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A DETAILED COMPARISON BETWEEN THE HOPPING CONDUCTIVITY AND THEORETICAL DATA OF THE $Ge_x Se_{100-x}$ GLASSY SYSTEM

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An investigation of the electrical properties of amorphous bulk samples of $Ge_x Se_{1oo-x}$ (with x = 5, 25, 28 and 30) has been carried out. Dc and ac electrical properties in the temperature range 289 to 338 K and at various frequencies from 10^2 to 10^5 Hz were the subject of the present work. Properties such as the dielectric constant, the loss factor and the electrical conductivities as functions of frequency and temperature are reported .The correlated barrier hopping model (CBH) of electrical conduction in amorphous materials has been used to describe this glass. A trial has been made to correlate the ac and dc conductivities with previously published theoretical data based on the effect of Ge on the homonuclear bond "excess bond ". The electrical properties were correlated with the coordination number N_c, the average heat of atomization H_s, the number of constraints N_{con}, the cohesive energy (CE) and the number of lone-pair electrons L. The comparison of the prediction with theoretical data shows very good agreement between the two.

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1. Introduction

The study of doped amorphous semiconductors is becoming of great interest to scientists. It was believed earlier [1] that impurities have little effect on the properties of amorphous semiconductors as each impurity atom can satisfy its valence requirements by adjusting its nearest-neighbor environment. However, several reports indicate that drastic changes in the conductivity and activation energy can be achieved by suitable preparation techniques [2-4]. Fritzsche and Kastner [5] have shown that the effect of charged additives in lone-pair semiconductors depends on whether the charged additives equilibrate or not with valence-alternation defects. Moreover, the variation of structural parameters corresponding to compositional changes may give further information about the influence of the type and degree of disorder on electronic properties. Measurement of ac conductivity of amorphous semiconductors has been extensively used to understand the conduction process in these materials [5]. The conductivity of semiconducting glasses is known to be frequency dependent what as expected, is due to conduction between localized states .The frequency dependence of the ac conductivity of glasses at a given temperature is often described by a power law [6]:

$$\sigma_T = \sigma_{dc} + \sigma_{ac}(\omega) = \sigma_{dc} + A\,\omega^s \quad (1)$$

Where σ_{dc} is the dc conductivity, $\omega = 2\pi f$ is the frequency and A and s are experimentally determined material constants. Correlated barrier hopping (CBH) of bipolarons (i.e. two electron hopping between charged defects D^+ and D^- [7,8]) and single polarons (holes hopping between D^0 and D^- and electrons between D^0 and D^+ [9,10]) are thought to dominate the ac conductivity of amorphous semiconductors. Although, numerous papers [11-15] have reported the effect of impurities on the conductivity in amorphous semiconductors, there are little data available from dielectric studies. The present study has twofold purposes; it determines the dc and ac conductivity as well as the dielectric constants and correlates these data with some " previously published " [11,14-18] theoretical data mainly with N_{co}, E_g, CE, Hs, L and some other related parameters.

2. Experimental procedure

Bulk $Ge_x Se_{100-x}$ samples with x = 5, 25, 28 and 30 were prepared from 5 N pure Ge and Se by using the conventional melt quenching technique. The appropriate compositions were loaded into a fused silica tubes [length 15 cm, internal diameter 1.5 cm]. The sealed tubes were heated in a rocking furnace. The furnace temperature was raised to 490 K (the melting point of Se), was kept there constant for two hours, raised up to 1233 K (the melting point of Ge), and maintained there for 8 hours. During this procedure the tubes were shaken vigorously to ensure alloy homogeneity and to prevent the escape of any dissolved or trapped gases from the molten mixture. After about 8, hours of heating the tubes were quenched in ice water. The ingots were confirmed to be completely amorphous by X-ray diffractions as well as Differential Thermal Analysis (DTA) as described in [11–14]. Polished samples, in the form of pellets were used for the measurements of ac and dc conductivity. A digital Keithely (E 616A) electrometer was used to measure dc electrical resistance (R_{dc}) directly. The dc conductivity σ_{dc} was calculated from $\sigma_{dc} = d / R_{dc}\, a$, where d is the thickness of the bulk samples and a is the cross sectional area. An automatic RLC bridge (PM 6304 Phillips) was used to measure the impedance Z, the capacitance C and the loss tangent (tan δ) directly. The total conductivity was calculated from the $\sigma_T(\omega) = d/Za$. The ac conductivity and the dielectric constant (ζ_1) were measured at various frequencies 10^2 to 10^5 Hz .The reproducibility of the results were checked by making runs at different times over the entire temperature and frequency range. It is observed that the conductivities and the dielectric constants were within ± 2 % error in different runs. However, only the result of one single run is reported here. The dielectric constant ζ_1 was calculated from

$\zeta_1 = dC / a\zeta_{o.,}$ where ζ_o is the permittivity of free space ($\zeta_o = 8.85 \times 10^{-12}$ F / m).

