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Electronic properties of liquid K and Cs metals and their binary alloys

S. DENIZ KORKMAZ*, Ş. KORKMAZ[a], E. TERKEN[b]
ESOGU, Education Faculty, Elementary Education Department, Meşelik Campus 26480 Eskişehir-TURKIYE
[a]*ESOGU, Arts and Sciences Faculty, Physics Department, Meşelik Campus 26480 Eskişehir-TURKIYE*
[b]*ESOGU, Graduate School of Applied and Natural Sciences, Meşelik Campus 26480 Eskişehir-TURKIYE*

A model potential which is derived from second order pseudopotential perturbation theory with the transferable electron-ion potential of Fiolhais and co-workers which was originally developed for the solid state is used for the comparative study of electrical resistivity of for liquid K, Rb, and Cs metals and liquid K-Cs and K-Rb alloys. In the present study electrical resistivity of liquid K, Rb, and Cs metals and liquid K-Cs and K-Rb alloys have been calculated using Ziman's formula, and modified Ziman's formula suggested by Ferraz-March and used by Khajil and Tomak (self consistent approximation). Previously no one has reported such comparative study using that pseudopotentials. In the electrical resistivity calculation we have used structure factor derived from the solution of Ornstein–Zernike equation with Rogers-Young closure. From present investigation it is found that self consistent formulation results are better than that of Ziman's formula. A successful application is evidence that our potential can predict physical properties of K-Cs and K-Rb alloys as well as K, Rb and Cs metals.

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1. Introduction

A number of calculations of the electrical resistivity using structure factor from various experiments or different forms of bare ion potential and dielectric function of liquid metals and alloys have been reported. Ziman formula [1] is one of the most widely used in the calculation of liquid metal resistivities and it was extended to liquid binary alloys by Faber and Ziman [2]. This expression involves a finite integral over the product $q^3S(q)\left|w(q)\right|^2\theta(2k_F-q)$. The unit step function $\theta(2k_F\text{-}q)$ cuts off the integration at $2k_F$ corresponding to a perfect sharp Fermi surface. Implicitly it is assumed that only those electrons whose wave vectors q lie on the Fermi surface are effective for the scattering. But it faces difficulties when applied to systems with strong electron-ion interaction and thus, strong, multiple electron scattering. The electron has a finite mean-free-path in such systems. The finite mean free path corresponds to a finite uncertainty in the electron momentum. Thus the Fermi surface is not perfectly sharp but it is blurred. One of the attempts to take into account this blurring has been made by Ferraz and March [3]. They have modified Ziman Formula. The formula supposed by Ferraz-March takes the mean-free-path of electron into account of calculation of resistivity. In the present work we have calculated electrical resistivities using the modified Ziman formula suggested by Ferraz-March for K, Rb and Cs liquid metals and $K_{0.5}Rb_{0.5}$, and $K_{0.5}Cs_{0.5}$, liquid metal alloys near the melting point. We have used the individual version of local pseudopotential proposed by Fiolhais and coworkers [4-5] which was developed for solid state and is transferable to the liquid metals and alloys [6-13] as interaction potentials. The static structure factor S(q) is determined from the solution of Ornstein-Zernike equation with Rogers-Young closure [14]. To the best of our knowledge, previously no one has reported such a study to investigate electrical resistivity using structure factor from this transferable pseudopotential and this closure. We have also calculated the electrical resistivities of the system studied present work using Ziman formula. We have compared our calculations with theoretical results obtained from modified Ziman formula suggested by Ferraz and March and Ziman formulas and experimental data.

2. Theory

2.1 Effective pair potential

We use the well-established second-order perturbation determination of the effective pair potential, $u_{ij}(r)$, which can be written as

$$u_{ij}(r)=\frac{Z_iZ_j}{r}\left[1-\frac{2}{\pi}\int_0^\infty F_{N_{ij}}(q)\frac{\sin qr}{q}dq\right] \tag{1}$$

where

$$F_{N_{ij}}(q)=\left(\frac{q^2}{4\pi}\right)^2\frac{1}{Z_iZ_j}w_i(q)w_j(q)\left[1-\frac{1}{\varepsilon(q)}\right]\left[1-G(q)\right]^{-1} \tag{2}$$

