JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 6, June 2007, p. 1710 - 1714

Effective pair potentials for molten Cu-Ge alloys

S. SENTURK DALGIC[a], M. CELTEK[b*], S. DALGIC[a]
[a]*Department of Physics, Trakya University, 22030, Edirne, Turkey*
[b]*Faculty of Education, Trakya University, 22030, Edirne, Turkey*

The local evanescent core type electron-ion potentials (EC) constructed by Nogueira and co-workers have been applied to molten Cu-Ge alloys at different compositions of Ge. The structure properties of liquid Cu-Ge alloys, such as partial static structure factors and pair distribution functions have been calculated using the variational modified hypernetted chain (VMHNC) integral equation theory of liquids. Comparison of the structural results with experimental data confirms the ability of the universal density dependent version of the EC potential to be used in the case of liquid Cu-Ge alloys. With the change of temperature, the diffusion coefficients of the pure components and alloy obtained from the average mean-square displacement can be fitted by the Arrhenius equation. The fit yields an activation energy and pre-exponential factor. The diffusion coefficients for pure components near their melting points are in a good agreement with experimental values.

(Received November 14, 2006; accepted April 26, 2007)

Keywords: Liquid Cu-Ge alloys, Structure, Pseudopotentials, Effective potentials

1. Introduction

Noble metals formed with polyvalent metals are characterized by specific physical properties in the liquid state. These physical properties are assumed to be caused by forming some clusters of unlike atoms in the liquid 'noble metal-polyvalent metal' systems. In this connection, it would be most interesting to determine by structural study whether the clusters containing different types of atoms in liquid alloys of noble and polyvalent metal really exist. From a theoretical of view, the study of metals and alloys can be studied with pseudopotentials [1]. Structure of the metals and alloys in their liquid state are well described using the effective inter-ionic interaction derived from the pseudopotential theory [1-3]. In principle the pseudopotentail can be of local or non-local character.

In this work we have concerned with a local evanescent core (EC) type model pseudopotential of Fiolhais *et al.* [4], so-called as the universal evanescent pseudopotential EC(U) in which the parameters R and α depend on the valence Z and the average electron density ρ, namely. $R(r_s,Z)$ and $\alpha(r_s,Z)$ was proposed by Nogueira, Fiolhais and Perdew [5]. We have presented the results of Fiolhais type pseudopotentials for liquids Fe, Co and Ni [6], and for liquid alkaline earth metals and metal alloys as the charge transferred alloys, such as Li-Ba liquid alloys in the zero alloy case [7]. On the other hand, in a recent work Dalgic and co-workers have been reported the structural calculations for the liquid hcp rare-earth metals using the effective pair potential derived from the EC type of Fiolhais' pseudopotentials with the VMHNC liquid state theory [8]. We have also shown that the universal choice of Fiolhais' potential predicts reasonable structural properties for liquid Ag, In and liquid Ag-In alloys [9]. Motivated by the success of the transferable local pseudopotential of Fiolhais *et al.* [4, 5] to predict the static structure of liquid simple metals and metal alloys, we examine the extent to considering the structural properties of liquid Cu-Ge alloys.

Copper-germanium system has been chosen for investigation in the present work due to several reasons. Copper and germanium are two elements which have very different physical properties and structures in the solid as well as in the liquid state. Upon melting, Ge undergoes a semiconductor-metal transition accompanied by significant structural changes. Chemical activity of germanium in binary melts is very high and it shows the tendency to interact with unlike atoms. Hoyer and co-workers have reported that the liquid Cu-Ge alloys have a pronounced extremum on the isothermal dependencies of physical properties near the concentration of the intermetallic compound [10]. Related to this, a maximum of the concentration dependency of the electrical resistivity of Cu-Ge liquid alloys has been observed at $Cu_{75}Ge_{25}$ [11]. X-ray patterns, structure factors, and radial distribution functions of liquid copper and germanium are very different. This fact suggests noticeable differences in the respective functions for various compositions of Cu-Ge melts.

To the best of our knowledge, universal version of EC potential EC(U) has not been extended to the case of liquid noble metal-polyvalent metal binary alloys and there is no published parameters of EC(U) for liquid Cu. It is thus interesting to examine how the structure factor and other structure-dependent characteristics evolve as a function of concentration from pure copper to pure germanium in the liquid Cu-Ge alloys. Therefore we only present the results for Cu and Cu-Ge with EC(U) model potential. We have also obtained the structural properties of liquid Cu-Ge alloys in comparison with the experimental data [12] and the molecular dynamics calculations [13]. We show that the universal choices of Fiolhais' potential predicts more reasonable structural properties for liquid Cu, Ge and liquid Cu-Ge alloys than others. In order to improve the reliable of model, we have calculated atomic dynamic properties, such as self-diffusion coefficient at different temperatures. We have seen Arrhenius type relation between self-diffusion coefficient and temperature.