3. Results and discussion

3.1 Temperature dependence of dc conductivity

Fig.1 depicts the variation of the dc conductivity with temperature. Over the entire temperature range it can be expressed as a sum of two activated processes of the form [6]

$$\sigma_{dc} = \sigma_1 \exp(-\Delta E_1 / kT) + \sigma_2 \exp(-\Delta E_2 / kT) \qquad (2)$$

The first term dominates. The pre-exponential factor σ_1 for chalcogenide glasses is found to depend on composition. ΔE_1 and ΔE_2 are the activation energies. The conductivity given by the second term arises from tunneling to unoccupied levels of nearest-neighbor centers [14-18]. Here σ_2 is smaller than σ_1, partly because of the smaller density of states and mainly because the charge carriers have a much lower mobility. For all the samples shown in Fig. 1, the electrical conductivity was found to be a negative exponential function of the absolute temperature, expressed by the first term of Eq. (2). At a given temperature, depending on the content, a deviation of the linear dependence is observed for all the samples under study. The kink temperature is of the order of 310 ± 10 K for all the $Ge_x Se_{1oo-x}$ glasses. The presence of two linear regions in the ln σ versus T^{-1} plots is most likely due to the appearance of two conduction mechanisms. Such behavior allows us to conclude that at low temperature the dominant conduction mechanism is due to hopping conduction. On the other hand, at higher temperature it may be due to the band conduction in the extended states. ΔE_1, $\sigma_{1,}$ ΔE_2, σ_2 and σ_{RT} were calculated from Fig. 1 for the different composition of $Ge_x Se_{1oo-x}$ and are listed in Table 1. An increase in Ge from x = 5 to 30 leads to a decrease in the thermal activation energy ΔE_1 from 0.533 to 0.199 eV as well as σ_1 from 16.3 to 2.9×10^{-5} Ω^{-1} $m^{-1,}$ ΔE_2 from 0.078 to 0.116 eV as well as σ_2 from 1.02×10^{-6} to 1.37×10^{-7} Ω^{-1} m^{-1} and σ_{RT} from 4.80×10^{-8} to 1.38×10^{-8} $\Omega^{-1}m^{-1}$. This behavior is similar to that given in [19]. The decrease of ΔE_1 could be due to a decrease in the band gap, the band gap was found to decrease with increasing x, as obtained from the optical measurements given in Ref. [15]. The value of the optical gap E_g is additionally listed in Table 1. It was also observed that ΔE_2 is fairly constant ≈ 0.1 eV, which means that impurities are ineffective. It was also found that $\Delta E_1 > \Delta E_{2.}$ Such results agree well with Mott and Davis prediction [20]. In order to emphasize the effect of the above

mentioned parameters on composition, the results are compared with the average heat of atomization H_s, given in Ref. [18], and are listed also in Table 1. In order to correlate H_s with ΔE_1 and E_g, it is reasonable to use the average coordination number N_c instead of the isostructure of crystalline semiconductors, the results of N_c given in Ref. [14] for the compositions under study are also listed in Table1. The increase of Ge leads to the decrease of ΔE_1, E_g and H_s /N_c, whereas N_c and H_s exhibit the opposite trend .To account for the observed correlation, one should consider the type and strength of bandings. Structural representation of IR and Raman spectra for $Ge_x\ Se_{100-x}$ has demonstrated that there are Ge-Se bonds in the Se-rich region ($x \leq 33$), but no Ge-Ge bonds [21] that follow from the smaller binding energy of Ge-Ge bonds compared with those of Se-Se. The binding energies (A-A) of homonuclear bonds are; 44 K cal / mol for Se and 37.6 k cal / mol for Ge. Hence by adding Ge to Ge_xSe_{100-x} the average strength of the compound decreases and consequently ΔE_1 will decrease. In order to emphasize the relation between ΔE_1 and E_g with H_s, we compare the above-mentioned parameters with H_s /N_c, which is the average single bond energy in the alloy. One observes that ΔE_1, Eg as well as H_s/N_c decrease with increasing the Ge content, which suggests that one of the main factors in determining the thermal activation energy is the average single bond in the alloy. According to Phillips' [22] proposal Ge_xSe_{100-x} ($x \leq 33$) in its glassy form contains fragments of layers of Ge $(Se_4)_{1/2}$ tetrahedra, which form corner-sharing chains cross-linked by edge-sharing bitetrahedra. These layers form randomly oriented clusters terminated in the direction of cross-linking by Se-Se bonds. The assumption given above is similar to the structural model proposed by Tronc et al. [23], based on the chemical ordering of $GeSe_4$ tetrahedral interconnected by a chain of chalcogenide atoms. This may explain the decrease of ΔE_1 from 0.533 to 0.199 eV with increasing x.

