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ELECTRICAL TRANSPORT PROPERTIES OF LIQUID Cd-BINARY ALLOYS

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The electrical transport properties viz. the electrical resistivity (ρ), the thermoelectric power (TEP) and thermal conductivity (σ) of several polyvalent alloys viz. $Cd_{1-X}Sn_X$, $Cd_{1-X}Pb_X$ and $Cd_{1-X}Bi_X$ were calculated from the pseudopotential form factors and Percus-Yevic (PY) hard sphere structure factors of Ashcroft and Langreth. The well recognized empty core model (EMC) potential of Ashcroft is used for the first time with seven local field correction functions due to Hartree (H), Hubbard-Sham (HS), Vashishta-Singwi (VS), Taylor (T), Ichimaru-Utsumi (IU), Farid et al. (F) and Sarkar et al. (S) in the present computation and found suitable for such study. It is conclude that, the comparison of present and experimental findings is highly encouraging.

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1. Introduction

During the last several years there has been an increasing interest in the properties of non-crystalline conductors such as liquid metals and liquid metallic alloys. Such a liquid exhibits metallic as well as fluid-like behaviour and hence can help to make a link between the theory of the liquid states and the theory of the electronic states in metals. And hence the study of electrical transport properties of liquid metals and their alloys remain one of the favourite quantities either experimentally or theoretically [1-11]. It was found that the electrical resistivities of the alloys obey two rules: (i) Nordheim's rule [12] and (ii) Linde's rule [13]. In the Nordheim's rule the resistivity of liquid alloys depends directly on the product of the atomic concentrations in the percentage of the guest and host elements [12]. While according to the Linde's rule [13], the resistivity derivative with respect to atomic concentration is directly proportional to the difference of the variables of the guest and host elements.

Despite the rich accumulation of experimental studies, the atomistic approach to the problem of the liquid metals had been very slow in progress; until Ziman [14] proposed the theory of electrical resistivity of liquid metals. Basically, there are three approaches for the theoretical investigations of transport properties of liquid metals. One is based on the nearly free electron picture [14], second one is the finite-mean-free path approach [5] and the third is based on tight-binding approximation [15]. The tight-binding approach usually involves either the average T-matrix approximation or the coherent potential approximation. A self-consisting approach corresponding to the finite mean-free-path is taking account of finite uncertainty in the electron momentum. In this article, we are intended to report the electrical resistivity (ρ), the thermoelectric power (TEP) and thermal conductivity (σ) of several polyvalent alloys viz. $Cd_{1-X}Sn_X$, $Cd_{1-X}Pb_X$ and $Cd_{1-X}Bi_X$ based on the well recognized empty core model (EMC) potential of Ashcroft [16]. Hence, both the second and third approaches are beyond the confines of present objectives of the paper as

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well as pseudopotential theory. So we will only be concerned and concentrate with the first approach of nearly free electron theory of Faber [14].

In the past, Faber-Ziman [17] could be extended the formula for pure liquid metals easily to the binary alloys. The two important ingredients of the formula are respectively the partial structure factors and the forma factors. When one is calculating the transport properties of binary alloys, problems arise from the partial structure factors rather then the form factors. Experimental data on the partial structure factors are scarce or the insufficient accuracy. In the present work, the partial structure factors are computed from the well known Percus-Yevic (PY) hard sphere model of Ashcroft and Langreth [3]. Seven different types of the local field correction functions proposed by Hubbard-Sham (HS) [18, 19], Vashishta-Singwi (VS) [20], Taylor (T) [21], Ichimaru-Utsumi (IU) [22], Farid et al. (F) [23] and Sarkar et al. (S) [24] are employed for the first time to investigate the influence of exchange and correlation effects with reference to the static Hartree (H) [25] screening function in the present computations.

