Electrical Resistivity of Na–K Binary Liquid Alloy Using Ab-Initio Pseudopotentials

Anil Thakur*, P. K. Ahluwalia

Department of Physics, Himachal Pradesh University, Shimla-171005, India

(Received 8 March 2005)

The study of electrical resistivity of simple binary liquid alloy Na–K is presented as a function of concentration. Hard sphere diameters of sodium (Na) and potassium (K) are obtained through the inter ionic pair potentials evaluated using Troullier and Martins ab-initio pseudopotentials, which have been used to calculate partial structure factors $S(q)$. The Ziman formula for calculating resistivity of binary liquid alloys has been used. Form factors are calculated using ab-initio pseudopotentials. The results suggest that the first principle approach for calculating pseudopotentials with in the frame work of Ziman formalism is quite successful in explaining the electrical resistivity data of compound forming binary liquid alloys.

PACS: 61. 25. Mv, 71. 15. Hx

The most popular method for study of electrical resistivity of liquid metals and their alloys is electrical conduction theory developed by Faber and Ziman[1,2] using the concept of model pseudopotential. This concept of pseudopotential for calculating various dynamic properties of metallic systems has been extremely useful over the last three decades.[3–5] However, this approach has not been found adequate to explain anomalous electrical properties of many liquid alloys at a specific composition.

More recently, the construction of pseudopotentials has been shifted from modelling to the ab-initio construction of pseudopotentials. Problem with model pseudopotentials is of their transferability. Because sometimes with change of environment, change of parameters are also required to obtain good agreement with experimental results. Ab-initio pseudopotentials are free from this defect. Moreover, ab-initio methods provide a lot of information about electronic, static and dynamic properties,[6] which enables us to have a comparison with experimental results.

The success of the computational efforts required to calculate the properties of complex crystals and liquids lies with the improvement of computational methods for the electronic structure calculations. In order to obtain reliable results, this effort is of utmost importance in spite of advances in computer technology. In ab-initio pseudopotentials the core electron wavefunctions of an atom remain essentially unchanged when placed into different chemical environments and since the core wavefunction's only major contribution to chemical bonding is to enforce the valence wavefunction's orthogonality to the core states, the true atomic potential can justifiably be replaced by a pseudopotential that effectively reproduces the effects of the core electrons. While calculating the ab-initio pseudopotential the main objective is to produce a pseudopotential that reproduces adequately the all electron behaviour outside the core region when placed in different chemical environment and should still be computationally efficient one.

There are many such pseudopotentials which satisfy the above criteria. One such example is the all-electron potential, i.e. a pseudopotential which is not pseudized at all. Thus the essence of the pseudopotential must lie in its computational efficiency and accuracy. A known aspect of the pseudopotential is that it gives nodeless pseudo wavefunctions for valence states. By removal the nodes of wavefunctions, we have a lower kinetic energy and a weaker potential, therefore a faster convergence. There are different types of pseudopotentials available to optimize the convergence: ab-initio pseudopotentials, empirical pseudopotential and model pseudopotentials. The ab-initio pseudopotential represents the start-of-art.

In the present work, ab-initio pseudopotentials have been applied to hard sphere diameters as a function of concentration by minimizing the interionic pair potentials in the determination of partial structure factors. Then in order to see the concentration dependence of observed electrical resistivity these partial structure factors have been used to calculate the of electrical resistivity of simple liquid alloy Na–K. As compared to the other simple binary liquid alloys, Na–K with weak scattering potentials gives excellent agreement with experiment using Ziman's formula. For other alkali metals the structure factor $S(q)$ data are less reliable.[7] Moreover, Na and K are $s-p$ bonded metals and therefore ab-initio pseudopotentials can be easily used to calculate the interionic pair potentials.

An important application of pseudopotentials is

* Email: anil_t2001@yahoo.com

©2005 Chinese Physical Society and IOP Publishing Ltd

the calculation of transport properties of disordered materials such as liquid or amorphous metals and alloys. Electrical resistivity of binary liquid alloys has been explained in detail by Faber and Ziman. We give here only the essentials of the Faber–Ziman theory. Further details can be found in Refs. [1,2]. Atomic units with $\hbar = 1$, $\hbar/(me^2) = a_o = 1$ and $m = 1/2$ are used throughout.