Table 1. Values of ΔE_1, σ_1, σ_2 ΔE_2, σ_{RT}, E_g, H_s, Nc and H_{s}/N_c for $Ge_x\ Se_{100-x}$ films.

Comp. Ge_xSe_{100-x}	ΔE_1 eV	σ_1 $\Omega^{-1}m^{-1}$	ΔE_2 eV	σ_2 $\Omega^{-1}\ m^{-1}$	σ_{RT} x10^{-8} $\Omega^{-1}\ m^{-1}$	E_g eV	H_s Kcal/g atom	N_c	H_s /N_c
X = 5	0.533	16.30	0.078	1.02x10^6	4.80	1.86	51.43	2.10	24.49
X =25	0.480	1.060	0.084	6.09x10^{-7}	2.18	1.74	59.55	2.50	23.82
X =28	0.432	0.146	0094	7.04x10^{-7}	1.75	1.73	60.38	2.54	23.77
X =30	0.199	2.9x10^{-5}	0.116	1.37x10^{-7}	1.38	1.72	61.58	2.60	23.68

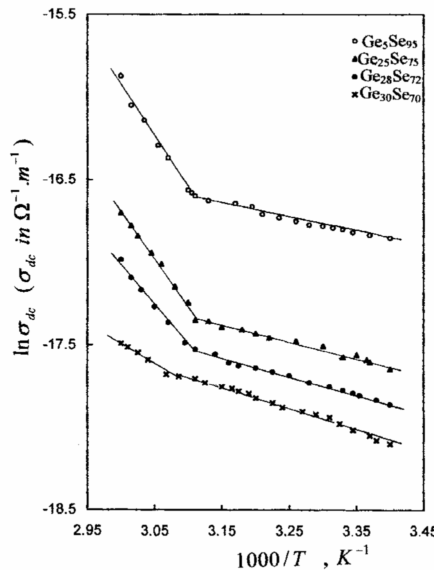

Fig 1. Temperature dependence of dc conductivity for $Ge_x\ Se_{100-x}$ (x = 5, 25, 28 and 30)

3.2 Temperature and frequency dependence of ac conductivity, dielectric constant and dielectric loss

Ac measurement is a powerful tool to determine the conduction mechanism in amorphous semiconductors. A common feature to all the amorphous semiconductors is the frequency-dependent conductivity σ_{ac} (ω). The ac conductivity, σ_{ac} (ω) of amorphous semiconductors is usually expressed by, σ_{ac} (ω) = σ_T (ω) - σ_{dc} = $A\omega^S$, where the frequency exponent s≤1 and, σ_{dc} part of the total conductivity σ_T (ω). Experimental results of σ_{ac} (ω) as a function of temperature (T) and frequency (ω) for the alloys under consideration are presented in Figs.2 & 3. As shown above the ac conductivity is independent on T in the considered range of temperature while, the frequency is found to have a pronounced effect on σ_{ac} (ω). Such a trend indicates that the Ge_x Se_{100-x} behaves as a semiconductor. It has been observed from Fig.4 for the Ge_5 Se_{95} and Ge_{25} Se_{75} as an example that, the parameter s does not change and remains constant around 0.95 over the temperature range 289-389 K. The parameter s is calculated from the slopes of the lines representing $\ln\sigma_{as}$ versus ln (ω) (Fig 3) and is listed in Table 2 for all the investigated compositions.

Table 2. Values of s, Tg, (ζ_1 and σ_{ac} at 330 K) for various composition of the Ge_x Se_{100-x} system.

