OBSERVATION OF FURTHER MEYER-NELDEL RULE FOR AC CONDUCTION IN GLASSY $Se_{70}Te_{30-x}Zn_x$

S. SRIVASTAVA, S. YADAV, R. K. SHUKLA, A. KUMAR*
Department of physics, Harcourt Battler Technological Institute, Kanpur

Temperature dependence of a.c. conductivity is studied in bulk glassy $Se_{70}Te_{30-x}Zn_x$ at different frequencies. At a particular frequency, a.c. conductivity is found to vary exponentially with temperature in certain temperature range. The activation energy is, however, found to be different at different frequencies. The pre-exponential factor is found to be correlated with activation energy following Meyer - Neldel (MN) rule. The observation of further MN rule in case of a.c. conductivity is also observed in the present case.

(Received February 26, 2010; wccepted March 15, 2010)

Keywords: Chalcogenide glasses, pre-exponential factor, activation energy

1. Introduction

Recently, the efforts have been devoted to the development of chalcogenide materials suitable for optoelectronics. The investigation of electrical and optical properties of Se based chalcogenide glasses have been a subject of active research for both solid state people and electronic engineers for their applications as photovoltaics [1] and memory switching [2] materials. Many amorphous semi-conducting glasses, especially, Se, exhibit a unique property of reversible transformation [3], which makes them very useful in optical memory devices.

Generally, conductivity of a semiconductor obeys the relation,

$$\sigma = \sigma_0 \exp(-\Delta E / kT) \quad (1)$$

where, ΔE is called the activation energy and σ_0 is called the pre-exponential factor. In most of the semiconducting materials, σ_0 does not depend on ΔE [4-12]. However, in some cases, σ_0 correlates with activation energy ΔE as,

$$\sigma_0 = \sigma_{00} \exp(\Delta E / kT_0) \quad (2)$$

Where, σ_{00} and kT_0 are constants for a given class of materials. σ_{00} is often called as MN pre-exponential factor, and kT_0, as the MN characteristic energy. Equation (2) is often referred as MN rule or the compensation rule. This rule in case of a.c. conductivity has been observed by many workers in some chalcogenide glasses [13-17].

Recently, further MN rule in thermally activated crystallization and high field conduction is observed by Mehta et. al. [18-19]

In the present work, we have tried to observe further MN rule in a.c. conductivity measurements in bulk samples of $Se_{70}Te_{30-x}Zn_x$. For this, we have measured the temperature dependence of a.c. conductivity at different frequencies.

2. Experimental

Samples of glassy $Se_{70}Te_{30-x}Zn_x$ (x = 0, 2, 4 and 8) alloys were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te and Zn elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4}gm. The materials were then sealed in evacuated (~ 10^{-5} Torr) quartz ampoules (length ~ 5cm and internal diameter ~ 8 mm). The ampoules containing material were heated to 1000^0C and were held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{0}C / minute. During heating, the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melt was cooled rapidly by removing the ampoules from the furnace and dropping them to ice-cooled water rapidly. The quenched samples were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by X-ray diffraction.

The glassy alloys thus prepared were crushed to a very fine powder and pellets (diameter ~ 6 mm and thickness ~ 1 mm) were obtained by compressing the powder in a die at a load of 5 Tons. The pellets were coated with silver paint to ensure good electrical contact between sample and the electrodes. The temperature measurement was facilitated by a copper-constantan thermocouple mounted very near to the sample. A vacuum of ~10^{-2} Torr was maintained over the entire temperature range.

The a.c. conductivity, conductance and capacitance were measured using a digital LCR meter. The parallel conductance was measured and a.c. conductivity was calculated. Three terminal measurements were performed to avoid the stray capacitances.

3. Results

The temperature dependence of a.c. conductivity in glassy $Se_{70}Te_{30-x}Zn_x$ (x = 0, 2, 4 and 8) alloy is studied at different frequencies. The results for glassy $Se_{70}Te_{30-x}Zn_x$ are shown in Figs 1- 4. It is clear from these figures that ln σ_{ac} vs 1000/T curves are straight lines at different frequencies for bulk glassy alloys of $Se_{70}Te_{30-x}Zn_x$.