Liquid binary alloy requires three partial structure factors for the calculation of electrical resistivity. Hoshino[8,10] using Hiroike's[9] solution of the Percus–Yevic equation has derived expressions for an m-component hard sphere system. We have calculated partial structure factors using Hoshino's expressions:

For the m-component hard-sphere mixture model, diameters are taken as $\sigma_1 < \sigma_2 < \sigma_3 - < \sigma_m$ and hard sphere ratio is given by $\gamma_{ij} = \frac{\sigma_i}{\sigma_j}$. The $2m-1$ parameters which describe the hard sphere system involve $x_i = \frac{n_i}{n}$, where n=$\frac{N}{V}$, $n_i = \frac{N_i}{V}$ and $\sum_{i=1}^{m} x_i = 1$ and packing fraction $\eta_i = \frac{\pi}{6}\eta_i\sigma_i^3$ satisfying $\eta = \sum_{i=1}^{m} \eta_i$

To calculate the partial structure factors for binary alloy, we use the hard sphere mixture matrix given by

$$S(k) = \begin{vmatrix} S_{11}(k) & S_{12}(k) \\ S_{21}(k) & S_{22}(k)) \end{vmatrix}. \qquad (1)$$

In order to calculate hard sphere diameters, interionic pair potential can be used by generalizing Harrison's[11] approach of pair-wise potential between the metallic ions.

The pair potential has the familiar form of the screened Coulomb potential

$$V_{ij} = \frac{Z_i^* Z_j^*}{R}\Big[1 - \frac{2}{\pi}\int_0^\infty F_{ij}^N(q)\frac{\sin(qR)}{q}dq\Big], \qquad (2)$$

where Z_i^* and Z_j^*[12–14] are effective valences and $F_{ij}^N(q)$ is a normalized energy wave number dependent characteristic that contains total band-structure effects in the alloy using the self-consistent electron screening. In many cases, especially for non-local pseudopotentials valence, Z is replaced by effective valence Z^*. We note that when a non-local pseudopotential is used, the calculation of $F^N(q)$ and Z^* requires the self-consistent solution of a system of coupled nonlinear equations.[12] The effective valence charges Z_i^* and Z_j^* are given in the form $Z_i^* Z_j^* = Z_i Z_j - \overline{Z}_i\overline{Z}_j$, where Z is the true valence and $\overline{Z}$ is the depletion hole charge that originates from orthogonality condition between valence and core electron wavefunctions. $F_{ij}^N(q)$ is given by

$$F_{ij}^N(q) = -\Big(\frac{q^2\Omega}{2\pi Z_i Z_j}\Big)F_{ij}(q), \qquad (3)$$

where $F_{ij}(q)$ in the general case is given by

$$F_{ij}(q) = -\Big(\frac{q^2\Omega}{8\pi}\Big)\Big[w_i(q)w_j(q)\frac{\epsilon^*(q)-1}{\epsilon^*(q)}\frac{1}{1-G(q)}\Big], \qquad (4)$$

Here the quantities $w_i(q)$ and $w_j(q)$ are the Fourier transforms of self consistent bare ion (unscreened) atomic pseudopotentials for metallic component of alloy, obtained by using generalized the first principle pseudopotential theory. We have used Troullier and Martins (TM)[15] unscreened pseudopotentials. In the present work, a semi-local form of pseudopotentials have been used to calculate pair potentials which relies essentially on a single reference level for each l component. With ab-initio pseudopotentials there is no effective charge and contribution of effective valence charge can be ignored. Here $G(q)$ is the exchange-correlation functional of Vashishta and Singwi,[16] $\epsilon^*(q)$ is a modified Hartree dielectric function. $\Omega = \Omega_{ideal} = (1-c_2)\Omega_1 + c_2\Omega_2$ with c_2 being the concentration of the second component in the alloy, and Ω_1 and Ω_2 are the atomic volumes of the pure elements. In the present work, Ω_1 and Ω_2 are atomic volumes of the pure elements taken from the density data.[8] The hard sphere diameters are determined using the relation $V_{ij}(\sigma_i) = V_{\min} + \frac{3}{2}K_BT$ at temperature $T = 373$ K for NaK alloy. Here $V_{\min}$ is the first minimum in the interionic pair potential. Pair potentials have been calculated by Eq. (2) using ab-initio pseudopotentials.

