A self-consistent pseudopotential applied to transport coefficients of liquid binary alloys of alkali metals

S Wang, S K Lai and C B So†
Department of Physics, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

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Abstract. The energy-independent model pseudopotential theory, developed and used previously for simple metals, is extended to the binary alloys of these simple metals and a self-consistent pseudopotential, which contains a detailed concentration dependence, is derived for the calculation of various properties of these alloys. This pseudopotential is applied within a low-order perturbation theory to calculate the form factors and transport coefficients for the K-Rb, Na-K and Na-Cs alloys in the liquid state. The calculated results show that a very significant fraction of the valence electrons is localised on the electronegative component in the liquid Na-Cs alloy, as compared with the other alloys considered, and, as a result, the electrical resistivity is very much greater for the liquid Na-Cs alloy than for the liquid Na-K and K-Rb alloys, as demonstrated in experiment. Finally, the applicability of the pseudopotential perturbation theory to the liquid alloys of simple metals is discussed.

1. Introduction

In an earlier paper (Woo et al 1975, to be referred to as I), an energy-independent model pseudopotential (EIMP) theory (which is essentially state dependent) was developed to obtain a self-consistent pseudopotential to calculate the electronic structure of simple metals. Subsequently, the EIMP theory was successfully applied to the calculations of various properties of the simple metals in both solid and liquid phases (see Matsuura et al 1975, So et al 1977a, b, Wang and So 1977, 1979, Lai et al 1978, to be referred to as II, III, IV, V, VI and VII respectively). It appears that the difference between the results obtained from the application of the EIMP theory and the other pseudopotential theories constructed from first principles (by which we mean that the theory does not contain any adjustable parameter), such as the Heine-Abarenkov-type model pseudopotential (Heine and Abarenkov 1964, Shaw 1968), is (i) small for the metals lighter than K and (ii) significant for the simple metals heavier than K (see II, III and V for example). This suggests that such a difference will also occur for the alloys of simple metals.

Therefore, in this paper we extend the EIMP theory to the binary alloys to derive a model pseudopotential in a self-consistent manner for use in the calculation of the electronic structure of the binary alloys of simple metals. We compare it with the results obtained by other authors from different pseudopotential theories of simple metals (Inglesfield 1969, Krasko and Gurskii 1972, Hallers et al 1974, Hafner 1976, 

† Present address: Material Science Branch, Atomic Energy of Canada Limited, Pinawa, Manitoba, R0E 1L0, Canada.
Hasegawa and Young 1977). Further, we apply the derived self-consistent pseudopotential and the theory of the electronic conduction, as described in V, to the calculation of the electronic transport coefficients of the K–Rb, Na–K and Na–Cs alloys and show why the electrical resistivity of the latter alloy is much greater than the former alloys.

2. Self-consistent pseudopotentials

In this section we derive expressions for the pseudopotential of a valence electron in an alloy of simple metals in the wave-vector space; these can be used in the pseudopotential calculation of the electronic structure of binary alloys.

2.1. Expression of pseudopotentials

The pseudopotential of a valence electron at position $r$ in an alloy consisting of two components is, in general, written as

$$ W(r) = \sum_{i=1}^{2} \sum_{\lambda(i)} w_i(r - R_\lambda) \equiv \sum_{i=1}^{2} \sum_{\lambda(i)} w_i^0(r - R_\lambda) + V_e(r) $$

(2.1)

where $w_i^0(r - R_\lambda)$ denotes the electronic bare pseudopotential due to an $i$th-type ion at the position $R_\lambda$, the sum $\sum_{\lambda(i)}$ extends over all the positions of the $i$th-type ions (i.e. to the $i$th component) and $V_e(r)$ represents the electronic potential due to the other valence electrons in the same alloys. Then the corresponding pseudopotential in the wave-vector space can be written, by transforming $r$ to $r + R_\lambda$ in the first term of equation (2.1), in the form

$$ \langle k + q | W(r) | k \rangle = \sum_{i=1}^{2} S_i(q) w_i^0(q) + V_e(q) $$

(2.2)

where $S_i(q) \equiv \sum_{\lambda(i)} \exp(-iq \cdot R_\lambda)/N$, being a partial-structure factor of the alloy consisting of $N_1$ type-1 ions and $(N - N_1)$ type-2 ions. Here, $w_i^0(k)$ is $\langle k + q | w_i^0(r) | k \rangle N$ and can be written, in general, as $w_i^0(q) = v_i(q) + f_i(k + q, k)$, where $v_i(q)$ and $f_i(k + q, k)$ are respectively the local and non-local parts of $w_i^0(q)$. $V_e(q)$ in equation (2.2) depends upon the pseudopotential chosen and must be calculated in a self-consistent manner. This can be done by following a procedure similar to that used by Shaw and Harrison (1967) and by using the pseudo-wavefunctions from a low-order perturbation theory, i.e.

$$ \chi_k = N_k \left( |k\rangle + \sum_q \frac{\langle k + q | W(r) | k \rangle}{E_k^0 - E_{k+q}^0} | k + q \rangle \right) $$

(2.3)

where the prime on the summation over $q$ means the exclusion of $q = 0$; $| k + q \rangle$ stands for a plane wave normalised in the volume of the alloy, i.e. in $N \Omega_0$ where $\Omega_0$ is the atomic volume; and $E_{k+q}^0$ is an eigenenergy of the unperturbed part of the Hamiltonian, $H^{ps} = T + W(r)$. $N_k$ in equation (2.3) is a normalisation constant and must be determined such that the true wavefunction $\psi_k(r)$ obtained using the normalised $\chi_k(r)$ from the equation connecting $\psi_k(r)$ and $\chi_k(r)$ (i.e. $\psi_k(r) = (1 - P) \chi_k(r)$ in which $P$ is the core-state projection operator) satisfies the normalisation condition of the true
A self-consistent pseudopotential wavefunctions, i.e. \( \langle \psi_k(r) | \psi_k(r) \rangle = 1 \). \( V_s(q) \) thus calculated for \( W(r) \) given by equation (2.1) is of the form

\[
V_s(q) = \sum_{i=1}^{2} S_i(q) \left\{ \left[ (v_i(q) | I(q) + v_{i,d}(q) \right]/\epsilon(q) \right] + g_i(q) \right\}
\]

