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Structure, electrical resistivity and knight shift of lithium based liquid alkali-alkali binary alloys: HFP technique

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ABSTRACT

In the present paper the partial liquid structure factors $S_{ij}(k)$ and the total structure factor $S(k)$ of lithium based alkali-alkali binary alloys have been computed on the lines of Ashcroft and Langreth[1] and Enderby and North[2] on the basis of Percus-Yevik hard sphere system for the equiatomic combination. The electrical resistivity $R(\mu\Omega cm)$ has been computed through Faber-Ziman formalism[3,6] and the Knight shift has been computed through Pake's formalism[4] which has been extended to the alloys on the lines of Faber-Ziman formalism. Reasonable agreement with the ideal value of obtained through the experimental data has been obtained. The form factor $w(k,q)$ needed for the computation of these properties has been obtained through the Harrison's First Principle (HFP) pseudopotential technique[5] which has been successfully used for the theoretical study of the variety of physical properties of metals and alloys.
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KEYWORDS

INTRODUCTION

Liquid metals and alloys have been favorite systems for the theoretical structural study as well as the study of their various physical properties in this decade. The study of the physical properties is hinged upon two ingredient namely the non-local screened form factor $w(k,q)$ which is potential dependent and the partial structure factor $S_{ij}(k)$ which are position dependent. The former has been computed through the HFP technique while the latter has been computed on the basis of Percus-Yevik hard sphere model on the lines of Ashcroft and Langreth[1] and Enderby and North[2]. The

electrical resistivity (R) and Knight shift (K%) have been computed through Faber-Ziman formalism[3,6] and extension of Pake's formalism[4] to binary alloys. In the subsequent sections we present the formalism, computation, result and observations as well as conclusion.

FORMALISM

The three partial structure factors for a binary liquid mixture can be expressed in terms of Fourier transform of direct correlation functions[1,2]:

$$S_{\alpha\alpha}(k) = \frac{[1 - n_\beta C_{\beta\beta}(q)]}{D_d(q)} \qquad (1)$$

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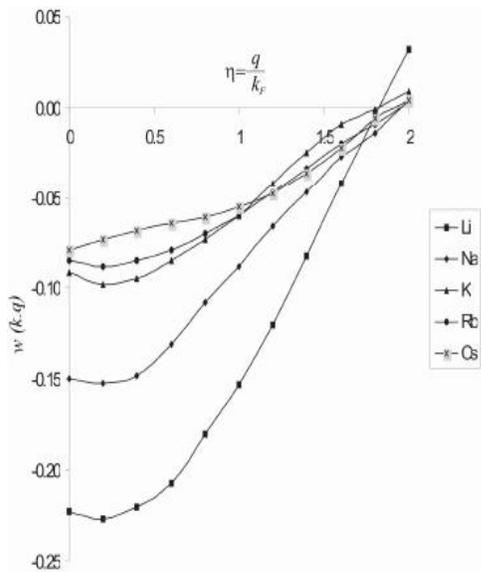
Figure 1 : Form factors of constituent metals

Figure 2 : The total structure factor for Li-based alloys (equiatomic composition) at 200°C

$$S_{\beta\beta}(k) = \frac{[1 - n_\alpha C_{\alpha\alpha}(q)]}{D_d(q)} \qquad (2)$$

$$S_{\alpha\beta}(k) = \frac{(n_\alpha n_\beta)^{1/2} C_{\alpha\beta}(q)}{D_d(q)} \qquad (3)$$

with

$$D_d(q) = [1 - n_\alpha C_{\alpha\alpha}(q)][1 - n_\beta C_{\beta\beta}(q)] - n_\alpha n_\beta C_{\alpha\beta}^2 \qquad (4)$$

$S_{\alpha\alpha}$, $S_{\beta\beta}$ and $S_{\alpha\beta}$ are called the Ashcroft-Langreth partial structure factors.