Composition Ge_x Se_{100-x}	s	T_g K	ζ_1	σ_{ac} $(\Omega m)^{-1}$
X = 5	0.91	364	53	6.97×10^{-3}
X =25	0.95	448	84.2	9.50×10^{-3}
X =28	0.96	483	49	5.97×10^{-3}
X =30	0.99	516	108.4	1.29×10^{-3}

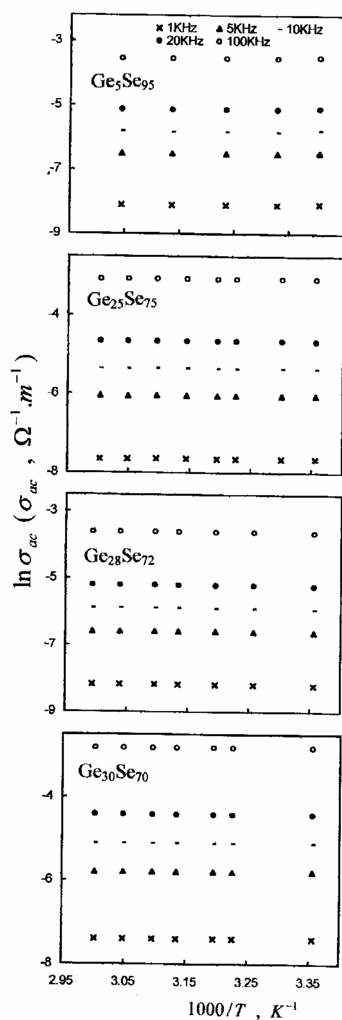

Fig 2. Variation of conductivity with temperature at different frequencies for Ge_x Se_{100-x} (x= 5, 25, 28 and 30)

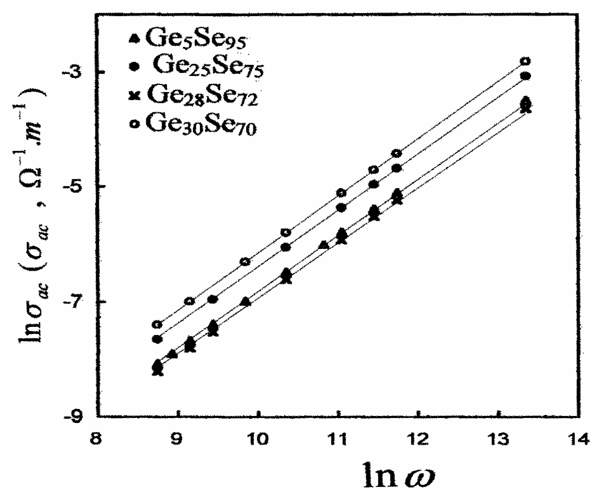

Fig 3. Frequency dependence of ac conductivity σ_{ac} (ω) for Ge_x Se_{100-x} (x = 5, 25, 28 and 30) at room temperature

Fig.5 shows the frequency and temperature dependence of the dielectric constant ζ_1 for Ge_5 Se_{95} and $Ge_{30}Se_{70}$ as a representative example. It is observed that the dielectric constant ζ_1 seems to be temperature and frequency dependent. On the other hand the decrease of ζ_1 with ω can be attributed to the contribution of multicomponents of polarizibility, deformational and relaxational components. The former polarizability concerns with electrons or ions, while the latter concerns with the orientational or interfacial [24] Increasing the applied field frequency tends to decrease the orientation polarization and hence the dielectric constant, since it takes more time than that for the electronic and ionic polarization. Such decreases tend to reduce the value of the dielectric constant with increasing the frequency.

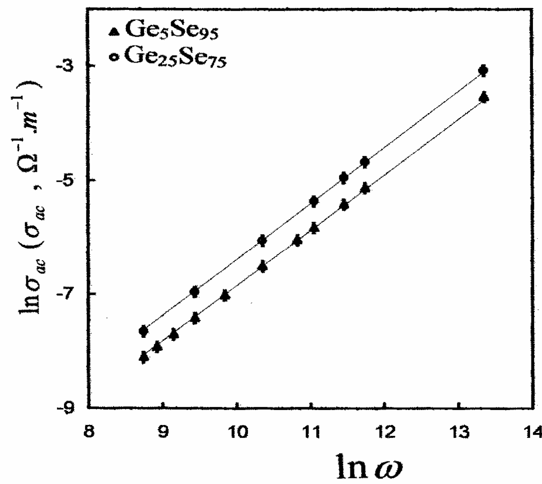

Fig 4. Frequency dependence of ac conductivity for Ge_5 Se_{95} and Ge_{25} Se_{75} at various temperatures range (295 to 324 K)