The Faber–Ziman formula for electrical resistivity of a binary alloy can be written as

$$R = \frac{3\pi}{\hbar^2 e^2}\frac{4\Omega}{V_F^2}\int_0^1 \Big[C_1V_1^2(q)S_{11}(q) + C_2V_2^2(q)S_{22}(q) + 2\sqrt{C_1C_2}V_1(q)V_2(q)S_{12}(q)\Big] \cdot (q/2k_F)^3 d(q/2k_F),$$

where $V_F = \Big(\frac{\hbar k_F}{m}\Big)$ is the Fermi velocity and $k_F = \Big(\frac{3\pi^2 Z_s}{\Omega}\Big)^{1/3}$ is the Fermi wave vector. Z_s is the mean number of valence electrons per atom and is given by

$$Z_s = [(1-c)Z_1 + cZ_2] - 2n_3,$$

where C_1, C_2, and C_3 are fractions of concentration of the elements and the alloy. $V_1(q)$ and $V_2(q)$ are the non-local screened pseudopotentials for the components of binary alloy.

For the calculation of ab-initio screened pseudopotentials we have used the Troullier and Martins (TM) method, because this method produces computationally efficient pseudopotentials with a plane-wave basis set. There is also no problem of transferability as compared to traditionally used model pseudopotentials.

TM pseudopotentials have proved their applicability with the calculations of systems of a larger number of elements in the periodic table in contrast to other ab-initio pseudopotentials like that of Bachelet *et al.*.[17] In the present work we have used the fhi98PP[18] code to generate TM ab-initio pseudopotentials. First the ab-initio pseudopotentials are constructed by all-electron calculation of free atom in a reference configuration and then the method of Troullier and Martins has been used to construct the screened pseudopotentials.

Table 1. Electronic configuration for constructing ab-initio pseudopotentials.

Metal	Electronic configuration
Na	$3s^{1.0}3p^{0.25}3d^{0.25}$
K	$4s^{1.0}4p^{0.0}4d^{0.0}$

Table 2. Pseudo-core radii for constructing ab-initio pseudopotentials.

Metal	Core Radii (a.u.)
Na	$r_c(s,p,d) = (2.4, 2.4, 2.4)$
K	$r_c(s,p,d) = (3.1, 3.1, 3.7)$

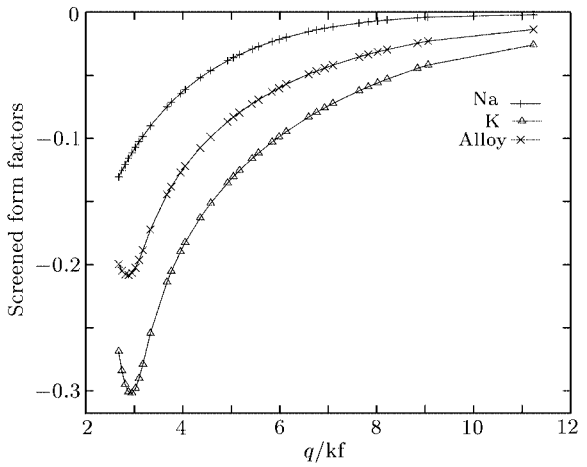


Fig. 1. Fourier transform of screened form factor for Na, K, and their alloy.

In the formulation of present work only one pseudopotential per atom has been used and pseudopotentials for angular momentum $l = 1$ have been calculated for both Na and K. Here general rule[19] has been applied that if atoms have states up to $l = l_c$ in the core then we need a pseudopotential up to angular momentum $l > l_c + 1$. Angular momentum $l > l_c + 1$ will feel the same potential as $l = l_c + 1$, because for all of them there is no orthogonality to core states. As a consequence, the pseudopotential should have projections on angular momentum up to l_c, and $l = l_c + 1$ should be a reference state for plane wave (PW) calculations. This rule, though not very strict, has been found to be very useful. In the present work, according to the configuration used for Na and K (Table 1) l_c is $= 0$ for both Na and K. Therefore, pseudopotentials can be calculated for $l_c + 1$, i.e. $l = 1$. Also, to have good a pseudopotential it should yield satisfactory results over a range of atomic environments, which is essential for ensuring transferability. Although thorough tests of transferability are complicated, in a simple way the same pseudopotential to calculate the eigenvalues and wavefunctions of several atomic configuration have been used. Pseudopotentials have been determined from the ground state atomic configuration and then used to calculate the eigenvalues of excited states. Transferability has been checked by comparing the obtained eigenvalues and wavefunctions with all electron calculations. The calculated values of electrical resistivity of Na–K alloy are shown in Fig. 2. as a function of percentage concentration along with the experimental results.[20] Calculated values agree reasonably both in magnitude and gradient. The good agreement is indicative of the free electron behaviour of this alloy. For the calculation of electrical resistivity, screened pseudopotentials have been shown in Fig. 1, which shows that the form factors in the alloy state have been found more negative than the form factors of constituent metals.