(2.4)

where

\[
v_{i,d}(q) = \frac{4\pi M_i(q)}{\Omega_0q^2} \int_{\Omega_{i,M}} \rho_i(r) \, dr = \frac{4\pi M_i(q)}{\Omega_0q^2} \rho_{i,d}
\]

(2.5)

in which \( M_i(q) \) is a modulating function (see I for details)

\[
\rho_i(r) = \sum_{k \in K_F} \left( \psi^*_k(r) \psi_k(r) - \chi^*_k(r) \chi_k(r) \right)_i
\]

in the atomic unit system and \( \Omega_{i,M} \) stands for the volume of the ion core of the \( i \)th component. Also from equation (2.4)

\[
\epsilon(q) = 1 - I(q) \equiv 1 - \frac{2}{\pi^2q^2} \int_{k \in K_F} \frac{|N_k|^2}{E_k - E_{k+q}}
\]

(2.6)

and

\[
g_i(q) = \frac{2}{\epsilon(q)\pi^2q^2} \int_{k \in K_F} \frac{|N_k|^2 f_i(k + q, k)}{E_k - E_{k+q}}
\]

(2.7)

Now, with the use of equation (2.4), equation (2.2) can be converted into

\[
\langle k + q | W | k \rangle = \sum_{i=1}^{2} S_i(q) w_{i,q}(k)
\]

(2.8)

with

\[
w_{i,q}(k) = \left[ (v_i(q) + v_{i,d}(q))/\epsilon(q) \right] + f_i(k + q, k) + g_i(q) \\
i = 1, 2
\]

(2.9)

which is the form factor for the \( i \)th component of the alloy. In the present non-local pseudopotential theory, \( v_i(q) \) in equation (2.9) is the Fourier transform of \(-Z_i/r\), i.e. \(-4\pi Z_i/(\Omega_0q^2)\), where \( Z_i \) is the valence charge of one of the \( i \)th-type ions. Hence \( v_i(q) \) plus \( v_{i,d}(q) \) in equation (2.9) is essentially

\[
v_i(q) + v_{i,d}(q) = -4\pi Z^*_i/(\Omega_0q^2)
\]

(2.10)

where \( Z^*_i = Z_i - M_i(q) \rho_{i,d} \) is an effective valence charge of one of the \( i \)th-type ions.

It then remains for us to determine \( |N_k|^2 \) and \( \rho_{i,d} \) in the low-order perturbation theory. \( |N_k|^2 \) can be determined from equation (4.4) of I by using \( W(r) \) given by equation (2.1) and \( \chi_k \) given in equation (2.3). The result thus calculated is

\[
|N_k|^2 = \left[ 1 + \sum_{i=1}^{2} C_i N \left( \frac{\partial}{\partial E_k} - \frac{\partial}{\partial E_k} \right) \langle k' | w_i(r) | k \rangle |_{\Omega_{i,M} \kappa = k} \right]^{-1}
\]

(2.11)

where \( C_i \) is the concentration of the \( i \)th component and \( E_k \) is the first-order electronic energy. In the same approximation \( \rho_{i,d} \) is calculated as

\[
\rho_{i,d} = \sum_{k \in K_F} |N_k|^2 \left( \frac{\partial}{\partial E_k} - \frac{\partial}{\partial E_k} \right) \langle k' | w_i(r) | k \rangle |_{\Omega_{i,M} \kappa = k} \]

(2.12)
using equation (4.6) of I for the ith component. Now, it may be concluded from the
above that \( v_{i,d}(q) \), \( \epsilon(q) \) and \( g_i(q) \), in the form factor given by equation (2.9), depend
upon the concentrations of the components in the alloy through \( |N_k|^2 \) given by
equation (2.11). However, such dependences were not quite appropriately included in
the previously published pseudopotential calculations of the alloys, such as those
mentioned in §1.

In deriving \( V_c(q) \) given by equation (2.4), the exchange-correlation effects of the
valence electrons in the alloy were not considered. To include such effects, we follow I
to write

\[
\begin{align*}
v_{i,d}(q) &= \frac{2}{\pi^2 q^2} \int_{k \leq k_F} dk \frac{|N_k|^2 v_{i,q}(k)}{E_k^0 - E_{k+q}^0} + v_{i,d}(q).
\end{align*}
\]  

(2.14)

2.2. Alternative expression of the pseudopotentials

In the preceding subsection the volume of the alloy under consideration was set equal
to \( N\Omega_0 \), \( \Omega_0 \) being a mean volume occupied by one of the ions. Hereafter this volume
will simply be called a cell. In this approximation it is equivalent to write \( W(r) \) given
by equation (2.1) in the form

\[
\begin{align*}
W(r) &= \sum_\lambda \left[ v_\lambda w_1(r - R_\lambda) + (1 - v_\lambda) w_2(r - R_\lambda) \right]
\end{align*}
\]  

(2.15)

where \( v_\lambda \) is unity, if the \( \lambda \)th cell is occupied by one of the first-type ions and zero
otherwise. Now, the summation over \( \lambda \) is to be taken over all the cells. Using the
concentrations of the two components in the alloy, \( W(r) \) can be rewritten as

\[
\begin{align*}
W(r) &= \sum_{i=1}^{2} \sum_\lambda C_i w_\lambda(r - R_\lambda) + \sum_\lambda (v_\lambda - C_1) \Delta w(r - R_\lambda)
\end{align*}
\]  