in these expressions, Z_i denotes the valences of the ions of the ith species. ε(q) is the Hartree dielectric function and G(q) local field correction. Here we employ the local density approximation (LDA) version of G(q) the correlation energy of VWN [15]. The $w_i(q)$ denotes pseudopotential form factor described by Fiolhais et al. [4-5] as

$$\begin{aligned}w_i(q)=4\pi Z_iR_i^{\,2}n\,[-\frac{1}{(qR_i)^2}+\frac{1}{(qR_i)^2+\alpha_i^{\,2}}\\+\frac{2\alpha_i\beta_i}{\left[(qR_i)^2+\alpha_i^{\,2}\right]^2}+\frac{2A_i}{\left[(qR_i)^2+1\right]^2}\end{aligned} \tag{3}$$

where n is number density and R_i, α_i, β_i and A_i denote the parameters of the potential tabulated by the authors (individual values are used).

2.2 Partial pair distribution functions and partial structure factors

With the effective pair potential known, total and direct correlations functions $h_{ij}(r)$ and $c_{ij}(r)$ can be determined from the solution of the Ornstein-Zernike equation given by

$$\gamma_{ij}(r)\equiv h_{ij}(r)-c_{ij}(r)=\frac{1}{2}\sum_{l=1}^{2}c_l n\int h_{il}(r)c_{lj}(r)dr\,, \tag{4}$$

which $h_{ij}(r)=g_{ij}(r)$-1 and $g_{ij}(r)$ is the pair distribution function, n is the number density of the system and c_l is the concentration of lth component. To solve the Ornstein-Zernike integral equation, one needs a closure between $h_{ij}(r)$ and $c_{ij}(r)$. In our case we use Rogers-Young [14] closure given by

$$\begin{aligned}g_{ij}(r)&=\exp\left(-\beta u_{ij}(r)\right)\\&\left(1.+\frac{\exp\left\{\left[h_{ij}(r)-c_{ij}(r)\right]f(r,\alpha)\right\}-1}{f(r,\alpha)}\right)\end{aligned} \tag{5}$$

where $\beta=1/k_BT$, k_B and T are the Boltzmann constant and temperature, respectively. In Eq. (5) f(r,α) is the mixing function given by

$$f(r,\alpha)=1-\exp(-\alpha r) \tag{7}$$

where α parameter is determined by the relation suggested by Lai and coworkers [16]. After the calculation pair distribution function, we computed the Ashcroft-Langreth's partial structure factors [17] by

$$S_{ij}(q)=1+\sqrt{c_ic_j}\,\rho\int\left[g_{ij}(r)-1\right]\exp(-i\overset{\varpi}{q}.\overset{\varpi}{r})d\overset{\varpi}{r} \tag{8}$$

where c_i is the concentration of the ith components.

2.3 Electrical resistivity of liquid metals and alloys

The well known Ziman formula [1] for the resistivity of a liquid metal is

$$\rho=\frac{3\pi m^2}{4Ze^2\eta^3n_{el}k_F^6}\int_0^\infty q^3S(q)\left|w(q)\right|^2\theta(2k_f-q)\,dq \tag{9}$$

where S(q) is the static structure factor, w(q) is the screened ion pseudopotential, n_{el} is the conduction electron density and it is related to Fermi wave vector k_F by $k_F=(3\pi^2n_{el})^{1/3}$, e is the electron charge, m is the electron mass and, h is planck constant. The unit step function θ is defined as

$$\begin{aligned}\theta(2k_F-q)\;&=0\quad\text{for}\quad q>2k_F\\&=1\quad\text{for}\quad q\le 2k_F\end{aligned}$$

The extension to a liquid metal binary alloy is done by Faber-Ziman [2] as

$$\begin{aligned}\rho=&\frac{3\pi m^2}{4Ze^2\eta^3n_{el}k_F^6}\times\\&[\int_0^\infty q^3\left[c_iw_i(q)^2S_{ii}(q)+c_jw_j(q)^2S_{jj}(q)\right]\theta(2k_f-q)\,dq\\&+\int_0^\infty q^3\left[2(c_ic_j)^{1/2}w_i(q)w_j(q)S_{ij}(q))\right]\theta(2k_f-q)\,dq]\end{aligned} \tag{10}$$

