Multi-component structure factor and Resistivity of complex formation model

Binary PbSn forms a low melting-temperature alloy which is extensively used for soldering materials in the electronic industry is generally a major environmental hazard and now there are massive efforts going on for searching alternatives of lead-free materials. For photonic and fiber device packaging, tin (Sn) solder is often used due to its ductility and relatively low melting temperature [A1]. The eutectic In-Sn has received much attention as a possible lead-free alternative of low temperature solders in electronic industry. Alloys of Sn-based systems are more promising in terms of solder mechanical properties and soldering performance [A2]. Many potentially suitable lead (Pb) free Solder Systems have been designed and their suitability tested for surface mount applications; one such system is Sn84.0In8.4Zn7.6 which have low melting temperature (187°C) soldering material. Hence we are motivated to determine the structure factor of Sn84.0In8.4Zn7.6 alloys [A3] and estimates the electrical resistivity using model potential proposed in the thesis.

In the present computation the electrical resistivity of Sn84.0In8.4Zn7.6 alloys is obtained with Faber-Ziman [A4] approach along with the local field correction functions due to Hartree (H) [A5], Taylor (TY) [A6], Ichimaru-Utsumi (IU) [A7], Sarkar-Sen et al. (SS) [A9], Farid et al. (FR) [A8] for the first time to investigate the influence of exchange and correlation effects.

THEORETICAL METHODOLOGY

In multi component hard sphere mixture model [A3], the diameter of i-th species is \( \sigma_i \) and we can choose the suffix without loss of generality as \( \sigma_1 < \sigma_2 < ... < \sigma_m \).

We define the hard sphere ratio by

\[
\alpha_{ij} = \frac{\sigma_i}{\sigma_j} (i < j) \tag{A1}
\]

where \( 0 \leq \alpha_{ij} \leq 1 \).

If there are \( N_i \) hard spheres with diameter \( \sigma_i \) \( (i = 1\sim m) \) in volume \( V \) and \( \sum_{i=1}^{m} N_i = N \), we define the concentration of i-th hard spheres by
\[ \chi_i = N_i / N = n_i / n \]  

(A2)

where \( n = N / V \), \( n_i = N_i / V \) and \( \sum_{i=1}^{m} x_i = 1 \).

By using the packing fraction \( \eta_i \) defined by

\[ \eta_i = \frac{\pi n_i \sigma_i^3}{6} \]  

(A3)

We can write the total packing fraction of the mixture as

\[ \eta = \sum_{i=1}^{m} \eta_i \]  

(A4)

From equations (A3) and (A4) we have

\[ \eta_i = \eta [x_i \sigma_i^3 (\sum_{j=1}^{m} x_j \sigma_j^3)^{-1}] \]  

(A5)

There are \((2m-1)\) parameters which specify the m-component hard sphere system: \( x_1 \sim x_{m-1}, \alpha_{12} \sim \alpha_{1m} \) and \( \eta \).

Hence for ternary system, \( m = 3 \), there are 5 parameters which specify the 3-component hard sphere system; \( x_1, x_2, \alpha_{12}, \alpha_{13} \) and \( \eta \).

To calculate the partial structure factors \( S_{ij}(k) \) we need to know the direct correlation function \( c_{ij}(r) \), which is obtained by solving the Percus-Yevick equation. For the m-component hard-sphere mixture considered here, Hiroike [A11] obtained the exact solution of the Percus-Yevick equation and gave the explicit forms of \( C_{ij}(r) \) as follows:

\[ -c_{ij}(r) = a_i + b_i r + dr^3 \quad \text{for} \quad r \langle \sigma_i \]  

(A6)

\[ -c_{ij}(r) = a_{ij} + b_{ij} r + dr^3 + \left( f_{ij} / r \right) \quad \text{for} \quad \lambda_{ij} \langle \sigma_{ij} \]

where

\( c_{ij}(r) = c_{ij}(r) \),

\( \sigma_{ij} = (\sigma_i + \sigma_j) / 2 \),

\( \lambda_{ij} = (\sigma_i \sigma_j) / 2 \),

\( a_{ij} = (a_i + a_j) / 2 \)

and \( b_{ij} = (b_i + b_j) / 2 \).
The explicit forms of the coefficients $a_i$, $b_i$, $d$ and $f_{ij}$ are given in [A11].