2. Theory

In a simple liquid metallic alloy, A_xB_{1-x}, the standard second-order perturbation theory leads to the effective interionic pair potentials, $\phi_{ij}(r)$, (i, j = A, B)

$$\phi_{ij}(r)=\frac{Z^i_{eff}Z^j_{eff}}{r}+\phi^{ij}_{ps}(r) \qquad (1)$$

in terms of A-type and B-type effective local pseudopotentials, which the Fourier transform of $\phi_{ps}^{ij}(r)$ given as

$$\phi_{ps}^{ij}(q) = \chi(q)\tilde{v}_{ps}^{i}(q)\tilde{v}_{ps}^{j}(q) \tag{2}$$

where $\tilde{v}(q)$ is the pseudopotential local form factor for species i and j and $\chi(q)$ is the response function of the electron gas. In the present work, we use the recent local pseudopotential proposed by Fiolhais *etal.* so called local evanescent core (EC) pseudopotential. An analytic expression for the form factor of this pseudopotential in Fourier space

$$\tilde{v}(q) = 4\pi Z_{eff} R^2 \left[-\frac{1}{(qR)^2} + \frac{1}{(qR)^2 + \alpha^2} + \frac{2\alpha\beta}{\left[(qR)^2 + \alpha^2\right]^2} + \frac{2A}{\left[(qR)^2 + 1\right]^2} \right] \tag{3}$$

where R is the core decay length, β and *A* parameters are given in terms of α namely,

$$\beta = \frac{\alpha^3 - 2\alpha}{4(\alpha^2 - 1)} \quad , \qquad A = \frac{\alpha^4}{4(\alpha^2 - 1)} \tag{4}$$

The values α and R can be obtained from the equilibrium condition of the solid state.

With the effective pair potential known, integral equations are able to provide us the liquid structure for metals and alloys. In our structural calculations, one of the integral equation theories which has shown to be very reliable theory of liquids VMHNC has been carried out [14, 15]. Like most liquid state theories the VMHNC solves the Ornstein–Zernike (OZ) equation which defines in terms of the partial direct correlation functions, $c_{ij}(r)$, the total correlation functions $h_{ij}(r)=g_{ij}(r)-1$, where $g_{ij}(r)$ denote the partial pair distribution functions and ρ_l denote the partial ionic number densities. The O-Z equation can be solved by minimizing the configurational Helmholtz free energy functional $f^{VMHNC}(\beta,\rho,x_l,\eta_\alpha)$ as

$$\frac{\partial f^{VMHNC}(\beta,\rho,x_1,\eta_\alpha)}{\partial \eta_k} = 0, \qquad k = 1,2,...,mn \tag{5}$$

with the exact closure relation of MHNC. The total structure factors for liquid alloys are determined as a linear combination of partial structure factors [16] using b_i and b_j neutron scattering amplitudes [17].

Among the atomic transport properties, the diffusion constants are important parameters for characterizing the liquid and as input into modelling heat and mass flow in crystal growth simulations. It is possible to compute the diffusion constant from two different time-dependent correlation functions. One is the normalized velocity autocorrelation function defined as

$$Z(t) = \frac{\langle \vec{v}(t) \cdot \vec{v}(0) \rangle}{\langle \vec{v}(0)^2 \rangle} \tag{6}$$

which allows one to obtain the self-diffusion constant trough the Green-Kubo (GK) type equation

$$D = \frac{k_B T}{M} \int Z(t)\, dt \tag{7}$$

where M is mass of atom. The other is the mean square displacement from which D is obtained using the Einstein (E) relation

$$D = \lim_{t\to\infty} \frac{\langle \Delta r^2(t) \rangle}{6t}. \tag{8}$$

The reader is referred to Refs. [18, 19] for details in dynamic structural calculations. The temperature dependence of our diffusion coefficient data exhibits the Arrhenius-type behaviour;

$$D(T) = D_0 \exp(-E_a / k_B T) \tag{9}$$

where D_0 is the self-diffusion prefactor and E_a is the diffusional activation energy.