2. Theoretical methodology

The Faber-Ziman [17] approach of investigating electrical resistivity of liquid metals assume the model of a gas of conduction electrons which interact with and are scattered by irregularly placed metal ions. As an external electric field drives the electron through the disordered medium, the scattering determines the electrical resistance which can be calculated using perturbation theory: the transition rate from an initial state $|\mathbf{k}\rangle$ to the final state $|\mathbf{k}+\mathbf{q}\rangle$ on the Fermi level with the density of state is given by

$$P(\theta)=\frac{2\pi}{\hbar}\left|\langle \mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle\right|^2 \frac{1}{2}N_{FE}(E_F), \tag{1}$$

where θ is the angle between k and $k+q$, the factor $(1/2)$ arises from the fact that electron spin does not change on scattering. Now the conductivity in the relaxation time approximation is given by

$$\sigma = \frac{1}{3}\, e^2\, v_F^2\, \tau\, N_{FE}(E_F). \tag{2}$$

Here e is electronic charge, v_F velocity of the electrons at the Fermi level and the relaxation time τ. The relaxation time τ is given by

$$\frac{1}{\tau}=\int(1-\cos\theta)P(\theta)d\Omega, \tag{3}$$

where θ is scattering angle, Ω is solid angle and $P(\theta)$ is probability for scattering through the angle θ.

Now assuming the free-electron distribution, an expression for the electrical resistivity of liquid metal in terms of the average of the product of the structure factor and pseudopotential matrix element can be written as [1-11, 14]

$$\rho=\frac{3\pi m^2}{4e^2\hbar^3 n k_F^6}\int_0^\infty S(q)|V(q)|^2\, q^3\, dq\, \theta(2k_F-q). \tag{4}$$

Where n the electron density is related to Fermi wave number and θ is the unit step function that cuts of the q-integration at $2k_F$ corresponding to a perfectly sharp Fermi surface. $S(q)$ is the structure factor and $V(q)$ is the screened ion pseudopotential form factor.

This method is initially applied to the liquid metals only, but later on the approach restructured to investigate the resistivity of $A_{1-X}B_X$ liquid binary alloys [1-11, 14]. Hence equation (4) is written as

$$\rho=\frac{3\pi m^2}{4e^2\hbar^3 n k_F^6}\int_0^{\infty}\lambda(q)q^3\,dq\,\theta(2k_F-q), \tag{5}$$

with

$$\lambda(q)=(1-X)\,S_{11}\,V_1^2(q)+2\sqrt{X(1-X)}\,S_{11}\,S_{22}\;V_1(q)\;V_2(q)+X\,S_{22}\,V_2^2(q). \tag{6}$$

Here $V_1(q)$ and $V_2(q)$ denote the model potentials for elements A and B, S_{ij} are the partial structure factors, X is the concentration of the second metallic component of $A_{1-X}B_X$ mixture. Here we have used Ashcroft-Lengreth's [3] formulations to generate the partial structure factor of the binary metallic complexes.

The expression of the thermoelectric power (TEP) is given by [2]

$$TEP=-\left(\frac{\pi^2 k_B^2 T_K}{3|e|E}\,\chi\right)_{E=E_F}, \tag{7}$$

with

$$\chi=3-2\xi, \tag{8}$$

where

$$\xi=\frac{\lambda(q)}{\rho}. \tag{9}$$

It is well known that if a temperature gradient is applied to a metal the conduction electrons will carry a heat current along it even though an electric current is prevented from flowing and that indeed they are responsible for the major part of the thermal conductivity. The expression of the thermal conductivity (σ) for the binary alloy can be written as [2]

$$\sigma=\left(\frac{\pi^2 k_B^2 T_K}{3|e|^2\rho}\right). \tag{10}$$

Here, e, E, E_F, T_K, k_B and χ are the electronic charge, energy, Fermi energy, temperature (in K), the Boltzmann's constants and the term of dimensionless thermoelectric power.

In the present work, we have calculated The electrical transport properties viz. the electrical resistivity (ρ), the thermoelectric power (TEP) and thermal conductivity (σ) of several polyvalent alloys by applying Ashcroft's well known empty core (EMC) model potential [16] including seven

different types of the local field correlation functions [18-25]. The form factor explored in the present investigation is of the form [16],

$$W(q) = \frac{-4\pi Z e^2}{\Omega_O q^2 \varepsilon(q)} \cos(qr_C), \tag{11}$$

where, Z is the valence, Ω_O the atomic volume, r_C the parameter of the potential and $\varepsilon(q)$ the modified Hartree dielectric function [27]. The parameter of the potential r_C may be set from appropriate experimental information (e.g., the Fermi surface or ionization energy). In this instance, it was determined by the known electrical resistivities of the pure liquid metals at the melting points.

3. Results and discussion

The input parameters and constants used in the present computations are narrated in Table 1. The computed results of electrical properties viz. the electrical resistivity (ρ), the thermoelectric power (TEP) and thermal conductivity (σ) are displayed in Figs. 1-9.