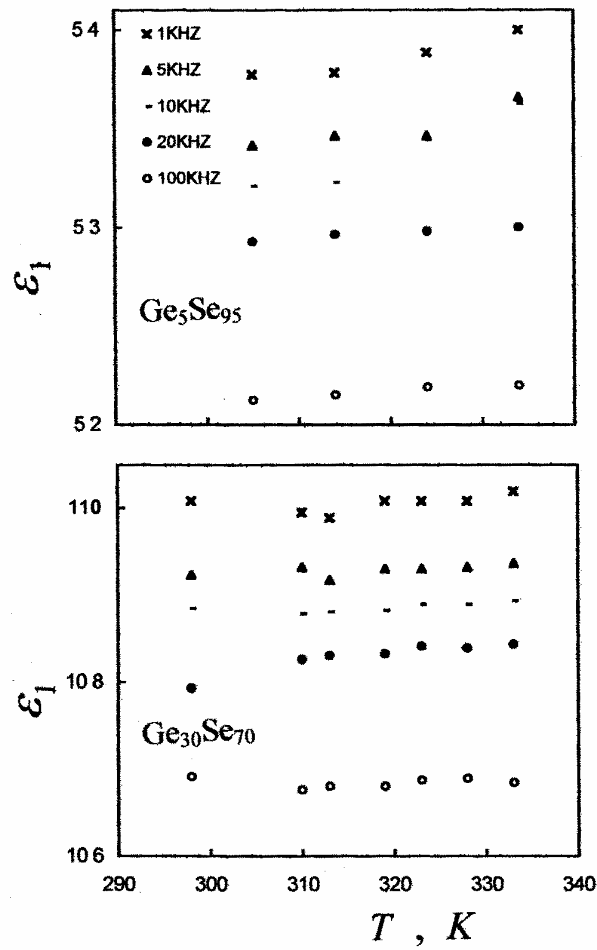

Fig 5. Variation of the real part of the dielectric constant ζ_1 with temperature at different frequencies for $Ge_x\,Se_{100-x}$ (x = 5 and 30)

The temperature and frequency dependence of ζ_2 of $Ge_5\,Se_{95}$ as a representative example is shown in Fig. 6. From the above figure, it is observed that ζ_2 increases slightly at high frequencies (10, 20, 100 K Hz), while at lower value of frequency (1 & 5 K Hz), ζ_2 increases obviously then decreases, on the other hand the process of increasing and decreasing of ζ_2 with temperature can be explained according to Stevels [24] who divided the relaxation phenomena into three parts, conduction loss, dipole loss and vibrational loss. At low temperature, the conduction loss has minimum values since it is proportional to (σ/ω). As the temperature increases, σ increases and so the conduction loss increases. This increases the value of ζ_2 with increasing temperature. In conclusion the ac results are consistent with Elliott's general views, concerning the amorphous semiconductor nature.

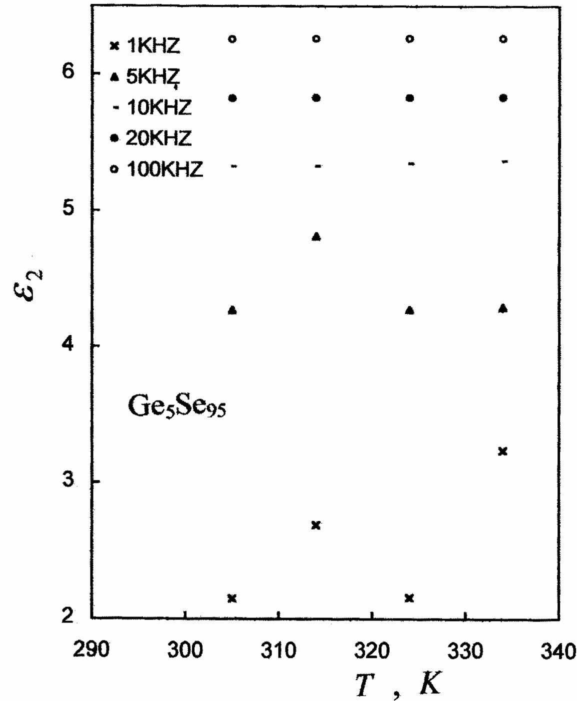

Fig 6. Variation of the imaginary part of the dielectric constant ε_2 with temperature at different frequencies for $Ge_5 Se_{95}$.