The above results show that, the variation of a.c. conductivity with temperature can be expressed by exponential relation,

$$\sigma_{ac} = \sigma_0 \exp(-\Delta E / kT) \quad (3)$$

where, ΔE is called the activation energy for a.c. conduction and σ_0 is called the pre-exponential factor.

The a.c. activation energy (ΔE) is determined from the slope of the straight lines in the resulting plots at different frequencies (Figs 1- 4). These straight lines are obtained by best fit to the experimental data using the least square method. The intercept of the line gives the value of ln σ_0.

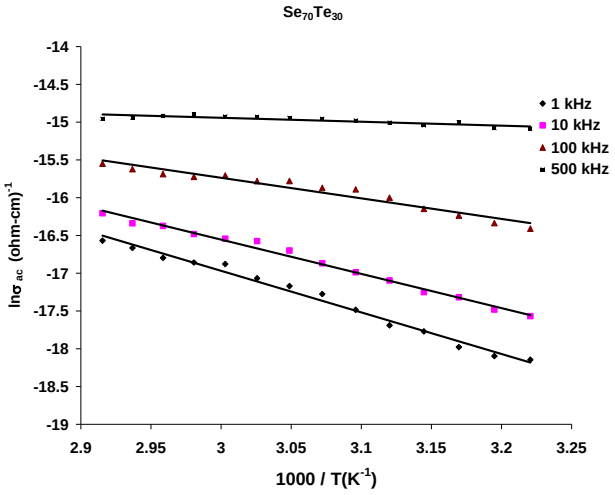

Fig.1 Plot of ln σ_{ac} vs 1000 / T for glassy $Se_{70}Te_{30}$ alloy

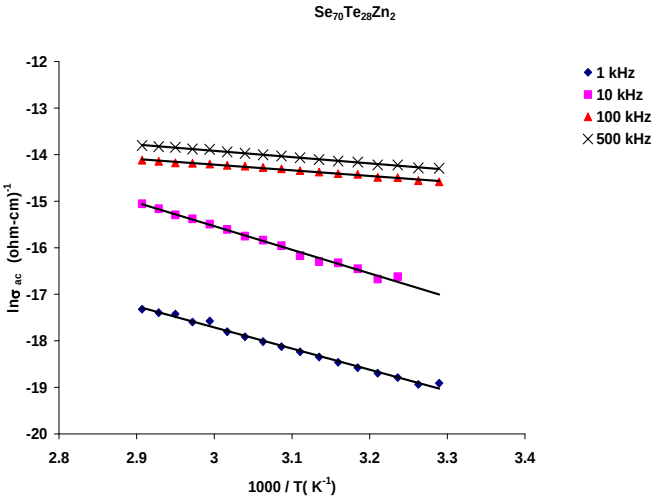

Fig.2. Plot of ln σ_{ac} vs 1000 / T for glassy $Se_{70}Te_{28}Zn_2$ alloy.