Table 1. The input parameters and constants.

Metal	Z	Hard Sphere Diameter (D) (au)	η	r_C (au)	Ω_O (au)
Cd	2	5.1401	0.456	1.4060	187.02
Sn	4	5.5180	0.44	1.3285	194.64
Pb	4	5.7448	0.456	1.4986	303.00
Bi	5	5.8959	0.456	1.5175	206.48

The concentration dependence of the electrical resistivity (ρ) is examined by varying $X = 0$ to $X = 1$ in the step size of 0.1. The results for the presently calculated electrical resistivities (ρ) for $Cd_{1-X}Sn_X$, $Cd_{1-X}Pb_X$ and $Cd_{1-X}Bi_X$ systems at 325 ^oC is shown with the experimental data [26-28] in Figs. 1-3. From the Figs. 1-3 it is seen that, among the seven employed local filed correction functions, the local field correction function due to H (without exchange and correlation) gives the minimum numerical value of the electrical resistivity, while the local field correction function due to F gives the maximum value. The present findings of the electrical resistivity (ρ) of Cd-based binary alloys due to HB, VS, T, IU and S local field correction functions are lying between H and F functions.

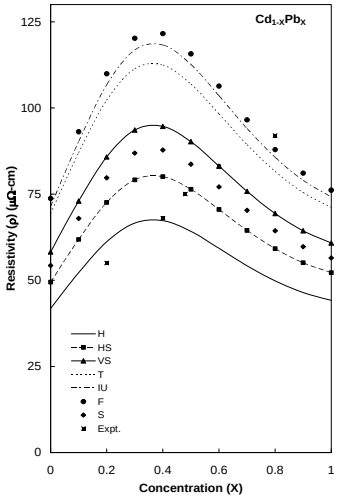

Fig. 1. Electrical resistivity (ρ) of $Cd_{1-X}Sn_X$ binary mixture.

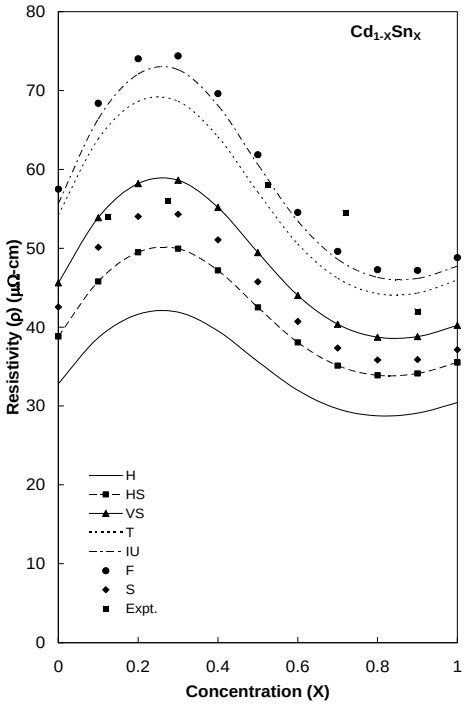

Fig. 2. Electrical resistivity (ρ) of $Cd_{1-X}Pb_X$ binary mixture.

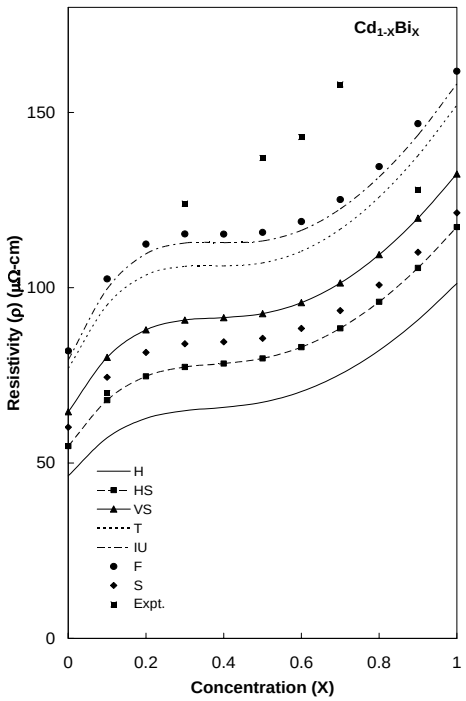

Fig. 3. Electrical resistivity (ρ) of $Cd_{1-X}Bi_X$ binary mixture.