(2.16)

where \( \Delta w(r - R_\lambda) = w_1(r - R_\lambda) - w_2(r - R_\lambda) \). We proceed to consider the corresponding
\( \langle k + q|W(r)|k \rangle \). Transforming \( r \rightarrow r + R_\lambda \) and using

\[
\begin{align*}
\sigma(q) &= \sum_\lambda \left[ (v_\lambda - C_1) \exp(-iq.R_\lambda) \right] / N \\
S(q) &= \sum_\lambda \left[ \exp(-iq.R_\lambda) \right] / N
\end{align*}
\]  

(2.17)

as a full structure-factor for the alloy, we obtain

\[
\begin{align*}
\langle k + q|W(r)|k \rangle = S(q) \sum_{i=1}^{2} C_i w_{1,q}^0(k) + \sigma(q) \Delta w_{q}^0(k) + V_c(q)
\end{align*}
\]  

(2.18)

where \( \Delta w_{q}^0(k) = w_{1,q}^0(k) - w_{2,q}^0(k) \). Although the form of \( \langle k + q|W(r)|k \rangle \) given in
equation (2.18) differs from equation (2.2), \( V_c \) in equation (2.18) can be calculated
in the same way as in the derivation of equation (2.4). $V_e$ thus obtained is of the form

$$V_e(q) = S(q) \sum_{i=1}^{2} C_i \left\{ \left[ (v_i(q) I(q) + v_{i,q}(q)) / \epsilon(q) \right] + g_i(q) \right\}$$

$$+ \sigma(q) \left\{ \left[ (v_1(q) I(q) + v_{1,q}(q)) / \epsilon(q) \right] + g_1(q) \right\}$$

$$- \left[ (v_2(q) I(q) + v_{2,q}(q)) / \epsilon(q) \right] - g_2(q) .$$

(2.19)

Substituting this into equation (2.18) and rearranging the terms, we arrive at

$$\langle k + q | W | k' \rangle = S(q) \sum_{i=1}^{2} C_i w_{i,q}(k) + \sigma(q) (w_{1,q}(k) - w_{2,q}(k))$$

(2.20)

where $w_{i,q}(k)$ is exactly the same as given by equation (2.9). It is given by equation (2.13) when the exchange-correlation effects of the valence electrons are included in the same way as in the derivation of equation (2.13). Obviously, equation (2.20), being another representation of the pseudopotential, is equivalent to equation (2.8). The use of these equations entirely depends on the system in question. Generally speaking, because of the presence of structure factors, equation (2.20) is generally appropriate for the ordered binary alloys. In contrast, equation (2.8) is, in general, appropriate for the disordered binary alloys, as will be seen in the following application.

2.3. Form factors in EIMP theory

In the EIMP theory as described in I, the Hamiltonian is written in the form

$$H_{ps} = T + W(r) = T + \sum_g \langle g | W(r) | g \rangle |g\rangle \langle g| + \sum_{g,g'} \langle g | W(r) | g' \rangle |g'\rangle \langle g' |$$

(2.21)

and the last term is taken as a perturbation. The corresponding unperturbed eigen-energies and eigenfunctions are respectively

$$E^0_k = \frac{1}{2} k^2 + \langle k | W(r) | k \rangle$$

(2.22)

and the plane waves, because the unperturbed Hamiltonian consisting of the first two terms on the left-hand side of equation (2.21) commutes with the operator of kinetic energy $T$. Accordingly, in the EIMP theory the linear combination coefficients, $C_q(k)$ say, in equation (2.3) are of the form

$$C_q(k) = \frac{\langle k + q | W(r) | k \rangle}{\langle k + q | W(r) | k \rangle - [\left( (k + q)^2 / 2 \right) + \langle k + q | W(r) | k + q \rangle]} .$$

(2.23)

Now, it is seen that in the perturbation theory just described, the form factor for a binary alloy has the same form as that of equation (2.13) with $E^0_k$ given by equation (2.22). This form factor is expected to improve the convergence of the non-local perturbation calculation, in which the whole $W(r)$ is taken as a perturbation and $C_q(k) = \langle k + q | W(r) | k \rangle / [\left( (k^2 / 2) - (|k + q|^2 / 2) \right]$ (for example, see Hafner 1976). This is because the whole $W(r)$ is stronger than the perturbation given by the last term in equation (2.21).
Further, in the EIMP theory the bare ionic pseudopotential \( w_i^0(r) \) is given by equation (2.2) of I. For \( w_i^0(r) \) thus determined, \( v_i(q) \) and \( f_i(k + q, k) \) in the form factor are respectively given just below equation (2.9) and

\[
f_i(k + q, k) = \frac{4\pi}{\Omega_0} \sum_i (2l + 1) P_i(\cos \theta_{k,k+q}) [I_{l,i}(|k + q|) J_{l,i}(k) - S_{l,i}(k, |k + q|)]
\]

(2.24)

from I. The symbols in equation (2.24) have the same meanings as in I. \( E_k^0 \) given by equation (2.22) can be converted into

\[
E_k^0 = \frac{k^2}{2} + \sum_{i=1}^{2} C_i N \langle k | w_i^0(r) | k \rangle = \sum_{i=1}^{2} C_i E_{i,k}^0
\]

(2.25)

where \( E_{i,k}^0 \) is of the form

\[
E_{i,k}^0 = \frac{k^2}{2} + 4\pi\Omega_0^{-1} \sum_l (2l + 1)(I_{l,i}(k) J_{l,i}(k) - S_{l,i}(k,k)).
\]

(2.26)

As for \( |N_k|^2 \) involved in a number of quantities in the form factor, it is to be calculated from equation (2.11) with \( \partial \partial E_k \) replaced by \( \partial k / \partial E_k (\partial / \partial k) \). The result thus calculated is

\[
|N_k|^2 = \frac{C_1 m_s^+(k) + C_2 m_s^+(k)}{C_1 m_s^+(k) N_{1,k}^{-2} + C_2 m_s^+(k) N_{2,k}^{-2}}
\]

(2.27)

where \( m_s^+(k) \) is the first-order density-of-states effective mass for a valence electron in the pure metal consisting of the ith-type ions and it takes the form

\[
m_s^+(k) = \left( 1 + 4\pi (k\Omega_0)^{-1} \sum_l (2l + 1)(I_{l,i}(k) J_{l,i}(k) + I_{l,i}(k) J_{l,i}(k) - S_{l,i}(k,k)) \right)^{-1}
\]

(2.28)

where the primes over \( I_{l,i}, J_{l,i} \) and \( S_{l,i} \) denote differentiation with respect to \( k \).