**Partial structure factors of ternary alloys:**

We use the following hard-sphere diameters

$$(4\pi/3)\sigma_i^3 = (4\pi/3)(4\sigma_i^3 + \sigma_2^3)$$  \hspace{1cm} (A7)$$

where $\sigma_2$ is assumed to satisfy the condition $\sigma_2 = (\sigma_1 + \sigma_2)/2$. The total packing fraction is taken to be 0.45, which is a typical value of the liquid metals and alloys near melting points.

For the ternary hard-sphere mixture the matrix $S(k)$ defined by equation

$$S(k) = \begin{pmatrix} S_{11}(k) & S_{12}(k) & S_{13}(k) \\ S_{21}(k) & S_{22}(k) & S_{23}(k) \\ S_{31}(k) & S_{32}(k) & S_{33}(k) \end{pmatrix}$$  \hspace{1cm} (A8)$$

$$S(k) = \begin{pmatrix} 1. - n_1 c_{11}(k) & -\sqrt{n_1 n_2 c_{12}(k)} & -\sqrt{n_1 n_3 c_{13}(k)} \\ -\sqrt{n_1 n_2 c_{21}(k)} & 1. - n_2 c_{22}(k) & -\sqrt{n_2 n_3 c_{23}(k)} \\ -\sqrt{n_1 n_3 c_{31}(k)} & -\sqrt{n_2 n_3 c_{32}(k)} & 1. - n_3 c_{33}(k) \end{pmatrix}$$  \hspace{1cm} (A9)$$

Taking the symmetries $S_{ij}(k) = S_{ji}(k)$ and $c_{ii}(k) = c_{ii}(k)$ into account, we obtain the six independent partial structure factors as follows:

$$S_{11}(k) = [(1 - n_1 c_{11}(k))(1 - n_3 c_{33}(k)) - n_2 n_3 c_{23}^2(k)] / D(k)$$

$$S_{22}(k) = [(1 - n_2 c_{22}(k))(1 - n_3 c_{33}(k)) - n_1 n_3 c_{13}^2(k)] / D(k)$$

$$S_{33}(k) = [(1 - n_1 c_{11}(k))(1 - n_2 c_{22}(k)) - n_3 n_3 c_{33}^2(k)] / D(k)$$

$$S_{12}(k) = [(1 - n_1 c_{11}(k))\sqrt{n_1 n_2 c_{12}(k)} + n_1 \sqrt{n_1 n_3 c_{13}(k)} c_{23}(k)] / D(k)$$

$$S_{13}(k) = [(1 - n_2 c_{22}(k))\sqrt{n_2 n_3 c_{23}(k)} + n_2 \sqrt{n_1 n_3 c_{13}(k)} c_{23}(k)] / D(k)$$

$$S_{23}(k) = [(1 - n_1 c_{11}(k))\sqrt{n_2 n_3 c_{23}(k)} + n_1 \sqrt{n_2 n_3 c_{12}(k)} c_{13}(k)] / D(k)$$  \hspace{1cm} (A10)$$

where direct correlation function is
Appendix

\[ \begin{align*}
D(k) &= \left| 1 - c(k) \right| \\
\text{and} \\
D(k) &= (1-n_c c_{11}(k))(1-n_c c_{22}(k))(1-n_c c_{33}(k)) - 2n_1 n_2 n_3 c_{12}(k)c_{13}(k)c_{23}(k) \\
&\quad - n_1 n_3 (1-n_c c_{22}(k))c_{12}^2(k) - n_1 n_2 (1-n_c c_{11}(k))c_{23}^2(k) \\
&\quad - n_2 n_3 (1-n_c c_{33}(k))c_{13}^2(k) \quad (A12)
\end{align*} \]

In figure A1 the results of the partial structure-factors are shown for Zn, In and Sn with the concentration of 0.076, 0.084 and 0.840 respectively.

The characteristic features are as follows:

- \( S_{33}(k) \) has a sharp high first peak and clear second and third peaks, while \( S_{11}(k) \) and \( S_{22}(k) \) are almost unity irrespective of \( k \).
- \( S_{13}(k) \) and \( S_{23}(k) \) oscillate around zero, while \( S_{12}(k) \) is very small. The height of the second peak of \( S_{33}(k) \) around \( 2<k<4\text{Å}^{-1} \) is reduced as shown below by the negative contribution of \( S_{13}(k) \) and \( S_{23}(k) \) there.
- The features (i) and (ii) mean that the free Zn and In ions behave like free particles with less correlation, while the Sn has a strong short range order.

