mechanical tunneling and hopping over barriers of charge carriers. Several authors [2, 3, 23] have evaluated, within the pair approximation, the ac conductivity for single-electron motion undergoing quantum mechanical tunneling and obtained an expression for s as

$$s = 1 - 4/\ln(1/\omega\tau_0), \tag{3}$$

where τ_0 is a characteristic relaxation time, often taken as the inverse of the optical phonon frequency. Equation (3) shows that s (about 0.81) is temperature independent but frequency dependent. Thus, this model is unable to explain the observed experimental results presented in figure 4.

A temperature dependent frequency exponent has been obtained within the framework of the quantum mechanical

tunneling model in the pair approximation by assuming that the carriers form non-overlapping small polarons [23], i.e., the total energy of a charge carrier is lowered by the polaron energy W_P resulting from the lattice distortion accompanying the occupation of the site by the carrier. The transpose of an electron between degenerate sites having random distribution of separations will generally involve an activation energy, the polaron hopping energy $W_H \approx W_P/2$. In this case, the frequency exponent becomes

$$s = 1 - 4/[\ln(1/\omega\tau_0) - W_H/k_B T]. \quad (4)$$

Now it is noted that s is temperature dependent, increasing with temperature. But this is contrary to the experimental results for s (figure 4) showing a decreasing trend with increasing temperature.

A mechanism for the polaron tunneling, where the polaron energy is derived from polarization changes in the deformed lattice as in ionic crystals and glasses was proposed by Long [3]. The resultant excitation is called a large or dielectric polaron. Because of the long range of the Coulomb interaction, its well will extend over many interatomic distances and overlap with the wells of other sites. This has important consequences for the frequency dependent loss because the activation energy associated with charge transfer between the overlapping sites reduces [2, 3] according to

$$W_H = W_{HO}\left(1 - \frac{r_p}{R}\right) \quad (5)$$

where r_p is the polaron radius and W_{HO} is given by

$$W_{HO} = e^2/4\varepsilon_p r_p \quad (6)$$

where ε_p is the effective dielectric constant. It is assumed that W_{HO} is constant for all sites, whereas the intersite separation R is a random variable. The ac conductivity for the overlapping large polaron tunneling model [23] is given by

$$\sigma_1(\omega) = \frac{\pi^4}{12}\frac{e^2(k_B T)^2[N(E_F)]^2\omega R_\omega^4}{2\alpha k_B T + W_{HO} r_p/R_\omega^2} \quad (7)$$

where R_ω is the hopping length at a frequency ω determined by the quadratic equation

$$R_\omega'^2 + [\beta W_{HO} + \ln(\omega\tau_0)]R_\omega' - \beta W_{HO} r_p' = 0 \quad (8)$$

where α is the inverse localization length and $R_\omega' = 2\alpha R_\omega$, $r_p' = 2\alpha r_p$ and $\beta = 1/k_B T$. Using the above expressions for the dependence of the conductivity on R_ω, it is straightforward to evaluate an expression for s:

$$s = 1 - \frac{8\alpha R_\omega + 6W_{HO} r_p/R_\omega k_B T}{[2\alpha R_\omega + W_{HO} r_p/R_\omega k_B T]^2}. \quad (9)$$

Thus this model predicts that s is a decreasing function of temperature. For large values of r_p', s continues to decrease with increasing temperature, eventually tending to a value of s predicted by the simple quantum mechanical tunneling model of non-polaron forming carriers, whereas for small values of r_p', s exhibits a minimum [23] at a certain temperature in a similar fashion to the case for the small polaron quantum mechanical tunneling model. Thus, it appears that the overlapping large polaron tunneling model might be an appropriate theory for explaining the data presented here.

Table 1. Parameters obtained from fits of the real part of ac conductivity and frequency exponent to the large polaron tunneling model for the xV_2O_5–$(1-x)$CdO glasses.

x	W_{HO} (eV) (±0.01)	r_p (Å) (±0.02)	α (Å^{-1}) (±0.02)	τ_0 (s) (±0.05 × 10^{-13})	$N(E_F)$ (eV^{-1} cm^{-3}) (±0.05 × 10^{23})
0.9	0.52	4.24	1.01	2.78×10^{-13}	2.27×10^{23}
0.8	0.50	3.05	1.53	2.74×10^{-13}	2.83×10^{23}
0.7	0.53	2.84	1.21	2.47×10^{-13}	2.55×10^{23}
0.6	0.52	1.54	1.11	1.58×10^{-13}	2.87×10^{23}

The experimental data for $\sigma_{total}(\omega)$ at different fixed frequencies are fitted to the ac conductivities calculated from equation (7) plus the dc conductivity (equation (1)). In the calculation we have used the value of τ_0 (table 1) obtained from infrared spectra [10]. The best fits of the total conductivity data for different frequencies are exhibited as solid lines in figure 2. Reasonable fits are also observed for other glass compositions. The values of the parameters obtained from the best fits for different compositions are shown in table 1. It may be noted that the values of the hopping energy are consistent with the high temperature activation energy of the dc conductivity [10]. The values of the inverse localization length, the density of states at the Fermi level and other parameters are also reasonable for localized states [23]. In figure 4(a) the frequency exponent s is also fitted to equation (9). The best fit of the experimental points is observed for the same values of the parameters (table 1) as are obtained from the best fits of the total conductivity.

The overlapping large polaron tunneling model (equation (9)) also predicts the frequency dependence of s. A detailed analysis shows that in the low temperature region ($k_B T/W_{HO} < 0.04$–0.05), s should increase with frequency. An opposite and more significant behavior should be observed in the high temperature region ($k_B T/W_{HO} > 0.05$). In the present work, significant frequency dependence of s was not observed.