The packing fraction η for the alloys was obtained by taking a linear average of the two components at each composition. Ashcroft and Lengreth [3] pointed out that the packing fraction η calculated by comparison of the working temperature and the liquidus temperature using $d\eta/dT$ for the components, does not differ significantly from the linear combination of the pure component

packing fraction. The present results are found in qualitative agreement with the available experimental findings [26-28]. One interesting features is noted herewith as concentration X of the B element increases electrical resistivity (ρ) increase and reaches the maximum value, after that the further increase in X decreases the ρ_L of the system.

In comparison with the presently computed results of the electrical resistivity (ρ) from static H-function, the percentile influences for $Cd_{1-X}Sn_X$ alloys of HB, VS, T, IU, F and S-functions are of the order of 19.72%-19.36%, 32.15%-33.91%, 51.07%-65.24%, 56.82%-73.34%, 60.40%-77.81% and 22.05%-29.78%, respectively. While those influences found for $Cd_{1-X}Pb_X$ binaries are of the order of 18.32%-19.03%, 37.76%-40.64%, 61.17%-67.27%, 68.04%-75.72%, 72.53%-80.67% and 27.99%-30.49%, respectively. Also, the percentile influences for $Cd_{1-X}Bi_X$ are found of the order of 15.88%-19.18%, 30.86%-40.28%, 50.20%-54.17%, 56.19%-74.84%, 58.80%-79.26% and 19.89%-30.16%, respectively.

The qualitative agreement with the experimental data may be indicative of the free electron behaviour of these mixtures in the whole concentration range. Here also, the calculated electrical resistivities of the Cd-systems increase like alkali-alkali systems. The peak of the curve increases with the increase of their electronegativity differences. The present study indicates the free electron behaviour of these mixtures in the whole composition range and all the constituent atoms are randomly distributed in the system.

The thermoelectric power (TEP) for $Cd_{1-X}Sn_X$, $Cd_{1-X}Pb_X$ and $Cd_{1-X}Bi_X$ binary systems are displayed in Figs. 4-6. It is seen that, as the concentration X of the B element increases thermoelectric power (TEP) decreases and reaches the maximum value, after that the further increase in X increase the thermoelectric power (TEP) of the system. Also, among the seven employed local filed correction functions, the local field correction function due to H (without exchange and correlation) gives the maximum numerical value of the TEP, while the local field correction function due to F gives the minimum value. The present findings of the TEP of Cd-based binary alloys due to HB, VS, T, IU and S local field correction functions are lying between H and F functions. The maximum depth position is found for $Cd_{1-X}Pb_X$ alloys. The experimental or theoretical data of TEP are not available for the further comparison. In the study of the thermoelectric power (TEP) for binary alloys, when two different metals are placed in contact, charge flows from one to another until a potential difference is setup such that $E_F^A = E_F^B$.

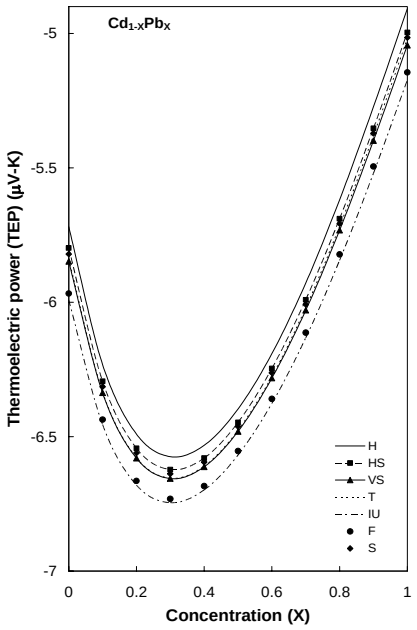

Fig. 4. Thermoelectric power (TEP) of $Cd_{1-X}Sn_X$ binary mixture.

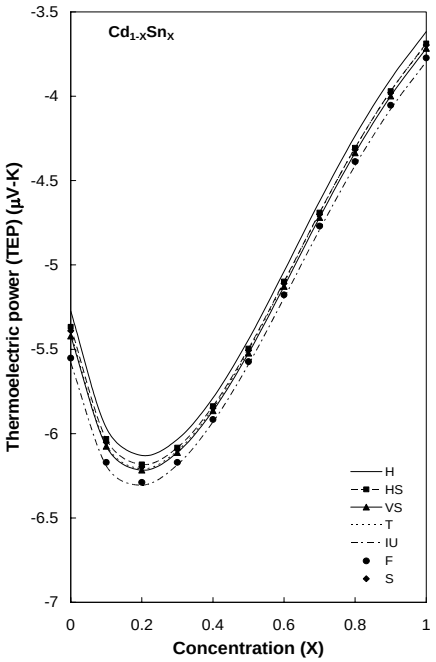

Fig. 5. Thermoelectric power (TEP) of $Cd_{1-X}Pb_X$ binary mixture.