In equation (2.27), \( |N_{i,k}|^{-2} \) has the same meaning as that of equation (4.8) in I and, for the present case, is of the form

\[
|N_{i,k}|^{-2} = 1 + m_s^+(k) x_i(k)
\]

(2.29)

where \( x_i(k) = 4\pi (k\Omega_0)^{-1} \sum_l (2l + 1)(I_{l,i}(k) J_{l,i}(k) - I_{l,i}(k) J_{l,i}(k)) \).

In a similar manner, \( \rho_{l,d} \) involved in \( v_{i,d}(q) \) given by equation (2.5) can be calculated from equation (2.12) to give

\[
\rho_{l,d} = \frac{\Omega_0}{\pi^2} \int_0^{k_F} dk m^+(k) x_i(k) (|N_k|^2)^2
\]

(2.30)

where \( m^+(k) \) is the first-order density-of-states effective mass for a valence electron in the alloy and has the form

\[
m^+(k) = \frac{m_s^+(k) m_s^+(k)}{C_1 m_s^+(k) + C_2 m_s^+(k)}
\]

(2.31)

and where the Fermi wave vector may be determined, as usual, from the equation

\[
k_F^2 = 3\pi^2 \Omega_0^{-1} \sum_{i=1}^{2} C_i Z_i.
\]

(2.32)
Accordingly, $\omega_{i,q}(k)$ in equation (2.13) in the EIMP theory is given by equation (2.9) with (i) $\nu_i(q) = -4\pi Z_i/(\Omega q^2)$; (ii) $\rho_{i,d}$, appearing in $\nu_{i,d}(q)$, given by equation (2.30); (iii) $f_i(k + q, k)$ given by equation (2.24); and (iv) $E_i^0$ and $|N_k|^2$, appearing in $\epsilon(q)$ and other quantities, given respectively by equations (2.25) and (2.27).

transition probability of the scattering $P_{k,k'}$ in the pseudopotential theory was argued to be

\[ P_{kF,kF} \propto |N_{kF}|^2 |N_{kF}|^2 |\langle \phi_{kF}|W(r)|\phi_{kF}\rangle|^2 \]

where $|N_{kF}|\phi_{kF}$ is a renormalised pseudo-Bloch state for an electron on the Fermi surface. It was subsequently written

\[ P_{kF,kF} \propto |N_{kF}|^2 |N_{kF}|^2 |\langle kF|W(r)|kF\rangle|^2 \]

by using the effective-mass theory with the effective mass $\langle m^*(kF)\rangle$, which is the density-of-states effective mass $m^*(kF)$ averaged over the Fermi surface. In this approximation the electrical resistivity $\rho$ was calculated to be

\[ \rho = \langle \langle m^*(kF)\rangle |N_{kF}|^2 \rangle \rho_\ell \]

where $\rho_\ell$ stands for the electrical resistivity in the Ziman-type theory and has the form

\[ \rho_\ell = \frac{3\pi \Omega}{4k_F^5} \int_0^{2\pi} dq q^3 |\langle k + q|W(r)|kF\rangle|^2 \]

within the atomic unit system. We note that $|\langle kF + q|W(r)|kF\rangle|^2$ can be written as $|S(q)|^2|\nu^F_{q}(kF)|^2$ for a pure simple liquid metal, characterised by the structure factor $S(q)$. As given by equation (3.2) $\rho$ has been successfully applied to the calculation of electrical resistivities for the pure simple liquid metals (see V). Also, equation (32) has been successfully applied to the calculation of $\rho$ for alkali metals in the solid phase, although $S(q)$ is much larger in these metals than in the pure simple liquid metals for the range of small $q$ where the form factor is large (III, So and Wang 1978, Kaveh and Wiser 1974). In view of this, in this section we apply $\langle k + q|W(r)|k\rangle$ derived in §2 to equation (3.2) to calculate the electrical resistivity and thermoelectric power from the $\rho$ calculated for binary alloys of the simple metals and we demonstrate why the electrical resistivity of the Na–Cs alloy is much greater than that of the Na–K alloy. Finally, we discuss the extent to which the low-order perturbation theory, which was used in deriving both the $V_{ij}(q)$ in §2 and equation (3.2), can really be applied to the calculations of transport coefficients of interest and other physical quantities of the binary alloys of simple metals.

3. Transport coefficients

In the calculation of transport coefficients for the pure simple metals in III and V, the

\[ P_{kF,kF} \propto |N_{kF}|^2 |N_{kF}|^2 |\langle \phi_{kF}|W(r)|\phi_{kF}\rangle|^2 \]

where $|N_{kF}|\phi_{kF}$ is a renormalised pseudo-Bloch state for an electron on the Fermi surface. It was subsequently written

\[ P_{kF,kF} \propto |N_{kF}|^2 |N_{kF}|^2 |\langle kF|W(r)|kF\rangle|^2 \]

by using the effective-mass theory with the effective mass $\langle m^*(kF)\rangle$, which is the density-of-states effective mass $m^*(kF)$ averaged over the Fermi surface. In this approximation the electrical resistivity $\rho$ was calculated to be

\[ \rho = \langle \langle m^*(kF)\rangle |N_{kF}|^2 \rangle \rho_\ell \]

where $\rho_\ell$ stands for the electrical resistivity in the Ziman-type theory and has the form

\[ \rho_\ell = \frac{3\pi \Omega}{4k_F^5} \int_0^{2\pi} dq q^3 |\langle k + q|W(r)|kF\rangle|^2 \]