Here electrical resistivity of these alloys is determined from Ziman type theory given by Jin et al [A3] by using the model potential [A12-A13]. In Table A1 Input parameters used in the calculation of resistivity of Sn-In-Zn system at 187°C is given.

Table A1: Input parameters and constants of Sn-In-Zn alloys

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration</th>
<th>( Z )</th>
<th>( \Omega ) a.u.(^3)</th>
<th>( \eta )</th>
<th>( k_F ) a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>0.840</td>
<td>4</td>
<td>100.1993</td>
<td></td>
<td>0.8392</td>
</tr>
<tr>
<td>In</td>
<td>0.084</td>
<td>3</td>
<td>183.3108</td>
<td>0.45</td>
<td>0.7853</td>
</tr>
<tr>
<td>Zn</td>
<td>0.076</td>
<td>2</td>
<td>191.0494</td>
<td></td>
<td>0.8525</td>
</tr>
</tbody>
</table>
Table A2: Estimated electrical resistivity of Sn-In-Zn alloys

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>29.1094</td>
<td>43.2354</td>
<td>45.621</td>
<td>36.8656</td>
<td>46.2308</td>
</tr>
</tbody>
</table>

Figure A1: Partial structure factor ($S_{ij}$) of Sn$_{84.6}$In$_{8.4}$Zn$_{7.6}$ ternary alloy.
The input parameters used in the calculation of partial structure factor and electrical resistivity of Sn$_{84.0}$In$_{8.4}$Zn$_{7.6}$ ternary alloys is shown in table A1. The comparisons of ternary structure factor and resistivity of Sn$_{84.0}$In$_{8.4}$Zn$_{7.6}$ systems are not available. Hence except some general remarks we are not able to make special comments. From Table A2 the resistivity is estimated between 36.8656 $\mu$Ω-cm (for SS [A8] screening function) to 46.0306 $\mu$Ω-cm (for F [A9] screening function) with respect to 29.3094 $\mu$Ω-cm due to H screening function. Thus the local field correction function affects the resistivity Sn$_{84.0}$In$_{8.4}$Zn$_{7.6}$ ternary alloys. Also figure A represents the nature of partial ternary structure factor of Sn$_{84.0}$In$_{8.4}$Zn$_{7.6}$ alloys. Here packing density of all the three components are taken to be constant at 0.45.

We conclude from the investigation of structure factor of ternary Sn$_{84.0}$In$_{8.4}$Zn$_{7.6}$ alloys and resistivity calculation that the results are very encouraging and this confirms the applicability of model potential [A12] in explaining the ternary Sn-In-Zn alloys.

REFERENCES

# Appendix

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Ph D (Thesis)</th>
</tr>
</thead>
</table>
(b) **Equation of state for Al-Li random alloys**

The enormous properties like ductility, light weight and high strength of aluminum makes it the best choice for many areas of constructive as well as other important engineering applications. It can, however, be improved. The little addition of Lithium in Aluminum will greatly increase the strength of the alloys with little change in ductility. Despite the fact that both element aluminum and lithium are quite normal metals, their alloys manifest rather unusual thermodynamics and electrochemical properties. The binary combination system of Al-Li alloys with their low density and high elastic modulus have been developed as potential replacements for conventional Aluminum alloys in the aerospace industry [B1-B5]. These alloys are of the age hardening type and develop their strength principally from the precipitation of small spherical particles that have an ordered structure, which combines high strength and high temperature resistance with low weight. The metallurgy of alloys based on the Al-Li system has been the subject of several comprehensive reviews. [B6-B8]

Equation of state (EOS) namely, the relationship between pressure, volume and temperature, i.e. the (P, V, T) relation, are of immense importance to theoreticians as well as experimentalists. In experimental physics, they are used as pressure calibration in high-pressure experiments and are needed to relate the measured pressure variation of some physical quantity (e.g. elastic constants, transport properties, specific heat, etc.) to the calculated volume variations. It also provides a test to the theoretical models of cohesion and predicts the onset of phase transition (insulator to metal, valence transition, solid to liquid, stable crystal structure, etc.). While studying EOS theoretically, the major difficulty arises from the question how to incorporate correctly the structurally complicated inter-particle interactions of the many-body problem. There are number of models or techniques in predicting the theoretical EOS, the tight-binding total-energy classical cell model [B9], model pseudopotential method [B17-B19], the generalized pseudopotential theory [B10], Debye - Gruneisen theory [B11], recent classical mean-field model [B12-B14], and linearised augmented plane-wave method with both the local density approximation (LDA) and generalized gradient approximation (GGA)using density functional methods [B15 -B16] etc. are the few extensively used techniques.