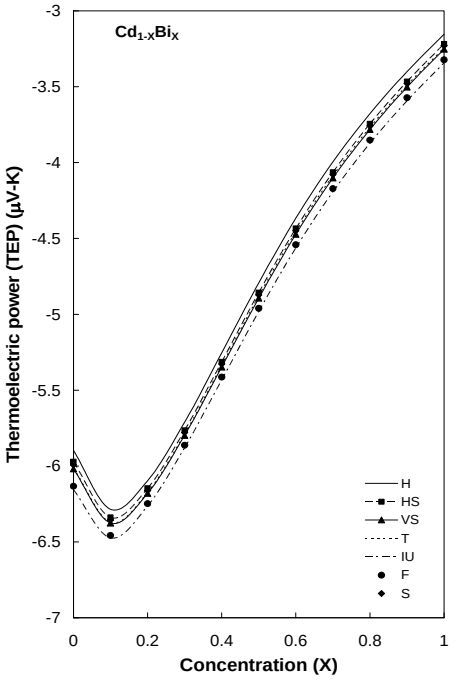

Fig. 6. Thermoelectric power (TEP) of $Cd_{1-X}Bi_X$ binary mixture.

In comparison with the presently computed results of the thermoelectric power (TEP) from static H-function, the percentile influences for $Cd_{1-X}Sn_X$ alloys of HB, VS, T, IU, F and S-functions are of the order of 0.80%-1.94%, 1.28%-2.86%, 1.09%-2.50%, 2.47%-5.81%, 2.21%-5.26% and 1.01%-2.21%, respectively. While those influences found for $Cd_{1-X}Pb_X$ binaries are of the order of 0.81%-1.80%, 1.22%-2.77%, 1.18%-2.28%, 2.54%-5.41%, 2.32%-4.83% and 0.96%-2.19%,

respectively. Also, the percentile influences for $Cd_{1-X}Bi_X$ are found of the order of 0.72%-1.80%, 1.22%-2.77%, 1.18%-2.28%, 2.54%-5.41%, 2.32%-4.83% and 0.96%-2.19%, respectively.

The thermal conductivity (σ) for $Cd_{1-X}Sn_X$, $Cd_{1-X}Pb_X$ and $Cd_{1-X}Bi_X$ binary systems are shown in Figs. 7-9. It is noted that, as the concentration X of the B element increases thermal conductivity (σ) decreases and reaches the maximum value, after that the further increase in X increase the thermal conductivity (σ) of the system except for $Cd_{1-X}Bi_X$, the reverse trend is observed. Also, among the seven employed local filed correction functions, the local field correction function due to H (without exchange and correlation) gives the maximum numerical value of the thermal conductivity (σ), while the local field correction function due to F gives the minimum value. The present findings of the thermal conductivity (σ) of Cd-based binary alloys due to HB, VS, T, IU and S local field correction functions are lying between H and F functions. The maximum depth position is found for $Cd_{1-X}Pb_X$ alloys. The experimental or theoretical data of thermal conductivity (σ) are not available for the further comparison.

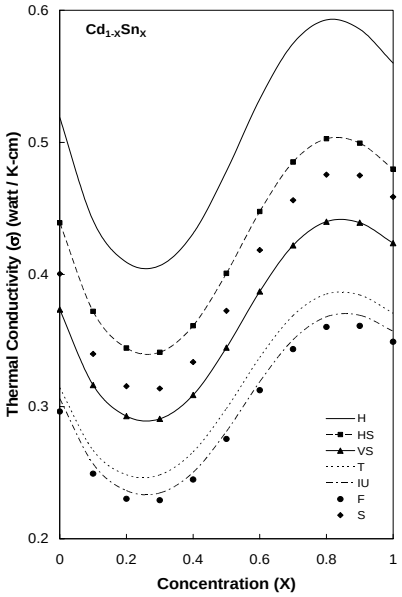

Fig. 7. Thermal conductivity (σ) of $Cd_{1-X}Sn_X$ binary mixture.