Here

$$C_{\alpha\beta}(q) = \int C_{\alpha\beta}(r) e^{iqr} d^3r \qquad (5)$$

The Fourier transform of the direct correlation functions stand as,

$$C_{\alpha\beta}(q) = -(4\pi/q^3)(A\sin q\sigma + B\cos q\sigma + C\sin q\lambda_{\alpha\beta} + D\cos q\lambda_{\alpha\beta}) \qquad (6)$$

$$C_{\alpha\alpha}(q) = -(4\pi/q^3)(A_\alpha \sin q\sigma_{\alpha\alpha} + B_\alpha) \qquad (7)$$

The explicit expression for the coefficients is,
The total structure factor is represented by

$$A = \alpha_\alpha + 2b_\alpha \sigma_{\alpha\alpha} + 4d\sigma_{\alpha\alpha}^3 - \frac{24d\sigma_{\alpha\alpha}}{d^2}$$

$$B = \frac{(2b_\alpha + 12d\sigma_{\alpha\alpha}^2)}{q} - \frac{24d}{q^3} - \sigma_{\alpha\alpha}(a_\alpha + \sigma_{\alpha\alpha}b_\alpha + \sigma_{\alpha\alpha}^3 d)q$$

$$A_\alpha = a_\alpha + 2b\sigma_{\alpha\alpha} + 4d\sigma_{\alpha\alpha}^2(\sigma_{\alpha\beta} + 2\lambda_{\alpha\beta}) - \frac{24d\sigma_{\alpha\beta}}{q^2}$$

$$B_\alpha = \frac{(2b + 12d\sigma_{\alpha\alpha}\sigma_{\beta\beta})}{q} - \frac{24d}{q^3} - (\sigma_{\alpha\beta}a_\alpha + \sigma_{\alpha\alpha}^2 b + \sigma_{\alpha\alpha}^3 d(\sigma_{\alpha\beta} + 3\lambda_{\alpha\beta}))q$$

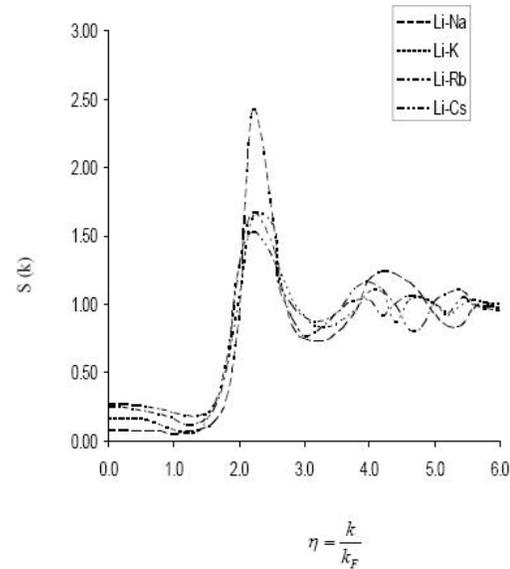$$C = \frac{24d}{q^3} - \frac{2b_\alpha}{q} = \frac{24\lambda_{\alpha\beta}d}{q^2}$$

$$D = \frac{(24d - 2bq^2)}{q^3}$$

$$S(k) = C_1 S_{11}(k) + C_2 S_{22}(k) + 2(C_1 C_2)^{1/2} S_{12}(k) \qquad (8)$$

where S_{11}, S_{22} and S_{12} are respectively denoting $S_{\alpha\alpha}(k)$, $S_{\beta\beta}(k)$ and $S_{\alpha\beta}(k)$ respectively. C_1 and C_2 are the concentrations of first and second species.

It was shown by Faber and Ziman[3,6] that the diffraction model formula for liquid metals proposed by Ziman[3,6] could easily be extended for binary alloys. For the sake of better representation, we express the resistivity of binary alloys as consisting of three distinct contributions, i.e.

$$R = R_{\alpha\alpha} + R_{\beta\beta} + R_{\alpha\beta} \qquad (9)$$

where the first two terms on right hand side arise due to the same particle correlation and the third term ($R_{\alpha\beta}$) is due to the cross term scattering. α and β represent here the constituent species of the binary alloys. The different contributions are given by

$$R_{\alpha\alpha} = \left(3\frac{\pi}{\eta}|e|^2\right)\left(\frac{\Omega}{Nv_F^2}\right)4\int_0^2 C_1|w_1(k,\eta)|^2 S_{11}(k)\eta^3 d\eta \qquad (10)$$

$$R_{\beta\beta} = \left(3\frac{\pi}{\eta}|e|^2\right)\left(\frac{\Omega}{Nv_F^2}\right)4\int_0^2 C_2|w_2(k,\eta)|^2 S_{22}(k)\eta^3 d\eta \qquad (11)$$

$$R_{\alpha\beta} = \left(3\frac{\pi}{\eta}|e|^2\right)\left(\frac{\Omega}{Nv_F^2}\right)4\int_0^2 2(C_1C_2)^{1/2}|w_1(k,\eta)||w_2(k,\eta)|S_{12}(k)\eta^3 d\eta \quad (12)$$