The (CBH) model is the most widely model used to describe the ac conductivity of amorphous semiconductors. Therefore we use this model to explain the effect of the addition of Ge to $Ge_x Se_{100-x}$. Elliott [7&8] has considered a model based on the nature of the defect centers in these materials proposed by Mott et al [25] in which spin pairing is believed to be energetically favored all defect centers, weather they were positively or negatively charges, and according to the (CBH) model electron pairs hope from doubly occupied D^+ stated to a nearly D^- center over the barrier separating the two sites. The (CBH) of bipolarons proposed by Elliott [26] has explained many features at relatively low temperature values of parameters s & A and its temperature dependence and the band gap dependence of σ_{ac} (ω, T) and it's temperature dependence [27].However, it does not predict the strong T dependence of σ (ω , T) which has been observed at high T in some materials.

Table 3. Values of E_g, N_{con} and L, compared with bond energies expected to occur in the $Ge_x Se_{100-x}$ system.

Composition $Ge_x Se_{100-x}$	E_g eV	N_{con}	L	Excess of Se-Se bonds	CE eV atom^{-1}
X = 5	1.86	2.205	3.80	170	2.050
X =25	1.74	3.125	3.45	50	2.621
X =28	1.73	3.350	290	32	2.706
X =30	1.72	3.645	2.70	20	2.765

The agreement between experiment and theory is in a good agreement for both single polaron and bipolaron cases; it is evident that the bipolaron is predominant in the system used in this work. Phillips [28] proposed that germanium chalcogenide glasses can be described as small chemically orders embedded in a continuous network .In view of this feature of Ge-Se glasses it can be said that the bipolarons hopping takes place due to the hopping of two electrons between the two charged states as previously mentioned.

According to [28-30] the value of the dielectric constant ζ_1 could be explained by assuming a decrease in the bond energies and hence one should consider the type and strength of bonding present in the system under study. Phillips [29] has also invoked his constraint theory to explain the effect of the increase in coordination number N_c and the corresponding modification in the chemical bond, on the optical and electronic properties of the alloys. It is proposed that observed changes in the electrical properties results from the local change in the chemical bonding. Also, the change in band gap that may results because of the mixing of two semiconductors that have different band gap values may also contribute to the observed changes in the optical and electrical data. The chemical bond approach has been used by Bicerano et.al [31] to explain the electrical behavior of amorphous systems. Such an approach explains the behavior in terms of the cohesive energy (CE) , which reflects the average bond strength at a given composition , at the same time it allows the determination of the number of possible bonds and there types (heteropolar and homopolar). As it was explained in details in Ref. [14] the (CE) reflects the average bond strength, and it allows the determination of bonds between like atoms if there is an excess of certain type of atoms, until all available valences for the atoms are saturated. Chalcogenide glasses are often called lone-pair (LP) semiconductors due to the fact that the lone-pair electrons (4p for Se) do not participate in the bonding, hence the chemical environment in the structure has influenced on the role of lone-pair electrons. The number of (LP) electrons obtained in Ref. [18] for the different composition of the Ge_x Se_{100-x} system is listed in Table 3. The previously obtained results of the optical gap E_g, the (CE), the number of homopolar bonds (excess bonds) and the number of constraints N_{con} are listed in Table 3. The observed data reveal that the addition of Ge leads to a decrease in, E_g and the number of (LP) L and the number of homopolar bonds (excess bonds). On the other hand, the frequency exponent s, the (CE) as well as N_{con} increase. The increase of the (CE) and other related parameters with increasing the Ge - content follows the ordering that would be expected from qualitative arguments concerning relative rigidities of network containing different percentage of x in the Ge_x Se_{100-x} system, and are in a very good agreement with the results and the explanations of the dc conductivity. A detailed analysis of the atomic arrangement in our binary system requires the determination of the radial distribution function which was also calculated by us from the RDF results given in Ref. [17]. The interatomic distance determined from the main peak is in a very good agreement with the experimental and theoretical studies given in this work.

4. Conclusions

In conclusion, we have studied the conductivity and dielectric constant for various alloys of the amorphous Ge_x Se_{100-x} semiconductor, at various temperature and frequency. Analysis of the results on the basis of the correlated barrier hopping (CBH) model reveals that the electronic conduction takes place via bipolaron hopping. A comparison between theoretical and experimental data was done. The agreement between the results is excellent and is also consistent with the theory used for explaining the conductivity and dielectric behavior.

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