3. Results and discussion

In this work, we have calculated the effective inter-ionic pair potentials using the EC(U). Pure copper and germanium and Cu-Ge alloys in liquid state have been investigated at a constant temperature of 1373 K. The presentation of the results is divided into two parts: the first one concern with the pure simple metals. The number densities of liquid Cu and Ge at 1373K are 0.0757at./A^3 and 0.0450 at./A^3, respectively. For liquid Cu and Ge, the parameter Z_{eff} are taken as 1.5 predicting the best result for g(r) comparing with experiment. The potential parameters α and R are 4.320 and 0.276(au) for Cu taken in Ref.[20]; 3.782 and 0.373(au) values determined for Ge. The second one deals with structure of Cu-Ge liquid alloys at different Cu compositions. The average number densities at there thermodynamic states are computed from the pure number densities of two component species.

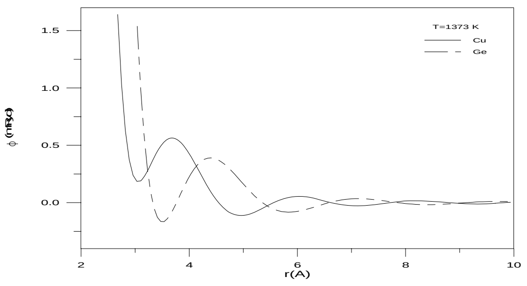
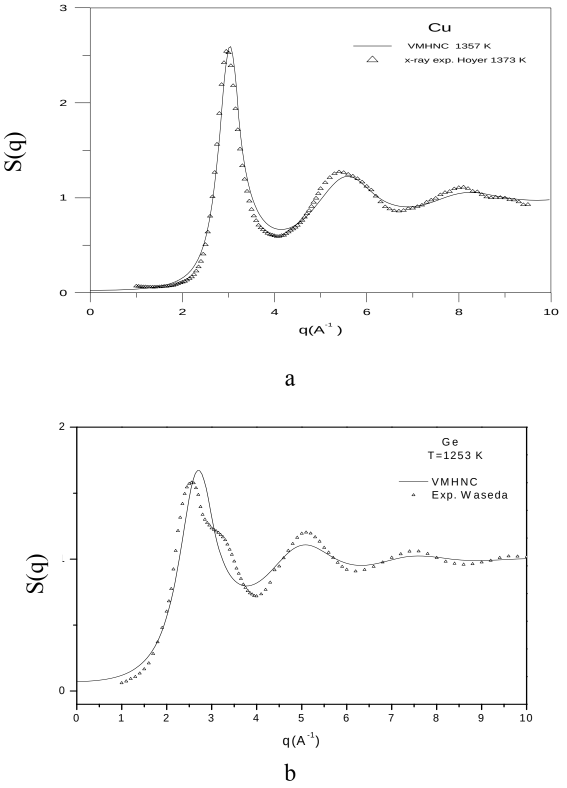


Fig. 1. Pair potentials for liquid Cu and Ge at T=1373 K.

In Fig. 1 we have also compared the calculated the EC(U) effective pair potentials of liquid Cu and Ge with those obtained from Fiolhais' potential. It is seen that the Cu exhibits solid state properties because of the presence positive minimum at small r values.

The VMHNC approximation is employed to calculate the liquid state structure factors S(q) of the pure systems. The S(q) for liquid Cu and Ge are shown in Figs. 2a,b along with the x-ray experimental data of Hoyer et al. [12] and Waseda [21]. The measured structure factor of Cu shows a symmetrical maximum at q=3.04 A^{-1}(2.95A^{-1} [12]) with a height of 2.59 (2.53 [12]). It is seen in Figs. 2 that the agreement between the calculated VMHNC results and experimental data is good for liquid Cu but for Ge, a major difference exists on the depth of the first minima of S(q).