In a composite form R can be expressed as

$$R = \left(3\frac{\pi}{\eta}|e|^2\right)\left(\frac{\Omega}{Nv_F^2}\right)\left\langle\sum_{\alpha,\beta}(C_1C_2)^{1/2}S_{ij}(k)w_\alpha(k,\eta)w_\beta(k,\eta)\eta^3\right\rangle \quad (13)$$

where $<>$ stands for

$$<> = [4\int_0^2 C_1 S_{11}(k)|w_1(k,\eta)|^2 + C_2 S_{22}(k)|w_2(k,\eta)|^2$$
$$+ 2(C_1C_2)^{1/2}S_{12}(k)|w_1(k,\eta)|\eta^3 d\eta \quad (14)$$

where $\eta=q/k_F$

Here $w_1(k,\eta)$ and $w_2(k,\eta)$ are the form factors of species 1 and 2 constituting the alloys; C_1, C_2 are the concentrations and $S_{11}(k)$, $S_{22}(k)$ & $S_{12}(k)$ are the partial structure factors of the alloy and $\eta=q/k_F$.

The frequency of nuclear magnetic resonance (NMR) associated with a metallic state is generally higher than the corresponding frequency for non-metallic state, such a shift of the NMR frequency is known as the Knight shift.

The Knight shift vide Pake[4] may be written as

$$K = \left(\frac{8\pi}{3}\right)\chi_p P_F \Omega \quad (15)$$

Here χ_p is the spin paramagnetic susceptibility of conduction electron per unit volume, Ω is the volume of the crystal and P_F the average electron density at the site of the nucleus from the conduction electrons with an energy E_F.

Knight shift may also be written as

$$K=K_0+K_1 \quad (16)$$

where K_0 and K_1 are zero order and first order terms. The variation of $\phi_k(R)$ in the core region is small thus we obtain

$$\frac{P_F^1}{P_F^0} = 2\,\text{Re}\left\langle N^{-1}\sum_\tau \phi'_{k_F}(R)\phi^0_{k_F}(R)\right\rangle$$
$$= \frac{2\Omega}{8\pi^3}P\int\frac{w(k,q)S(k)}{E_k-E_{k+q}}d^3q \quad (17)$$

where P is the Cauchy's Principal value. Assuming the form factor $w(k,q)$ and structure factor $S(k)$ to be spherically symmetric we get

$$\frac{K_1}{K_0} = \frac{P_F^1}{P_F^0} = -\frac{3Z}{4E_F k_F^2}\int_0^\alpha S(k)w(k,q)q\ln\left|\frac{q+2k_F}{q-2k_F}\right|dq \quad (18)$$

TABLE 1 : Computed electrical resistivity R($\mu\Omega$cm) and Knight shift (K%) of Lithium based alloys at 200°C for equiatomic composition

Alloys	R_{th}	R^{id}	Knight Shift					
			Theoretical			experimental		
			$(K_0)_A$	$(K_0)_B$	$(K\%)_{th.}$	$(K\%)_A$	$(K\%)_B$	$(K\%)_{id.}$
Li-Na	17.5	17.0	0.05	0.15	0.09	0.03	0.12	0.07
Li-K	26.0	19.3	0.05	0.32	0.20	0.03	0.26	0.15
Li-Rb	33.7	25.0	0.05	0.56	0.30	0.03	0.66	0.34
Li-Cs	37.7	30.4	0.05	1.08	0.55	0.03	1.44	0.73

where E_F is the Fermi energy, k_F is the Fermi wave vector and the other symbols have their usual significance. For the alloys the integrand of Eq. (6.10) is replaced by

$$I_k = \int_0^\infty\left[\begin{array}{c}C_1 S_{11}(k)w_{11}(k,q)+C_2 S_{22}(k)w_{22}(k,q)+\\2(C_1C_2)^{1/2}w_{11}(k,q)S_{12}(k)\end{array}\right]q\ln\left|\frac{q+2k_F}{q-2k_F}\right|dq \quad (19)$$