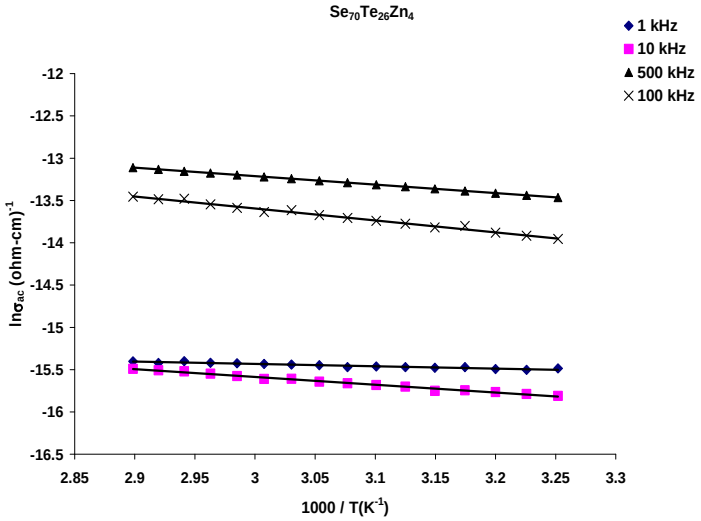

Fig.3. Plot of ln σ_{ac} vs 1000 / T for glassy $Se_{70}Te_{26}Zn_4$ alloy

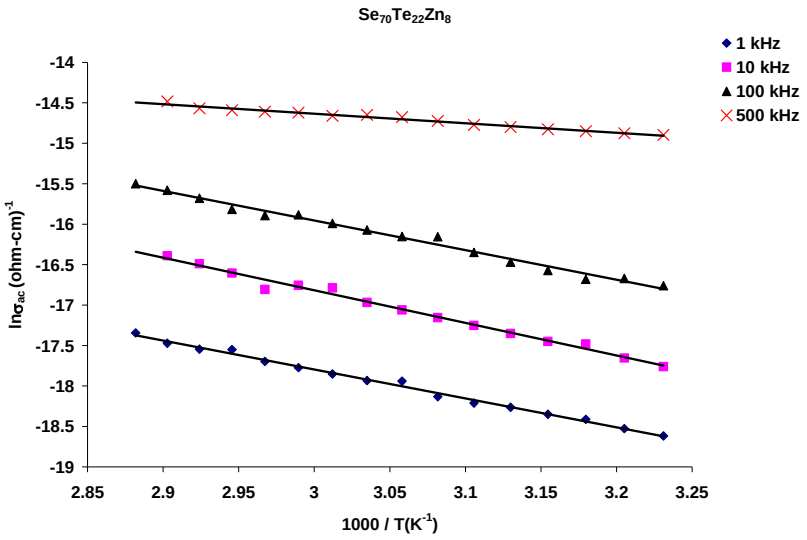

Fig.4. Plot of ln σ_{ac} vs 1000 / T for glassy $Se_{70}Te_{22}Zn_8$ alloy.

The values of ΔE and $\ln\sigma_0$ are given in Tables 1- 4 for $Se_{70}Te_{30-x}Zn_x$ alloys. Figs 5-8 show the plots of $\ln\sigma_0$ vs ΔE for different glassy alloys, which are straight lines indicating that σ_0 varies exponentially with ΔE following the relation as given by Equation (2).

Table 1. Values of activation energy and pre-exponential factor of $Se_{70}Te_{30}$ alloy.

Frequency(KHz)	ΔE (eV)	ln σ_0(ohm-cm)$^{-1}$
1	0.394	-2.864
10	0.239	-7.405
100	0.427	-2.086
500	0.058	-13.728

Table 2. Values of activation energy and pre-exponential factor of $Se_{70}Te_{28}Zn_2$ alloy.

Frequency(KHz)	ΔE (eV)	lnσ_0(ohm-cm)$^{-1}$
1	0.394	-3.996
10	0.343	-3.739
100	0.116	-9.875
500	0.106	-10.524

Table 3. Values of activation energy and pre-exponential factor of $Se_{70}Te_{26}Zn_4$ alloy

Frequency(KHz)	ΔE (eV)	lnσ_0(ohm-cm)$^{-1}$
1	0.025	-14.533
10	0.074	-12.455
100	0.110	-9.436
500	0.080	-12.568

Table .4 Values of activation energy and pre-exponential factor of $Se_{70}Te_{22}Zn_8$ alloy.

Frequency(KHz)	ΔE (eV)	$\ln\sigma_0(\text{ohm-cm})^{-1}$
1	0.34	-4.709
10	0.31	-5.090
100	0.18	-9.606
500	0.09	-11.317

Recently, it is reported that the relaxation time formula is activated, and it includes the Meyer-Neldel rule term rather than its simple activated form [20]. The chalcogenide glassy material during a.c. conduction can be considered as a medium consisting of network of resistors and capacitors [21]. If the local conductivity is thermally activated, and all capacitors are assumed to be equal, then the resistance and capacitance between pairs of site is given by:

$$R=R_o \exp (W/ k T) \quad (4)$$

and $$C = C_o$$

where R_o & C_o are constant. For the whole system, a broad distribution of energy barriers [21] P (W) can be anticipated, and resistance of sample is given by

$$R=R_o P (W) \exp (W/ k T) \quad (5)$$

Time constant of circuit is

$$\tau = RC = R_o C_o P (W) \exp (W/kT) \quad (6)$$

where $R_o C_o = \tau_o$

For P (W) = constant, the relaxation time has an Arrhenius form.

If the distribution of the energy barriers has an exponential form [21-25]
P (W) ~ exp (-W/ k T_o) where T_o is the characteristic temperature, then equation (6) becomes

$$\tau = \tau_o \exp(W/k T) \exp (-W/k T) \quad (7)$$

This is exactly the same as MN rule formula.