within the atomic unit system. We note that $|\langle kF + q|W(r)|kF\rangle|^2$ can be written as $|S(q)|^2|\nu^F_{q}(kF)|^2$ for a pure simple liquid metal, characterised by the structure factor $S(q)$. As given by equation (3.2) $\rho$ has been successfully applied to the calculation of electrical resistivities for the pure simple liquid metals (see V). Also, equation (32) has been successfully applied to the calculation of $\rho$ for alkali metals in the solid phase, although $S(q)$ is much larger in these metals than in the pure simple liquid metals for the range of small $q$ where the form factor is large (III, So and Wang 1978, Kaveh and Wiser 1974). In view of this, in this section we apply $\langle k + q|W(r)|k\rangle$ derived in §2 to equation (3.2) to calculate the electrical resistivity and thermoelectric power from the $\rho$ calculated for binary alloys of the simple metals and we demonstrate why the electrical resistivity of the Na–Cs alloy is much greater than that of the Na–K alloy. Finally, we discuss the extent to which the low-order perturbation theory, which was used in deriving both the $V_{ij}(q)$ in §2 and equation (3.2), can really be applied to the calculations of transport coefficients of interest and other physical quantities of the binary alloys of simple metals.

3.1. Transport coefficients of liquid binary alloys of simple metals

It appears from the present theory of the structure factors that the pseudopotential written in terms of the partial-structure factors is generally suitable for liquid alloys. Hence, at this point it is better to apply equation (2.8) with the exchange-correlation
effect included to the calculation of the matrix element in equation (3.3). When this is applied, we obtain

$$\rho_f = \frac{3\pi \Omega_0}{4k_F^6} \int_0^{2k_F} dq \; q^3 \left( \sum_{i=1}^2 C_i a_i(q) \left| w_{r,q}^E(k_F) \right|^2 + 2(C_1 C_2)^{1/2} a_{12}(q) \left| w_{1,q}^E(k_F) \right|^2 \right)$$

(3.4)

where \(|S_i(q)|^2 = a_i(q) C_i/N\) and \(S_1(q) S_2(q) = a_{12}(q)(C_1 C_2)^{1/2}/N\) and where \(a_i(q)\) and \(a_{12}(q)\) are the liquid partial structure-factors, corresponding respectively to \(S_i(q)\) and \(S_{12}(q)\) in the work of Ashcroft and Langreth (1967).

Having determined the expression for \(\rho\), we may proceed to calculate the thermoelectric power from the widely used equation (Bradley et al 1962, Evans 1970)

$$Q = \frac{T(\pi k_B)^2}{3E_F} \left( \frac{\partial}{\partial \ln E} \left( \ln \rho(E) \right) \right)_{E = E_F}.$$  

(3.5)

Substituting \(\rho\) given by equation (3.2) with \(\rho_f\) given in equation (3.4), we have, after using straightforward algebra,

$$Q = -\frac{2\langle m^*(k_F) \rangle T(\pi k_B)^2}{3k_F^2} (\zeta + \xi)$$

(3.6)

where \(\xi = [3 - 2A - (B/2)] [1 - (2\langle m^*(k_F) \rangle) - 1 k_F \langle \partial m^*(k) \partial k\rangle_{k = k_F}]^{-1}\). Here

$$A = \left( \sum_{i=1}^2 C_i a_i(q) \left| w_{r,q}^E(k_F) \right|^2 + 2(C_1 C_2)^{1/2} a_{12}(q) \left| w_{1,q}^E(k_F) \right|^2 \right)_{q = 2k_F} J^{-1}$$

(3.7)

and

$$B = k_F \left( \sum_{i=1}^2 C_i a_i(q) \left( \partial w_{r,q}^E(k) \right)^2 \right)_{k = k_F}$$

$$+ 2(C_1 C_2)^{1/2} a_{12}(q) \left( \partial w_{1,q}^E(k) \right)_{k = k_F} J^{-1}.$$  

(3.8)

\(J\) has the form

$$J = \left( \sum_{i=1}^2 C_i a_i(q) \left| w_{r,q}^E(k_F) \right|^2 + 2(C_1 C_2)^{1/2} a_{12}(q) \left| w_{1,q}^E(k_F) \right|^2 \right)$$

(3.9)

and the symbol \(\langle f(q) \rangle\) has the same meaning as in \(V\). \(\zeta\) in equation (3.6) is given by

$$\zeta = k_F \left| N_{k_F} \right|^2 \left( \frac{\partial |N_k|}{\partial k} \right)_{k = k_F} - \frac{k_F}{\langle m^*(k) \rangle} \left( \frac{\partial \langle m^*(k) \rangle}{\partial k} \right)_{k = k_F}$$

(3.10)

which arises from the factor \(\langle m^*(k_F) \rangle \left| N_{k_F} \right|^2\) in equation (3.2) and is a correction to \(Q\) in the Ziman-type free-electron theory.

3.2. Application to K–Rb, Na–K and Na–Cs alloys at 100°C

In applying the equations just derived above for \(\rho\) and \(Q\) to the liquid binary alloys, we need to know the partial structure-factors. Theoretically, these factors can be calculated by using the interatomic potentials in the alloys as in the calculation of the
liquid structure-factors for simple metals (Murphy and Klein 1973). However, the computer work involved in such a calculation is very time consuming. Because of this, we take the partial structure-factors directly from the Ashcroft–Langreth work, which is based on the hard-sphere model of liquids (see V and VII for the applicability of this model to the metallic calculations). The partial structure-factors, as derived by Ashcroft and Langreth, are written in terms of C, σ2, η2, η and x = σ1/σ2. Here, C, σ2 and η2 are respectively the concentration, the hard-sphere diameter and the partial packing density for the heavier component of the alloy, η2 being given by

$$\eta_2 = \frac{C\eta}{C + (1 - C)x^2} = \frac{\pi C\sigma_2^2}{6\Omega_0}.$$  \hspace{1cm} (3.11)

$$\eta = \eta_1 + \eta_2$$ where η1, the partial packing density of the lighter component, has the form