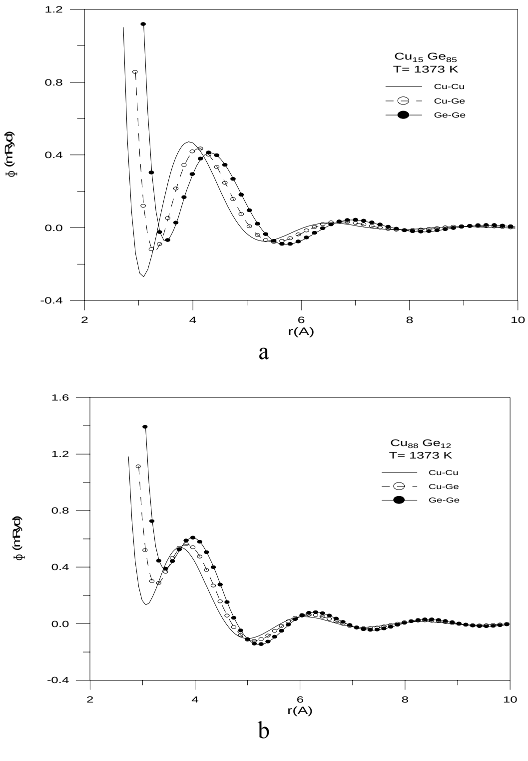
The parameters of the elemental systems for the EC(U) potential discussed above have been adopted for the further use in the present study of alloy.



a

b

Fig. 2.(a) Structure factors for liquids (a)Cu and (b)Ge at melting temperature along with the experimental data of Hoyer at 1373K [12] and Waseda [21], respectively.



a

b

Fig. 3. Interatomic pair potentials: (a)$Cu_{15}Ge_{85}$, (b) $Cu_{88}Ge_{12}$.

The interatomic partial pair potentials obtained with the EC potentials for different Cu compositions at 1373K are shown in Figs. 3a and 3b. It can be seen in Fig. 3a and 3b that the pair potentials for two different alloy composition exhibit rather different trends with each other. From Figs. 3a, it is clear that the depth of the primary potential well of $\phi_{GeGe}(r)$ is shallower than that of than that of $\phi_{CuCu}(r)$.

Total structure factors, S(q), and pair correlation functions, g(r), obtained for liquid Cu-Ge alloys at the specific thermodynamic states given in Ref. [12] are show in Fig. 4a and 4b.

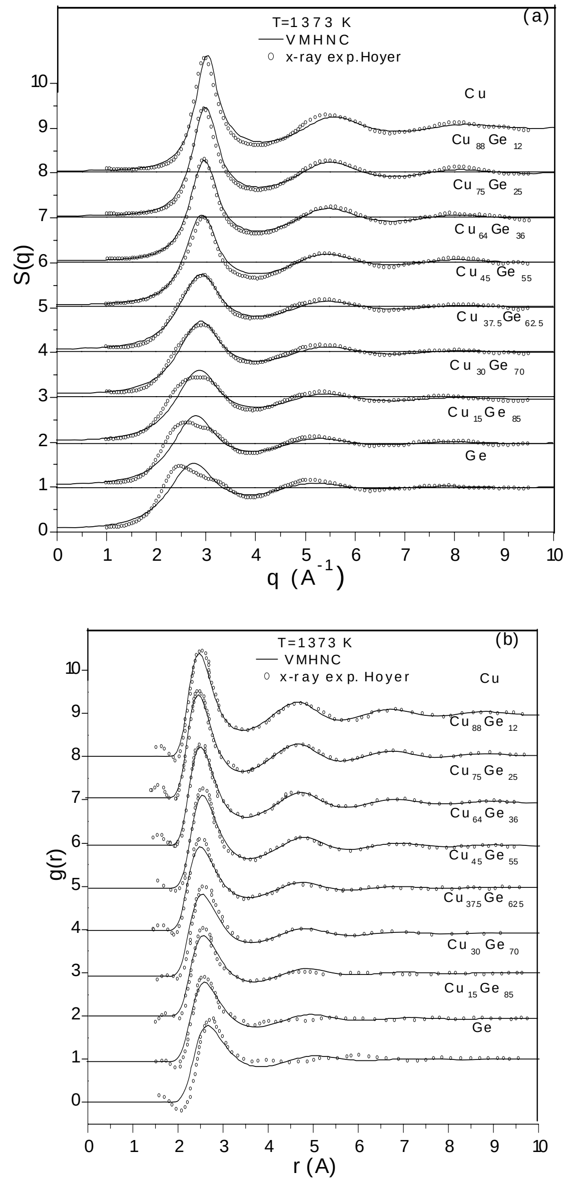


Fig. 4. (a) Total structure factors and (b) pair correlation functions for liquid Cu-Ge alloys.

As it can be seen from Fig.4a, the total structure factors of copper-rich alloys change slightly and are very like this one of pure Cu. With increasing Ge content the height of the main peak decreases and it becomes broader.

Structure factors show a remarkable asymmetry of the maxima. Nevertheless, the first maximum of S(q) remains at the same position as in pure Cu to $Cu_{37.5}Ge_{62.5}$. Beginning with this Ge- concentration the main peak shifts to lower q-values and structure factors show a similar behaviour as that of pure Ge at larger q-values.