In the present case also, the activation energy of a. c. conduction decreases with increase in frequency and it satisfies MN relation with pre-exponential factor. This may be due to compensation effect in relaxation time as suggested by Abdel-Wahab for some chalcogenide glasses [21].

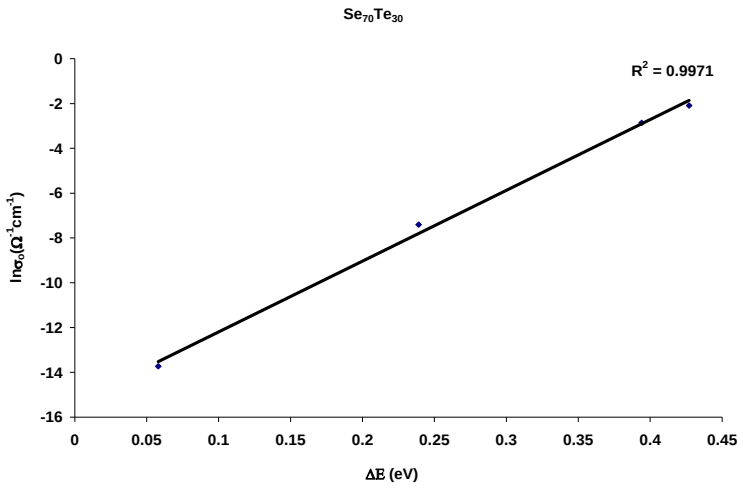

Fig.5. Plot of pre exponential factor ln σ_0 vs ΔE for glassy $Se_{70}Te_{30}$ alloy

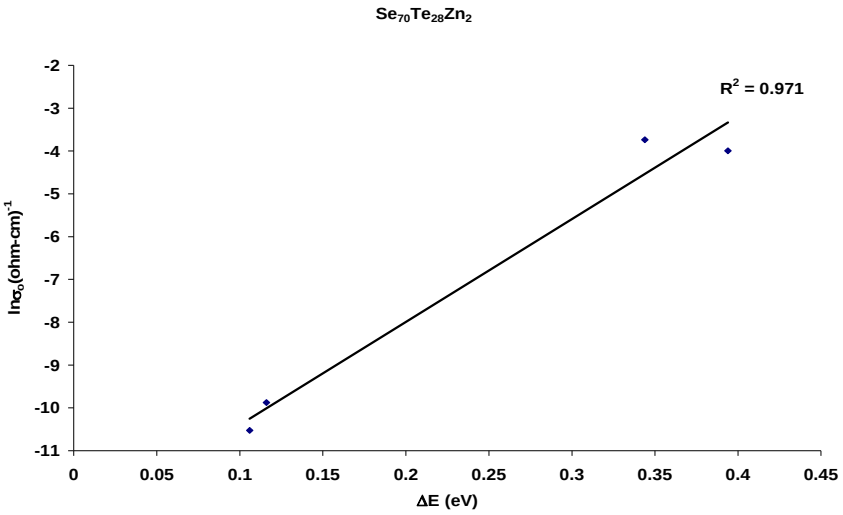

Fig.6. Plot of pre exponential factor ln σ_0 vs ΔE for glassy $Se_{70}Te_{28}Zn_2$ alloy

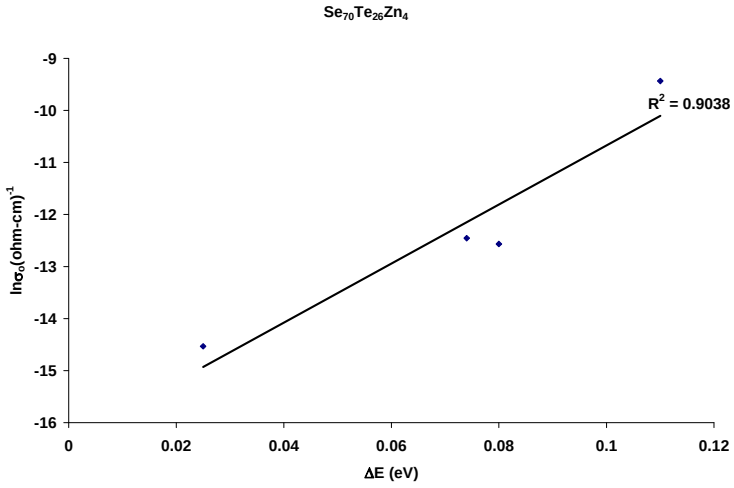

Fig.7. Plot of pre exponential factor ln σ_0 vs ΔE for glassy $Se_{70}Te_{26}Zn_4$ alloy