In order to study the effect of lithium additions on Aluminum we have used second order perturbation theory to calculate equation of states for various
concentration of lithium in aluminum. A well established model potential, depending on an effective core radius but otherwise parameter free, is employed to study the equation of state by incorporating the proper electron-ion interactions. An enhanced criterion for the selection of the exchange and correlation effects is put forward. The pressure – volume (P-V) relation for pure Aluminum, Lithium and addition of concentrations of 5, 10, 15 and 20 % of Lithium in Aluminum have been studied. The basic theory is as follows.

The following form of the well established model potential \([B17-B19]\) is employed to reveal the electron-ion interaction under the pseudo-alloy atom (PAA) consideration:

\[
W(q) = -\frac{8\pi Z}{\Omega_0 q^2 \varepsilon(q)} \left[ \cos(qr_c) - \frac{q^2 r_c^2}{1 + q^2 r_c^2} \right]
\]  

(B1)

The present model local pseudopotential is simple to envisage and easy to apply either to pure metals or to alloys. The virtue of the momentum-space formalism rests on its simplicity. Here real-space integral is replaced by a simple summation over reciprocal vectors, and hence convergence is very rapid because of the smooth pseudopotential used in place of the real potential, which are singular at the origin. And the fast and rapid convergence of form factor in q-space is the special characteristics of this potential which makes this potential unique and physically justifiable as it is the requisite criteria for quasi-static nature of electron-ion interaction \([B17-B19]\).

The constants and parameters used in the present investigation are tabulated in Table B1. To determine the input parameters and other constants for PAA model, the following definitions for binary alloys Al\(_{1-x}\)B\(_x\) are adopted.

\[
Z = (1-x)Z_{Al} + xZ_{Li}
\]  

(B2)

\[
\Omega_0 = (1-x)\Omega_{0,Al} + x\Omega_{0,Li}
\]  

(B3)

\[
r_{c} = (1-x)r_{c,Al} + xr_{c,Li}
\]  

(B4)

\[
k_{F} = (1-x)k_{F,Al} + xk_{F,Li}
\]  

(B5)
Here, $x$ is the concentration of second component. From the second order perturbation theory and in the PAA model, the total crystal energy can be written as

$$E = E_0 + E^0 + E^1 + E^2$$  \hspace{1cm} (B6)

The first term in above expression is given by

$$E_i = -\frac{\alpha Z^2}{R_a}$$  \hspace{1cm} (B7)

Where, $R_a = r_s Z^{1/3}$ and $\alpha$ is the Ewald constant, which depends on crystal structure

$$E^{(0)} = Z \left[ \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - (0.115 - 0.031\ln(r_s)) \right]$$  \hspace{1cm} (B8)

In which $r_s$ is the dimensionless parameter which is defined as

$$r_s = \left( \frac{3}{4\pi\rho Z} \right)^{1/3} \frac{1}{a_0}$$  \hspace{1cm} (B9)

The contribution of $E^{(1)}$ term is given by

$$E^{(1)} = \lim_{q \to 0} \left[ \frac{4\pi Z^2 e^2}{\Omega q^2} + Z W_\beta(q) \right]$$  \hspace{1cm} (B10)

For our model potential, above expression reduces to

$$E^{(1)} = \frac{9Zr_c^2}{r_s^3} = \frac{12\pi Z^2 r_c^2}{\Omega_0}$$  \hspace{1cm} (B11)

The Band structure energy for the metal is written as

$$E^{(2)} = \frac{\Omega_0}{16\pi} \sum q^2 W_\beta(q)^2 \left[ \frac{\varepsilon(q) - 1}{1 + \varepsilon(q) - 1} \right]$$  \hspace{1cm} (B12)

In the above expression prime on the summation sign suggest exclusion of $q = 0$ term. Here $W_\beta(q)$ is the effective bare ion potential, $\varepsilon(q)$ dielectric response function.
and \( f(q) \) is the local field correction function to introduce the exchange and correlation effects.

For the present computation the local field correction due to Ichimaru-Utsumi (IU) [21] is used to incorporate the exchange and correlation among the conduction electrons in the dielectric screening. The IU screening function is preferred since it satisfies all the important sum rules for a response function, in particular the compressibility sum rule which is most important criterion for obtaining the repulsive diameter of the ion correctly [22] for the exchange and correlation criterion.