The most probable interatomic distance, estimated as a peak position in total pair correlation functions, is similar to one of pure Cu (Fig. 4b). With addition of Ge, the first coordination maximum shows the decrease in its height and growing of asymmetry. In the point of these views, it can be say that distances between Ge atoms are fared and their distribution is slightly correlated. Self-associated groups of Ge atoms are dominant in atomic arrangement at higher concentration of Ge. The tendency to preferred interaction of like kind atoms exists not only in the region of miscibility gap but also in Cu-enriched molten alloys.

Table 1. D for the liquid Cu, Ge and Cu-Ge alloys at different temperatures.

Metal	T(K)	$D(A^2ps^{-1})$				
		EC(U)		D^b	D^c	D^d
		GK	E			
Cu	1357	0.299	0.393		0.365 ± 0.07	0.397
	1423	0.315^a	0.409^a	0.303 ± 0.04		0.471
Ge	1253	1.184	1.330			1.370
	2000	2.342	2.505			2.440
		Self-diffusion from E				
		Cu	Ge			
$Cu_{30}Ge_{70}$	1373	0.776	1.234			
$Cu_{75}Ge_{25}$	1373	0.496	0.843			

[a][20], [b]Results of Alemany [18],[c]Results of Mei [22], [d]Experimental [23]

The self-diffusion coefficients, D, can be obtained velocity autocorrelation function (GK) or from the mean square displacement (E) by using these Fiolhais' pair potentials and static structures. Calculated values of D of pure Cu and Ge are listed in Table 1 along with the Cu and Ge in $Cu_{30}Ge_{70}$ and $Cu_{75}Ge_{25}$ alloy. It is seen that GK and E method give consistent results with each other and available experimental values.

We have plotted logarithmic representation displayed in the Arrhenius type diagram, with D as a function of 1000/T for Ge in Fig.5 and for $Cu_{30}Ge_{70}$ and $Cu_{75}Ge_{25}$ liquid alloys in Fig 6.

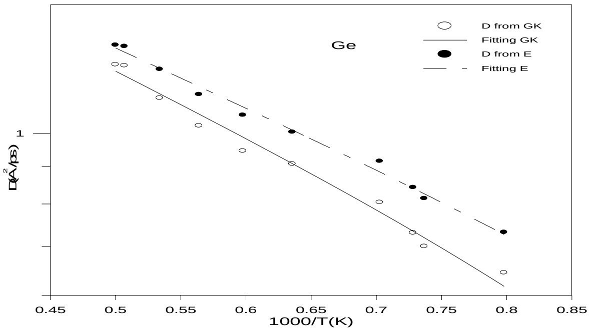


Fig.5. The calculated D for the liquid Ge at different temperatures.

The solid line in Figs. 5, 6 represent an Arrhenius best fit for the curve through data points calculated from GK relation. Dashed line corresponds to fit for E. It is seen in Figs. 5, 6 that the values of D computed by using GK and E relations are mutually consistent.

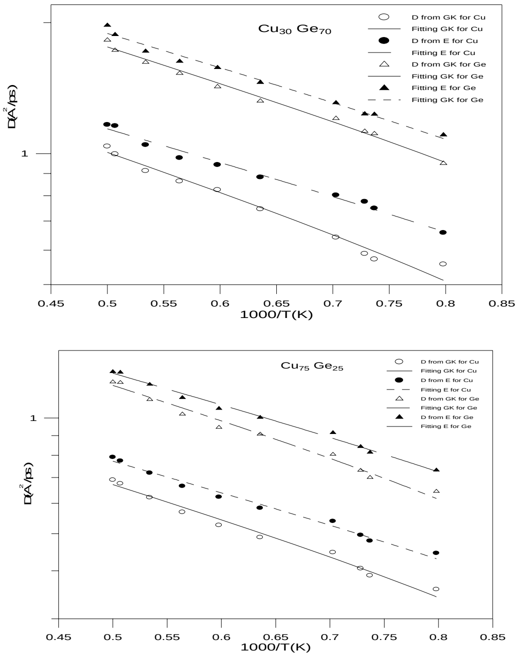


Fig. 6.The coefficients of self-diffusion D for $Cu_{30}Ge_{70}$ and $Cu_{75}Ge_{25}$ at different temperatures.