The experimental data presented here can also be analyzed in terms of classical barrier hopping models [22, 24]. The barrier hopping models, which correlate the relaxation variable W with the intersite separation R, were developed initially by Pike [24] for single-electron hopping and later extended by Elliott [22] for two electrons hopping simultaneously. For neighboring sites at a separation R, the Coulomb wells overlap, resulting in a lowering of the effective barrier height from W_M to a value W, which for the case of one electron transition is given by [24]

$$W = W_M - e^2/\pi\epsilon\epsilon_0 R. \quad (10)$$

The ac conductivity (real part) in this model in the narrow band limit is expressed by

$$\sigma_1(\omega) = \frac{\pi^3}{24} N^2 \omega R_\omega^6 \epsilon\epsilon_0 \quad (11)$$

where N is the concentration of pair sites and R_ω is the hopping distance given by

$$R_\omega = e^2/\pi\epsilon\epsilon_0[W_M + k_B T \ln(\omega\tau_0)]. \quad (12)$$

The frequency exponent s for this model is evaluated as [15]

$$s = 1 - 6k_B T/[W_M + k_B T \ln(\omega\tau_0)]. \quad (13)$$

Thus, the barrier hopping models predict a temperature dependent exponent with s decreasing with increasing temperature similar to the experimental data presented in figure 4. We have tried to fit equation (13) to the experimental data in figure 4(b). It may be noted that the experimental data and the prediction of the barrier hopping models do not agree. Also reasonable fits of the experimental data to the barrier hopping model based on two electrons hopping simultaneously [22] were not obtained.

Thus, out of several models discussed above, the large polaron tunneling model is the best for interpreting the ac conductivity of the present cadmium vanadate glasses. But why this particular model is suitable for the present system is not clear at present due to the absence of adequate knowledge of the local structure of these glasses. A preliminary structural study [10] of these glasses reveals that CdO drastically changes the layer structure of V_2O_5 giving a strong dependence of the vanadium site spacing on the CdO content and thus suggesting non-overlapping of site potentials. However, detailed studies of the local structure can reveal the situation. The ac results for the present glasses can be compared with those for the conventional $x V_2O_5$–$(1-x)P_2O_5$ glasses [16]. It was observed that the large polaron tunneling model [3] could adequately explain the frequency and temperature dependences of the ac conductivity of the $x V_2O_5$–$(1-x)P_2O_5$ glasses [16] being similar to those for the present glasses, although the dc conductivity mechanism for these glasses [12] is different from that of the present glasses [10]. Thus the effect of the structure on the ac electrical properties is no so significant, in contrast to the case for the dc electrical properties of these glasses.

4. Conclusions

The frequency dependent (ac) conductivity of the cadmium vanadate semiconducting glasses has been investigated in the frequency range 10 Hz–2 MHz and in the temperature range 93–343 K. Of the various theoretical models for ac conduction in amorphous semiconductors, the overlapping large polaron tunneling model is consistent with the ac conductivity and its frequency exponent. Fits using this model are in good agreement with the experimental data for all measurement temperatures and frequencies. Other models such as simple quantum mechanical tunneling of electrons and the classical barrier hopping models did not agree with the experimental data.

References

[1] Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
[2] Austin I G and Mott N F 1969 *Adv. Phys.* **18** 41
[3] Long A R 1982 *Adv. Phys.* **31** 553
[4] Ghosh A 1988 *J. Appl. Phys.* **64** 2652
[5] Livage J, Jollivet J P and Tronc E 1990 *J. Non-Cryst. Solids* **121** 35
[6] Sakuri Y and Yamaki J 1985 *J. Electrochem. Soc.* **132** 512
[7] Peng B, Fan Z, Qui X, Jiang L, Tang G H, Ford H D and Huang W 2005 *Adv. Mater.* **17** 857
[8] Rao C B, Ramesh K V and Sastry D L 2006 *Physica* B **382** 81
[9] Ramesh K V and Sastry D L 2006 *Mater. Sci. Eng.* B **126** 66
[10] Ghosh A, Bhattacharya S, Bhattacharya D P and Ghosh A 2007 *J. Phys.: Condens. Matter* **19** 106222
[11] Owen A E 1977 *J. Non-Cryst. Solids* **25** 370
[12] Sayer M and Mansingh A 1972 *Phys. Rev.* B **6** 4629
[13] Ghosh A and Chakraborty D 1993 *Phys. Rev.* B **48** 5167
[14] Bhattacharya S and Ghosh A 2002 *Phys. Rev.* B **66** 132203
[15] Mansingh A, Tandon R P and Valid J K 1980 *Phys. Rev.* B **21** 4829
[16] Murawski L 1984 *Phil. Mag.* B **50** L69
[17] Ghosh A 1990 *Phys. Rev.* B **41** 1479
[18] Bhattacharya S and Ghosh A 2003 *Phys. Rev.* B **68** 224202
[19] Ewiss M, El-Zayat M Y and Nothhelfer-Richter R 2005 *Phys. Chem. Glasses* 43 **165**
[20] Jung W H 2000 *J. Phys. D: Appl. Phys.* **33** 444
[21] Mogus-Milankovic A, Santic A, Licina V and Day D E 2005 *J. Non-Cryst. Solids* **351** 3235
[22] Elliott S R 1987 *Adv. Phys.* **36** 135
[23] Mott N F and Davis E A 1979 *Electronic Process in Non-Crystalline Materials* 2nd edn (Oxford: Clarendon)
[24] Pike G E 1972 *Phys. Rev.* B **6** 1572
[25] Hariharan K and Kaushik R 1987 *J. Mater. Sci.* **22** 3335
[26] Jonscher A K 1977 *Nature* **267** 673