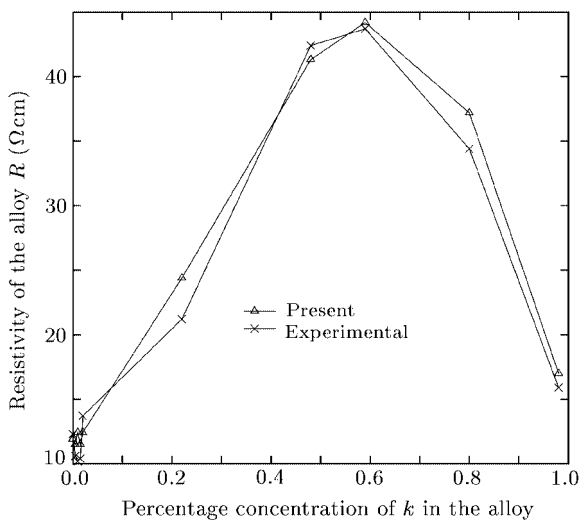


Fig. 2. Electrical Resistivity of Na–K alloy as a function of concentration.

Electronic configurations along with the core radii of Na and K are listed in Tables 1 and 2, respectively. In most cases, atomic ground states work very well for the occupied atomic orbital. However, a specific way for the configuration to resemble the solid state can be used if it does not change the result much. As in the present work the electronic configuration of Na is taken as shown in Table 1.

It is clear from Fig. 2. that the calculated electrical resistivity varies smoothly with the concentration of each constituent and well defined "electrical resistivity surface" pattern of continuity is followed.

These results suggest that the Ziman formalism when used with ab-initio pseudopotentials is successful in explaining the electrical resistivity of simple binary liquid alloys.

References

[1] Faber T E and Ziman J M 1965 *Philos. Mag.* **11** 153
[2] Ziman J M 1961 *Philos. Mag.* **6** 1013
[3] Mishra A K, Sahay B B and Mukherjee K K 1990 *Phys. Status Solidi* **157** 85
[4] Mishra A K, Singh R N and Sahay B B 1990 *Physica* B **167** 7
[5] Helen M 1994 *Ph.D. Thesis* (India: Bhagalpur University)
[6] Gonzalez L E, Gonzalez D J and Lopez J M 2001 *J. Phys.: Condens. Matter* **13** 7802
[7] Srivastava S K and Sharma P K 1970 *Physica* **48** 225
[8] Hoshino K 1983 *J. Phys. F: Met. Phys.* **13** 1981
[9] Hiroike K 1969 *J. Phys. Soc. Jpn.* **27** 1415
[10] Hoshino K 1983 *J. Phys. F: Met. Phys.* **13** 1981
[11] Harrison W A 1966 *Pseudopotentials in the Theory of Metals* (New York: Benjamin)
[12] Zhao M and Rice S A 2001 *Phys. Rev.* B *63* 85409
[13] Moriarty J A 1988 *Phys. Rev.* B **38** 3199
[14] Woo C H, Wang S and Matsuura M 1975 *J. Phys.* F **5** 1836
[15] Trouiller N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[16] Vashishta P and Singwi K S 1972 *Phys. Rev.* B **6** 875
[17] Bachelet, Hamann D R and Schulter M 1982 *Phys. Rev.* B **26** 4199
[18] Fuchs Martins and Scheffler Matthias 1999 *Computer Physics Commun.* **119** 67
[19] Gonze X, Stumpf and Scheffler 1991 *Phys. Rev.* B **44** 8503
[20] Hennephof J, Van Der Luget, Wnnght G W and Marien T M 1972 *Physica* **61** 146