The finite mean free path corresponds to a finite uncertainty in the electron momentum. Thus the Fermi surface is not perfectly sharp but it is blurred. Some attempts have been made to take into account this blurring. Ferraz- March approach [3] yields in place of Eq.(6)

$$\rho=\frac{3\pi m^2}{4Ze^2\eta^3n_{el}k_F^6}\int_0^\infty q^3S(q)\left|w(q)\right|^2\Gamma(q,k_f,l)\,dq \tag{11}$$

where

$$\begin{aligned}\Gamma(q,k_F,l)=&\frac{2}{\pi}\times[\tan^{-1}(ql)\\&-\frac{1}{2}\tan^{-1}\frac{2ql}{1+4(k_Fl)^2-(ql)^2}\\&-\frac{\pi}{2}\Theta\left(q-\left(\frac{1}{l^2}+4k_F^{\,2}\right)\right)]\end{aligned} \tag{12}$$

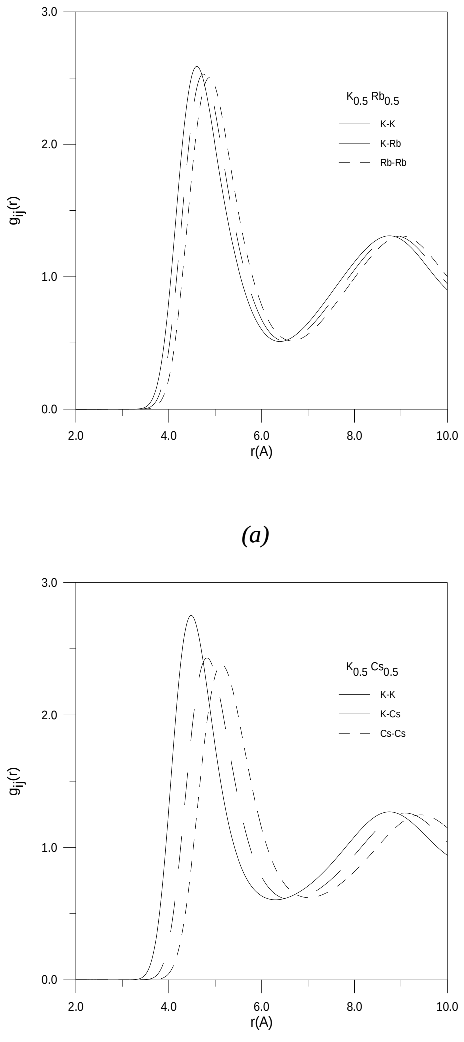
The mean free path *l* can be determined self consistently. The first step in the self consistency loop is to calculate ρ using with *l* =∞. A new "*l*" is then calculated from Drude relation as

$$\rho_L = \frac{\eta k_F}{ne^2 l} \tag{13}$$

the iterations are continued till ρ_L converges. The extension of the Ferraz-March expression to binary alloys is straightforward with θ replaced by $\Gamma(q,k_F,l)$ in Eq. 8 [18].