$$\eta_1 = \frac{(1 - C)\eta x^2}{C + (1 - C)x^2} = \frac{\pi(1 - C)\sigma_1^2}{6\Omega_0}$$ \hspace{1cm} (3.12)

the hard-sphere diameter being σ1. Because the concentration dependence of x can be ignored, this set of parameters can be determined by calculating first η1 and η2 from equations (3.11) and (3.12), and then η, if Ω0 and the values of σ1 and σ2 for the pure liquid metals are known. However, because the accurate Ω0 is not yet available for many binary alloys, we follow an alternative method of determining the parameters involved. The alternative way is as follows: (i) we first find η for C ≠ 0 from a linear interpolation from the known η1⁰ = η(C = 0) and η2⁰ = η(C = 1) at T of interest; (ii) we then use η thus obtained and x from σ1 and σ2 for the pure metals to find η1 and η2 for C ≠ 0 using equations (3.11) and (3.12); and (iii) we finally use η1 and σ1 (or η2 and σ2) to determine Ω0 for a given concentration C. The parameters thus determined at C = 0:5 for those alloys, for which η1⁰ and η2⁰ can easily be obtained from the literature, are summarised in table 1. At this point it should be noted that the values of Ω0 given in this table do not differ significantly from the experimental values (Huijben et al 1975, 1976) not only for C = 0:5 but also for the other values of C. We also note that the change in volume on the alloying of two components, i.e. ΔΩ satisfying the equation

$$\Omega_0 = (1 - C)\Omega_{1,0} + C\Omega_{2,0} + \Delta\Omega$$ \hspace{1cm} (3.13)

(Ω1,0 and Ω2,0 being the respective ionic volumes of the two components before alloying), is negative with a largest value around C = 0:55 for the alloys considered here.

Table 1. Values used for input data, σi, ηi⁰ and Ωi,0 (Ashcroft and Lekner 1966, Hennephof et al 1978, Hâlers et al 1974); the values determined here for (i) various packing densities, (ii) the atomic volume and (iii) the change in the atomic volume for the liquid K–Rb, Na–K and Na–Cs alloys at C = 0:5 and T = 100°C; σi and various atomic volumes are in atomic units.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>σ1</th>
<th>σ2</th>
<th>η1⁰</th>
<th>η2⁰</th>
<th>Ω1,0</th>
<th>Ω2,0</th>
<th>η</th>
<th>η1</th>
<th>Ω0</th>
<th>−ΔΩ</th>
</tr>
</thead>
<tbody>
<tr>
<td>K–Rb</td>
<td>7.64</td>
<td>8.10</td>
<td>0.44</td>
<td>0.43</td>
<td>534.4</td>
<td>640.7</td>
<td>0.44</td>
<td>0.20</td>
<td>587.3</td>
<td>0.17</td>
</tr>
<tr>
<td>Na–K</td>
<td>6.20</td>
<td>7.64</td>
<td>0.45</td>
<td>0.44</td>
<td>277.7</td>
<td>534.4</td>
<td>0.44</td>
<td>0.15</td>
<td>403.9</td>
<td>2.07</td>
</tr>
<tr>
<td>Na–Cs</td>
<td>6.20</td>
<td>8.84</td>
<td>0.45</td>
<td>0.42</td>
<td>277.7</td>
<td>854.5</td>
<td>0.44</td>
<td>0.11</td>
<td>557.0</td>
<td>9.12</td>
</tr>
</tbody>
</table>
We now turn to the consideration of the on-Fermi-level form factor \( w^{EC}(k) \) in the formulae of \( \rho \) and \( Q \). This form factor can be calculated by a computer using equation (2.13) with \( F(q) \), as suggested in III and used in IV–VII. As an indication of the change in the form factors on alloying, among the results thus calculated for a number of concentrations, those for \( C = 0, 0.5 \) and 1 are shown in figures 1 (a), (b) and (c) for the three alloys considered here. In addition, in order to see the change in the effective valence charge \( Z_r^* \) on alloying, the values of \( Z_r^* \) involved in the calculation of the form factors for \( M(q) = 1 \) (which has been used for all \( q \) in the orw pseudopotential theory) are displayed in table 2. One aspect of the calculated \( Z_r^* \) merits emphasis; namely, in going from pure metals to alloys, the effective valence charge of the lighter component decreases, while that of the heavier component increases. Physically, this implies that some fraction of the valence electrons is localised on the electronegative ion, which is Na for Na–K and Na–Cs, and K for K–Rb. Accordingly, the valence electrons in an alloy cannot move as freely as those in the pure metals of the alloy.

Hence, it is natural to conclude from the above that the valence-electron density-of-states effective mass for the liquid binary alloys considered, such as \( \langle m^*(k_F) \rangle \) in equations (3.2) and (3.6), (i) is greater than both \( \langle m^*(k_F) \rangle_{C=0} \) and \( \langle m^*(k_F) \rangle_{C=1} \), being respectively the density-of-states effective masses for the lighter and heavier components and (ii) has a maximum at a value of \( C \) corresponding to the largest magnitude.
of $\Delta \Omega$ among the $\langle m^*(k_F) \rangle$ of different $C$. Before proceeding further, we note from the information about $\langle m^*(k_F) \rangle$ as given in IV and V for the pure metals that it is reasonable to use $\langle m^*(k_F) \rangle_C = 0.0$ equal to 1.046, 1.03, 1.04 and 1.08 respectively for the sodium, potassium, rubidium and caesium metals at 100°C. Accordingly, the value of the maximum of $\langle m^*(k_F) \rangle$ occurring at $C \approx 0.55$ for the alloys considered here is greater than (i) 1.04 for K–Rb, (ii) 1.046 for Na–K and (iii) 1.08 for Na–Cs.