4. Conclusions

We present the calculated the effective inter-ionic pair potentials using the EC(U) and the static structure for pure liquids Cu, Ge and Cu-Ge liquid alloys at different composition of Ge in conjunction with the VMHNC. The overall agreement with experimental data is good. We may note that the potential parameters for liquid Ge can be revised to give the best results for the static structure factor. The analysis of the results for liquid Cu-Ge alloys confirm the ability of the EC(U) potential to describe the interaction in the liquid ‘noble metal-polyvalent metal’ systems. Temperature and concentration dependence on the self diffusion coefficients are reported. The results for D seem to be exhibit Arrhenius behaviour. The values of D computed for pure systems are comparable to experiment. These results for D, static structural functions of these systems show satisfactory agreement with the available values leads us to conclude that transferability of the potential for liquid metal-polyvalent metal alloys.

Acknowledgements

The authors want to thank Professor W. Hoyer for sharing the experimental data.

References

[1] W. A. Harrison, Pseudopotentials in the Theory of Metals (Benjamin, New York, 1966); M. L. Cohen, V. Heine, Solid State Physics, Vol. 24 (Academic Press, New York, 1970).
[2] J. A. Moriarty, Phys. Rev. **B1**, 1363 (1970); Phys. Rev. **B5**, 2066 (1972); Phys. Rev. **B6**, 1239 (1972); Phys. Rev. **B42**, 1609 (1990).
[3] S. Dalgic, S. Dalgic, G. Dereli, M. Tomak, Phys. Rev. **B50**, 113 (1994).
[4] C. Fiolhais, J. P. Perdew, S. Q. Armster, J. M. MacLaren, M. Brajczewska, Phys. Rev. **B53**, 13193 (1995); ibid. Phys. Rev. **B51**, 14001 (1995).
[5] F. Nogueira, C. Fiolhais, J. P. Perdew, Phys. Rev. **B59**, 2570 (1999).
[6] S. S. Dalgic, S. Dalgic, G. Tezgor, Phys. Chem. Liq. **40**, 539 (2002).
[7] H. Kes, S. S. Dalgic, S. Dalgic, G. Tezgor, J. Optoelectron. Adv. Mater. **5**, 1281 (2003).
[8] S. S. Dalgic, S. Dalgic, M. Celtek, S. Sengul, J. Optoelectron. Adv. Mater. **5**, 1274 (2003).
[9] H. Kes, S. S. Dalgic, S. Dalgic, J. Optoelectron. Adv. Mater. **7**(4), 2047 (2005)
[10] A. Il’inskii, I. Kaban, Yu. Koval, W. Hoyer, S. Slyusarenko, J. Non-Cryst. Solids **345-346**, 251 (2004).
[11] H.J. Güntherodt, Y. Tieche, Helv. Physica Acta, **41**, Fasc. 6/7 (1968) 855
[12] I. Kaban, Th. Halm, W. Hoyer, J. Non-Cryst. Solids **288**, 96 (1998).
[13] M. I. Mendelev, J. Non-Cryst. Solids **232**, 560 (1998).
[14] Y. Rosenfeld, J. Stat. Phys. **42**, 437 (1986).
[15] L. E. Gonzalez, D. J. Gonzalez, M. Silbert, Physica **B168**, 39 (1991); L. E. Gonzalez, D. J. Gonzalez, M. Silbert, Phys. Rev. **A45**, 3803 (1992)
[16] G. Tezgor, S. S. Dalgic, U. Domekeli, J. Optoelectron. Adv. Mater. **7**, 1983 (2005).
[17] V. F. Sears, Thermal-Neutron Scattering Lengths and Cross Sections For Condensed-Matter Research, Atomic Energy of Canada, Ltd. Report AECL-8490, June, 1984.
[18] M. M. G. Alemany, C. Rey and L. J. Gallego, Phys. Rev. **B 58**, 685 (1998).
[19] S. Dalgic, M. Colakogullari, S. Senturk Dalgic, J. Optoelectron. Adv. Mater. **7** (4), 1993 (2005)
[20] S. Dalgic, to be submitted
[21] Y. Waseda, The Structure of Non-Crystalline Materials-Liquids and Amorphous Solids (McGraw-Hill, New York, 1981).
[22] J. Mei, J.W. Davenport, G.W. Fernando, Phys. Rev. **B43**, 4653 (1991)
[23] M. M. G. Alemany, C. Rey and L. J. Gallego, J. Chem. Phys. **109,** 5175 (1998).

---

[*] Corresponding author: m_celtek14@yahoo.com