3. Results and discussion

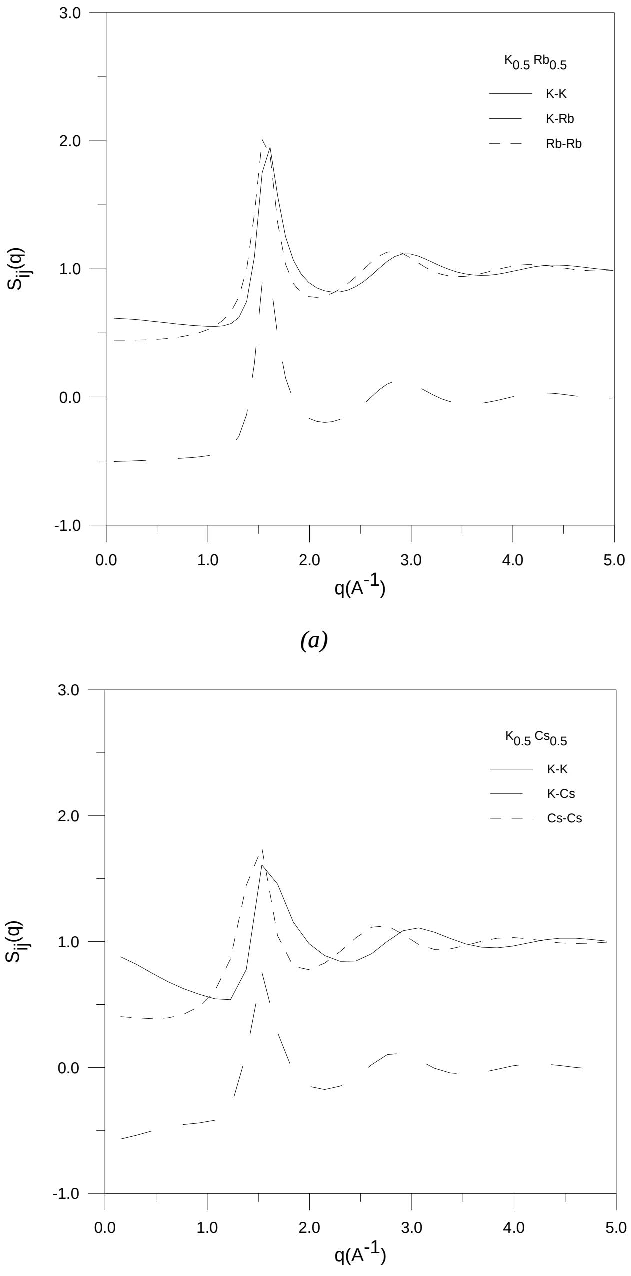
In Fig. 1 we display the partial pair distribution functions and in Fig. 2 Ashcroft-Langreth partial structure factors for $K_{0.5}Rb_{0.5}$ and $K_{0.5}Cs_{0.5}$ alloys. As is seen from Fig. 1, first peak of $g_{K\text{-}Rb}(r)$ is in the middle between $g_{K\text{-}K}(r)$ and $g_{Rb\text{-}Rb}(r)$ first peaks. The peaks have similar height. First peak of $g_{K\text{-}Cs}(r)$ is also in the middle between $g_{K\text{-}K}(r)$ and $g_{Cs\text{-}Cs}(r)$ first peaks. The highest peak is $g_{K\text{-}K}(r)$. These features are signaling a very weak tendency towards phase separation.



(a)

(b)

Fig. 1. Partial pair distribution functions and ashcroft-langreth partial structure factors (a) for $k_{0.5}rb_{0.5}$ and for $k_{0.5}cs_{0.5}$ alloys.



(a)

(b)

Fig. 2. Ashcroft-langreth partial structure factors (a) for $k_{0.5}rb_{0.5}$ and (b) for $k_{0.5}cs_{0.5}$ alloys.

We have calculated electrical resistivity for each system studied in this work using Eqs. (6-11). Calculated values of electrical resistivity are summarized in Table 1 together with available experimental data [19-25].

In the cases of K-Cs alloys, the results of electrical resistivity calculated from both formulas are similar to each other. In the cases of K, Rb and Cs the resistivities calculated using the expression based on Ziman formula by Ferraz-March are greater than the results from Ziman formula and they are in good agreement with experimental data.

Table 1. The calculated values of electrical resistivity for liquid k, rb and cs liquid metals and $k_{0.5}rb_{0.5}$ and $k_{0.5}cs_{0.5}$ alloys together with available experimental data [19-23]at 378 k.

	ρ_{Ziman} ($\mu\Omega$cm)	$\rho_{\text{Ferraz-March}}$ ($\mu\Omega$cm)	ρ_{exp} ($\mu\Omega$cm)
K	13.6	14.72	15.6 (130 °C)
Rb	18.6	24.3	33.0 (160 °C)
Cs	20.7	30.4	45.0
K	15.3	14.7	
$K_{0.5}Rb_{0.5}$	20.8	20.1	
Rb	21.4	20.8	
K	15.2	15.5	15.0
$K_{0.5}Cs_{0.5}$	31.3	32.2	56.5
Cs	24.6	26.0	44.6

4. Conclusions

We investigated the electronic transport properties of liquid alkali metals and alloys using the modified Ziman formula (self consistent approach) and Ziman formula. To calculate the resistivity using both formulas, we computed the static structure factor and partial structure factor using the individual version of pseudopotential proposed by Fioalhais and coworkers with LDA screening with the correlation energy of VWN and Ornstein Zernike integral equation with Rogers-Young closure.

We calculated the resistivities of liquid alkaline metals using Ziman and the modified Ziman formula and we compared our results with each other and the experimental data. Our integral equation for the resistivity of liquid alkaline metals and alloys shows that the electrical resistivities calculated using the modified Ziman formula provides better results than the Ziman's formula by using Fiolhais pseudopotential and Rogers-Young closure.

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[*] Corresponding author: sduysal@ogu.edu.tr