The increase in $\langle m^*(k_F) \rangle$ on alloying depends, of course, on the valence-electron fraction localised on the electronegative ion. As can be seen from table 2, this fraction is (i) small for K–Rb, (ii) larger than in K–Rb for Na–K and (iii) much larger than in K–Rb for Na–Cs. Then, for the maximum value of $\langle m^*(k_F) \rangle$ it is fair to use (a) 1.06 for K–Rb, (b) 1.1 for Na–K and (c) 1.3 for Na–Cs. It is interesting to note that 1.1 and 1.3 are the approximate density-of-states effective masses due to the crystal periodic potential for the potassium and caesium metals respectively in the solid phase (see IV). Having determined $\langle m^*(k_F) \rangle_C = 0.0$ and the maximum value of $\langle m(k_F) \rangle$ occurring at $C \approx 0.55$ for the alloys considered here, the values of $\langle m(k_F) \rangle$ for other $C$ to be used in the calculation of $\rho$ and $Q$ may be determined by a linear interpolation between the maximum value of $\langle m^*(k_F) \rangle$ and $\langle m^*(k_F) \rangle_C = 0$ or $\langle m^*(k_F) \rangle_C = 1$, for $C$ between $C = 0.55$ and $C = 0$ or 1. The values thus determined for $\langle m^*(k_F) \rangle$ are summarised in table 3 to show the $C$ dependence of the valence-electron density-of-states effective mass. It is worth emphasising at this point that in this work $\langle m^*(k_F) \rangle$ is introduced to treat the valence electrons in the pseudo-Bloch states as the free particles, as in V, and cannot be compared directly with the density-of-states effective mass obtained from the usual calculation of electron density of states, which include the effects of the full electron–ion interactions.

The calculation of $\rho(C)$ as described above is applied to the K–Rb, Na–K and Na–Cs alloys at 100°C. The results thus calculated are displayed in figures 2(a) and (b) to compare with the corresponding experimental values (Hennephof et al 1972, 1978). In these figures, in order to see the effect of the difference between $\langle m^*(k_F) \rangle$ and 1 on

### Table 2. Values of the effective valence charge $Z_e$ in atomic units for the liquid K–Rb, Na–K and Na–Cs alloys at 100°C.

<table>
<thead>
<tr>
<th>$C$</th>
<th>0.0</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
<th>0.7</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>K–Rb $Z_{ke}$</td>
<td>1.251</td>
<td>1.247</td>
<td>1.241</td>
<td>1.235</td>
<td>1.229</td>
<td>1.224</td>
<td>1.000</td>
</tr>
<tr>
<td>K–Rb $Z_{1ke}$</td>
<td>1.000</td>
<td>1.334</td>
<td>1.335</td>
<td>1.327</td>
<td>1.319</td>
<td>1.312</td>
<td>1.308</td>
</tr>
<tr>
<td>Na–K $Z_{ke}$</td>
<td>1.134</td>
<td>1.129</td>
<td>1.119</td>
<td>1.111</td>
<td>1.104</td>
<td>1.098</td>
<td>1.000</td>
</tr>
<tr>
<td>Na–K $Z_{1ke}$</td>
<td>1.000</td>
<td>1.326</td>
<td>1.306</td>
<td>1.288</td>
<td>1.272</td>
<td>1.257</td>
<td>1.251</td>
</tr>
<tr>
<td>Na–Cs $Z_{ke}$</td>
<td>1.134</td>
<td>1.123</td>
<td>1.105</td>
<td>1.091</td>
<td>1.080</td>
<td>1.072</td>
<td>1.000</td>
</tr>
<tr>
<td>Na–Cs $Z_{1ke}$</td>
<td>1.000</td>
<td>1.608</td>
<td>1.540</td>
<td>1.484</td>
<td>1.437</td>
<td>1.398</td>
<td>1.396</td>
</tr>
</tbody>
</table>

### Table 3. Values of various valence-electron density-of-states effective masses in atomic units for the liquid K–Rb, Na–K and Na–Cs alloys at 100°C.

<table>
<thead>
<tr>
<th>$\langle m^*(k_F) \rangle$</th>
<th>0.0</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
<th>0.7</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle m^*(k_F) \rangle_{K–Rb}$</td>
<td>1.030</td>
<td>1.035</td>
<td>1.048</td>
<td>1.055</td>
<td>1.052</td>
<td>1.045</td>
<td>1.040</td>
</tr>
<tr>
<td>$\langle m^*(k_F) \rangle_{Na–K}$</td>
<td>1.046</td>
<td>1.055</td>
<td>1.080</td>
<td>1.095</td>
<td>1.085</td>
<td>1.050</td>
<td>1.030</td>
</tr>
<tr>
<td>$\langle m^*(k_F) \rangle_{Na–Cs}$</td>
<td>1.046</td>
<td>1.100</td>
<td>1.200</td>
<td>1.290</td>
<td>1.220</td>
<td>1.130</td>
<td>1.080</td>
</tr>
</tbody>
</table>
the electrical resistivities, the theoretical results from equation (3.2) for $\langle m^*(k_F) \rangle = 1$, denoted by $\rho_0(C)$, are also displayed. Further, in order to show the influence of the renormalisation of the pseudoscattering matrix element on the electrical resistivities, the theoretical results from equation (3.2) for $\langle m^*(k_F) \rangle |N_{k_F}|^2 = 1$ are also given in figure 2(b) for the K–Rb alloy. At this point, it is worth noting that the renormalisation of the pseudo-scattering matrix element here is significant, as in the calculation of optical conductivities (VI), not only for K–Rb but also for Na–K and Na–Cs alloys. Also, the calculation of $Q(C)$ as described above is carried out. The results obtained for the Na–Cs alloy, for which the previously published work was unable to predict the $C$ dependence of $Q$ correctly, are displayed in figure 3 along with the theoretical results of Feitsma et al (1978) and their interesting experimental values. There are
three aspects of the results calculated here that merit emphasis and these are given below.

(i) The theoretical electrical resistivity increases abruptly in going from the Na–K alloy to the Na–Cs alloy, as does the experimental result.

(ii) $\rho(C)$ or $\rho_0(C)$ has a maximum at $C \approx 0.55$ for both the Na–K and Na–Cs alloys, while $\rho$ of the K–Rb alloy has no maximum.