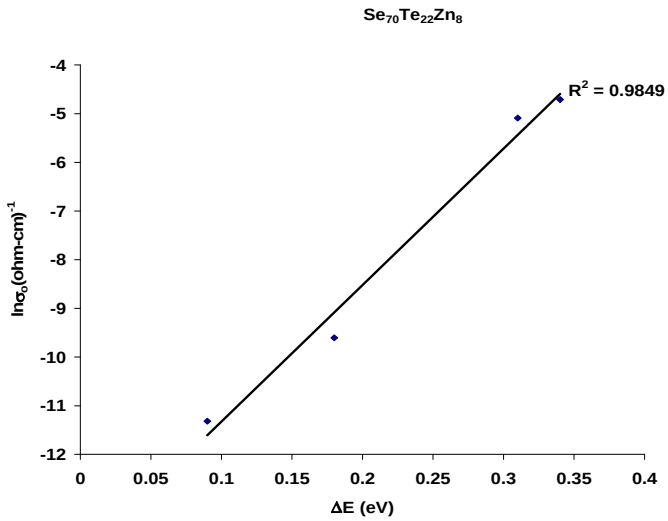

Fig.8. Plot of pre exponential factor ln σ_0 vs ΔE for glassy $Se_{70}Te_{22}Zn_8$ alloy

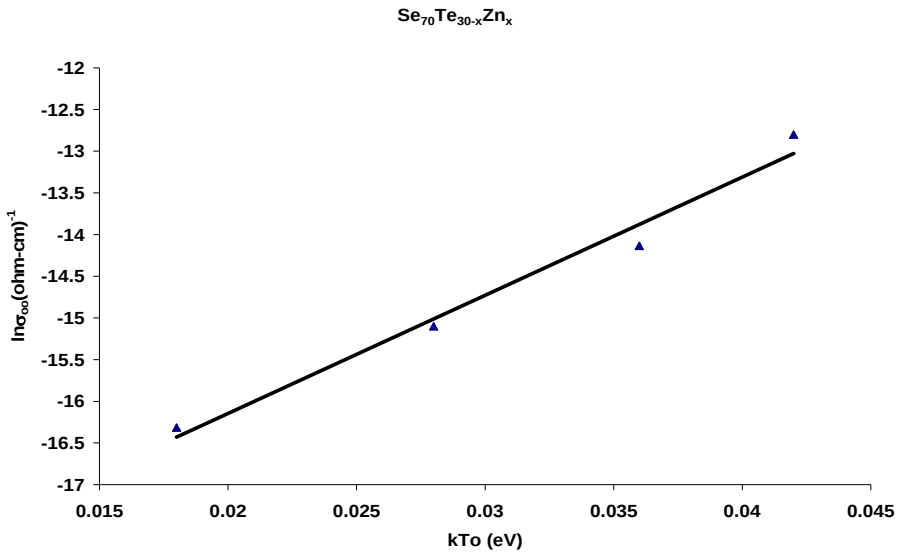

Fig.9 Plot of pre exponential factor ln σ_{00} vs kT_0 for glassy $Se_{70}Te_{30-x}Zn_x$ alloy

It is interesting to note that the value of MN conductivity pre- exponential factor σ_{00} is different at different frequencies. The value of the characteristic energy kT_0 is also different at these frequencies, as shown in Table 5. On plotting ln σ_{00} as function of kT_0, a straight line is obtained (Fig. 9) which indicates that a strong correlation exists between these quantities which can be described by the following relation:

$$\sigma_{00} = \sigma'_{00}\exp(kT_0 / \varepsilon) \tag{8}$$

where ε is a constant.

Table 5. The ln σ_{00} and (kT_0)for different compositions.