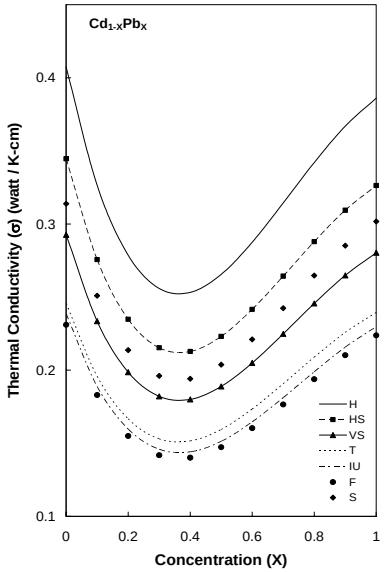

Fig. 8. Thermal conductivity (σ) of $Cd_{1-X}Pb_X$ binary mixture.

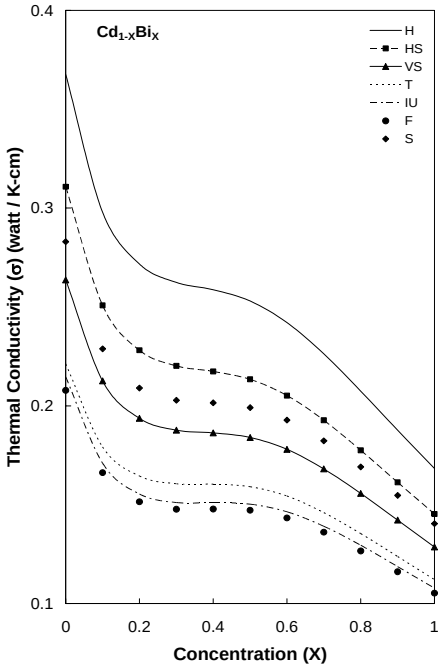

Fig. 9. Thermal conductivity (σ) of $Cd_{1-X}Bi_X$ binary mixture.

In comparison with the presently computed results of the thermal conductivity (σ), from static H-function, the percentile influences for $Cd_{1-X}Sn_X$ alloys of HB, VS, T, IU, F and S-functions are of the order of 14.32%-16.21%, 24.34%-28.32%, 33.80%-39.46%, 36.23%-42.32%, 37.66%-43.76% and 18.07%-22.94%, respectively. While those influences found for $Cd_{1-X}Pb_X$ binaries are of the order of 15.49%-15.97%, 27.40%-28.91%, 37.97%-40.21%, 40.48%-42.99%, 42.04%-44.67% and 21.86%-23.37%, respectively. Also, the percentile influences for $Cd_{1-X}Bi_X$ are found of the order of 13.67%-16.08%, 23.59%-28.71%, 33.39%-39.85%, 35.95%-42.80%, 37.43%-44.24% and 16.58%-23.20%, respectively.

The numerical values of the electrical transport properties viz. the electrical resistivity (ρ), the thermoelectric power (TEP) and thermal conductivity (σ) are found to be quite sensitive to the selection of the local field correction function and showing a significant variation with the change in the function. Thus, the calculations of the electrical transport properties viz. the electrical resistivity (ρ), the thermoelectric power (TEP) and thermal conductivity (σ) are one of the sensitive tests for the proper assessment of the form factor of the model potential and in the absence of experimental information such calculations may be considered as one of the guidelines for further investigations either theoretical or experimental.

It is apparent that for all cases, using the resistivity model of Ashcroft and Langreth [3], better calculated agreement with experimental values was obtained by allowing variation in atomic volume. One could conclude from this information that structure information in resistivity models seems to be required.

4. Conclusions

There are reported for the first time that, the electrical transport properties viz. the electrical resistivity (ρ), the thermoelectric power (TEP) and thermal conductivity (σ) of several polyvalent alloys viz. $Cd_{1-X}Sn_X$, $Cd_{1-X}Pb_X$ and $Cd_{1-X}Bi_X$ using EMC model potential and Percus-Yevic (PY) hard sphere model with seven different types of local field correction functions. The EMC model potential with more advanced IU, F and S-local field correction functions generate consistent results regarding the electrical transport properties. Hence, the EMC model potential is found suitable for

studying the electrical transport properties of polyvalent alloys. Also, the present investigation predicts that the present study of the electrical transport properties is sensitive to the selection of the proper local field correction function.

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