Also Z, E_F and k_F are those of the alloys evaluated through $X=C_1 X_1+C_2 X_2$ where C_1 and C_2 are the concentrations of the constituents. Here X_1 and X_2 are the input parameters of the metal viz., Z, E_F, k_F and Ω_0 and X is that for the binary alloy.

RESULT AND COMPUTATIONS

The form factors of the constituent alkali metals have been computed through the HFP technique and shown in figure 1 for Li, Na, K, Rb and Cs. These form factors have been used to compute the electrical resistivity (R) and Knight shift (K%) of the alloys Li-Na, Li-K, Li-Rb and Li-Cs. The partial structure factors $S_{ij}(k)$ have been computed through the formalism given in the previous section. The total structure factor $S(k)$ has been depicted in figure 2. The computed electrical resistivity $(R)_{th}$ alongwith R^{id} and Knight shift $(K\%)_{th}$ alongwith $(K\%)^{id}$ at 200°C have been given in TABLE 1 for comparison. The experimental values of R and K% are not available in the literature at the equiatomic composition for the alloys under investigation.

OBSERVATIONS

Form factors

From figure 1 the form factors of the constituent elements Li, Na, K, Rb and Cs show their usual nature

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starting from their limiting value at $\eta=0$ and crossing over the x-axis between $\eta=1.5$ to $\eta=2$ (where $\eta=\dfrac{q}{k_F}$).

Total structure factors

From figure 2 the nature of the total structure factors of Li-Na, Li-K, Li-Rb and Li-Cs has been illustrated. For Li-Na the principal peak lies at $\eta=2.2$ having magnitude 2.4 and the secondary peaks lies at $\eta=4.2$ and $\eta=5.8$ with peak heights 1.2 and 1.01 respectively. For Li-K the principal peak also lies at $\eta=2.2$ having peak height 1.6 and the secondary peaks lies at $\eta=4.2$ and $\eta=6.0$ with peak heights 1.08 and 1.004 respectively. For Li-Rb the principal peak lies at $\eta=2.2$ having peak height 1.67 and the secondary peaks lies at $\eta=4.0$ and $\eta=5.2$ with peak heights 1.03 and 1.028 respectively. Finally, for Li-Cs the principal peak lies at $\eta=2.2$ having peak height 1.52 and secondary peaks at $\eta=4.0$ and $\eta=5.4$ with peak heights 1.07 and 1.1 respectively. Thus it is observed that the principal peaks of all these alloys lies near $\eta=2.2$. The positions of the first secondary peaks slightly vary within $\eta=4.0$ and $\eta=4.2$. The positions of the next secondary peaks are between $=5.2$ to $\eta=6.0$ (where $\eta=\dfrac{k}{k_F}$).

Electrical resistivity (R)

From TABLE 1 if is observed that the computed electrical resistivity of Li-Na is in good agreement with the ideal value (17.5 against 17.0 $\mu\Omega$cm). For other alloys the computed resistivities are not in such a close agreement with the ideal value. For Li-K, Li-Rb, Li-Cs the difference between the theoretical and ideal values is 6.7, 8.7 and 7.3$\mu\Omega$cm respectively. This indicates that these alloys do not show ideal behavior at equiatomic composition. If the experimental values were available we could be able to arrive at better conclusion.

Knight shift (K%)

The theoretical and experimental Knight shifts of the constituent elements and the alloy have been shown in TABLE 1 from which (K%)id has been computed.

It is observed that except for Li-Cs all the computed Knight shifts are in reasonable agreement with the ideal value.

CONCLUSION

Thus it may be concluded that the HFP technique in conjunction with the Ashcroft & Langreth and Enderly and North technique for the computation of the form factor and partial structure factors respectively may be safely used to study the electrical resistivity and Knight Shift of the alloys through Faber-Ziman's and Pake's extended formalisms.

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