Sample	$\ln\sigma_{00}$ (ohm-cm)$^{-1}$	(kT_0)(eV)
$Se_{70}Te_{30}$	-15.10	0.028
$Se_{70}Te_{28}Zn_2$	-12.80	0.042
$Se_{70}Te_{26}Zn_4$	-16.31	0.018
$Se_{70}Te_{22}Zn_8$	-14.13	0.036

The correlation between σ_{00} and kT_0 has been reported by Shimakawa and Abdel-Waheb [26] in the case of chalcogenide glasses and is called as further MN rule. The observation of the correlation between MN pre-factor σ_{00} and MN energy can also be explained by multiple excitations stimulated by optical phonon energy as describe by Yelon and Movaghar[27-28].

4. Conclusions

To observe the presence of Meyer - Neldel rule in bulk samples of $Se_{70}Te_{30-x}Zn_x$ (x =0, 2, 4, 8), the variation of activation energy is measured at different frequencies for bulk sample of $Se_{70}Te_{30-x}Zn_x$. The pre-exponential factor σ_0 changed with activation energy for all glassy alloys. It is found that σ_0 varies with ΔE at different frequencies. Here, a co-relation between σ_{00} and kT_0 is also observed indicating the presence of further MN rule as observed in other thermally

activated processes. This is explained by Yelon and Movaghar in terms of multiple excitations stimulated by optical phonon energy.

References

[1] Rowlands J & Kasap S, Phys. Today **50**, 24 (1997)
[2] Segura A, Guesdon J P, Besson J M & Chevy, J. Appl. Phys. **54**, 876 (1983)
[3] Kenawy M A, El-Shazly A F, Afify M A Zayad H A et al, Thin Solid Films **200**, 203 (1991)
[4] R. Arora, A. Kumar, Phys. Status Solidi (a) **125**, 273 (1991).
[5] A. Many, E. Harnik, D. Gerlick, J. Chem. Phys. **23**, 1733 (1955).
[6] S. K. Dwivedi, M. Dixit, A. Kumar, J. Mat. Sci. Lett. **17**, 233 (1998).
[7] S. W. Johnston, R.S. Crandall, A. Yelon, Appl. Phys. Lett. **83**, 908 (2003)
[8] M. Kikuchi, J. Appl. Phys. **64**, 4997 (1988).
[9] K. Morii, T. Matsui, H. Tsuda, H. Mabuchi, Appl. Phys. Lett. **83**, 908 (2003).
[10] J. Fortner, V, G. Karpov, M. Saboungi, Appl. Phys. Lett. **66**, 997 (1995).
[11] K. L. Narashimhan, B. M. Arora, Solid State Commun. **55**, 615 (1985).
[12] G. Kemeny, B. Rosenberg, J. Chem. Phys. **52**, 4151 (1970).
[13] F. Abdel-Waheb, J. Appl. Phys. **91**, 265 (2002).
[14] F. Abdel-Waheb, Turk. j. Phys.**28**, 133 (2004).
[15] N. Mehta D. Kumar, A. Kumar, Matter. lett. **61**, 3167 (2007).
[16] N. Mehta S. Kuamr, A. Kumar, Eur. Phys. J. Appl. Phys. **37**, 123 (2006).
[17] N. Mehta, D. Kumar, A. Kumar Glasss Physics and Chemistry **34**, 42 (2008)
[18] N. Mehta, A. Kumar journal of Non crystalline solids **354**, 5347 (2008)
[19] N. Mehta, V. S. Kushwaha, A. Kumar, Vaccum **83**, 1169 (2009)
[20] Abdel-Wahab F. Turk .J. Phys **28**, 133 (2004)
[21] J.C. Dyre, J. Appl. Phys. **64**, 2456 (1988)
[22] Hvam JM, Brodsky MH. Phys. Rev. Lett. **46**, 371 (1981)
[23] J.C. Dyre, J. Phys. C**19**, 5655 (1986)
[24] J.C. Dyre, J. Phys. **C21**, 2431 (1988)
[25] J.R.Macdonald,J. Appl.Phys.**58**, 1955 (1985)
[26] K. Shimakawa, Abdel – Wahab, Appl. Phys. Lett. **70**, 652 (1997).
[27] Yelon, B. Movaghar, Phys. Rev. Lett., **65**, 618 (1990).
[28] A. Yelon, B. Movaghar, H. M. Branz, Phys. Rev. B, **46**, 12244 (1992).

*Corresponding author: ysarish@yahoo.com