(iii) The thermoelectric power $Q(C)$ calculated using equation (3.6) is in reasonably good agreement with experiment. However, when the contribution from $\zeta$ in equation (3.6) is excluded, $Q$ reverses its sign and takes a negative value, which is very much smaller in magnitude than the negative value calculated by Feitsma et al (1978) using an equation like equation (3.6) with $\zeta = 0$. It is easy to understand the first aspect, by recalling that the localisation of the valence electrons on the electronegative component in the Na–Cs alloy is much larger than that in the Na–K alloy. Coming to the second aspect, we note that if the valence-electron fraction localised on the electronegative component in K–Rb were larger than that from the calculated effective valence charges, then the corresponding $\langle m^*(k) \rangle$ would become larger and the electrical resistivity versus concentration for the K–Rb alloy would also have a maximum. Hence, the second aspect occurs, just because the charge transfer in K–Rb is small as compared with that in the Na-based alloys. The third aspect implies that (a) the form factor as described in §2 for the binary alloys differs significantly from that used by Hallers et al (1974) and (b) the correction $\zeta$ to the Ziman-type free-electron theory in equation (3.6) may play an important role in some cases.

3.3. Applicability of a low-order perturbation theory to liquid binary alloys

The partial structure-factors $a_1$, $a_2$ and $a_{12}$ are, in general, not so small as the liquid structure-factors of the pure metals in the range of small $q$ (see figure 4), in which the form factors are very large (see figure 1). Consequently, the pseudopotential in the small-$q$ range is quite large and one may question the applicability of a low-order perturbation theory to the calculation of the properties of liquid binary alloys. Thus,

![Figure 4](image_url)
in this subsection we examine the reliability of the low-order pseudopotential theory as described and used in the previous sections. To this end, we apply equation (2.20) with the exchange–correlation effect of the valence electrons included to equation (3.2) to rewrite $\rho_t$ in the form

$$\rho_t = \frac{3\pi\Omega_0}{4kF^2} \int_0^{2kF} dq \, q^3 \left[ a(q) \left( \sum_{i=1}^{2} C_i^2 |w_{i,F}(kF)|^2 + 2C_1 C_2 w_{1,F}(kF) w_{2,F}(kF) \right) + C_1 C_2 (w_{1,F}(kF) - w_{2,F}(kF))^2 \right].$$

(3.14)

This is essentially the same as that derived by Faber and Ziman (1965). Here, the liquid structure-factor $a(q)$ came from $|\tilde{S}(q)|^2$ in writing equation (3.14) and is a full structure-factor for the binary alloy under consideration. It has been shown in the literature (Ashcroft and Langreth 1967) that as $\sigma \rightarrow 1$ or $\sigma_1 \rightarrow \sigma_2$,

$$a(q) \rightarrow (1 - C(q)\Omega_0^{-1})^{-1}$$

(3.15)

where $C(q)$ takes the form

$$C(q) = -4\pi\sigma^3 \int_0^{1} ds \, s^2 \frac{\sin sq}{sq} (f + gs + hs^3).$$

(3.16)

In this equation $f = (1 + 2\eta)^2(1 - \eta)^{-4}$, $g = -6\eta[1 + (\eta/2)]^2(1 - \eta)^{-4}$ and $h = (\eta/2)(1 + 2\eta)^2(1 - \eta)^{-4}$ with $\eta = \pi\sigma^3(6\Omega_0)^{-1}$. Now, we can also apply equation (3.2) with $\rho_t$ given by equation (3.14) and $a(q)$ given by equation (3.15) to calculate $\rho$ for the K–Rb alloy, because the $x$ value of this alloy nearly satisfies $x \rightarrow 1$, as required for $a(q)$ given by equation (3.15). The results thus obtained using the same input data as in the preceding subsection are given in table 4. The values of $a(q)$ involved in this part of the calculation are also displayed in figure 4. It is now seen that the $a(q)$ of interest here is about the same as the liquid structure-factors of the pure simple liquid metals even in the small-$q$ range. Accordingly, the reliability of the calculation of $\rho(C)$ as described above for K–Rb is as good as the application of the low-order perturbation theory to the calculation of $\rho$ for the pure simple liquid metals. Then, from the comparison of the results in table 4 with those displayed in figure 2(b) (they differ by about 4%) and from the overall success of the calculation of transport coefficients in the preceding subsection, it appears that the applicability of a low-order perturbation theory, such as that described in §2 and used in §§3.1 and 3.2, to the calculation of the properties of liquid binary alloys of the simple metals is generally as good as that for the pure simple liquid metals.

| Table 4. Values of $\rho(C)$ calculated using equation (3.2) with $\rho_t$ given by equation (3.14) and the structure factor $a(q)$ given in equation (3.15) for the K–Rb alloy at 100°C. |
|---|---|---|---|---|---|---|---|
| $C$ | 0.0 | 0.1 | 0.3 | 0.5 | 0.7 | 0.9 | 1.0 |
| $\rho(C)$ | 14.79 | 16.12 | 19.09 | 22.08 | 24.85 | 27.52 | 28.80 |
4. Conclusions

In this paper the EIMP theory developed previously for simple metals was extended to the binary alloys of these simple metals and a self-consistent pseudopotential was derived for use in the calculation of the electronic structure of the binary alloys with arbitrary concentration. The self-consistent pseudopotential thus derived contains a more extensive concentration dependence than those already available in the literature. It has been applied to calculate (i) the form factors, (ii) the electrical resistivities and (iii) the thermoelectric power in a low-order pseudopotential perturbation theory for the K–Rb, Na–K and Na–Cs alloys in the liquid phase. The calculated results show that a very significant fraction of the valence electrons is localised on the electronegative component in the Na–Cs alloy, as compared with the other alloys considered here, and hence the electrical resistivity is very much greater for Na–Cs than for Na–K and K–Rb alloys. The calculated results also show that the applicability of the pseudopotential perturbation calculation to the liquid binary alloys of simple metals is generally as good as that for the pure simple liquid metals.

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