The pressure (\( P \)) is obtained from the first derivative of the crystal energy with respect to the atomic volume which is given by

\[
P = \frac{dE}{d\Omega_0} = -\frac{r_s}{3\Omega_0} \frac{dE}{dr_s}
\]

(B13)

Using the set of above expressions, the total crystal energy of pure Al, Li and combination of their alloys in different compositions has been computed. In the calculation of band structure energy term in total energy calculations enough care has been taken to achieve proper convergence. The individual terms contributing to the total crystal energy per atom are tabulated in Tables B2 to Table B6. It is observed here that the total crystal energy for pure aluminum and lithium predicted using present findings is matched very well with experimental values [B30,B31] and other such reported theoretical work [B9, B10, B17]. The deviation of the results in their percentage error is shown in the tables. The present results obtained by our model potential in the pseudo-alloy-atom model are encouraging for pure metals and hence we extended it for prediction of the combination of Al-Li alloys. Because of the unavailability of experimental total crystal energy of these alloys in various concentration proportions in literature, we have compared the presently obtained values at concentration of \( x = 0 \) and \( 1 \) with the experimental value of pure components.
Table B1: Input parameters used for the present calculations

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$Z$</th>
<th>$r_s$ (Å)</th>
<th>$k_f$ (Å$^{-1}$)</th>
<th>$\Omega_0$ (Å$^3$)</th>
<th>$r_c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3</td>
<td>2.073889</td>
<td>0.925391</td>
<td>112.089838</td>
<td>1.17646</td>
</tr>
<tr>
<td>Al$<em>{0.95}$Li$</em>{0.05}$</td>
<td>2.9</td>
<td>2.106782</td>
<td>0.910943</td>
<td>113.591342</td>
<td>1.16682</td>
</tr>
<tr>
<td>Al$<em>{0.90}$Li$</em>{0.10}$</td>
<td>2.8</td>
<td>2.140921</td>
<td>0.896417</td>
<td>115.092847</td>
<td>1.15425</td>
</tr>
<tr>
<td>Al$<em>{0.85}$Li$</em>{0.15}$</td>
<td>2.7</td>
<td>2.176415</td>
<td>0.881798</td>
<td>116.594351</td>
<td>1.13800</td>
</tr>
<tr>
<td>Al$<em>{0.80}$Li$</em>{0.20}$</td>
<td>2.6</td>
<td>2.213388</td>
<td>0.867068</td>
<td>118.095856</td>
<td>1.11707</td>
</tr>
<tr>
<td>Li</td>
<td>1</td>
<td>3.237344</td>
<td>0.592819</td>
<td>142.119927</td>
<td>0.79210</td>
</tr>
</tbody>
</table>

Table B2: Total Crystal Energy and Pressure for Al

<table>
<thead>
<tr>
<th>Energy (Ryd/atom)</th>
<th>Expt. value</th>
<th>Other results</th>
<th>% error</th>
<th>Pressure (Kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_e(r_e)$ = -5.3913</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_e$ = -2.3585×10$^3$</td>
</tr>
<tr>
<td>$E_e(r_e)$ = -0.0607</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_e$ = 728.3502×10$^3$</td>
</tr>
<tr>
<td>$E_1(\Omega)$ = 4.1895</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_1$ = 5.4982×10$^3$</td>
</tr>
<tr>
<td>$E_2$ = -2.8574</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_2$ = -3.8680×10$^3$</td>
</tr>
<tr>
<td>$E = -4.1199$</td>
<td>-4.1423</td>
<td>-4.343, [B23,B24]</td>
<td>0.5389</td>
<td>$P = -1.7444×10^{-4}$</td>
</tr>
</tbody>
</table>

Table B3: Total Crystal Energy and Pressure for Al$_{0.95}$Li$_{0.05}$

<table>
<thead>
<tr>
<th>Energy (Ryd/atom)</th>
<th>Expt. value</th>
<th>Other results</th>
<th>% error</th>
<th>Pressure (Kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_e(r_e)$ = -5.0156</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_e$ = -2.1651×10$^3$</td>
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<td>$E_e(r_e)$ = -0.0834</td>
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<td>-</td>
<td>-</td>
<td>$P_e$ = 663.5395×10$^3$</td>
</tr>
<tr>
<td>$E_1(\Omega)$ = 3.8001</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_1$ = 4.9212×10$^3$</td>
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<tr>
<td>$E_2$ = -2.5094</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_2$ = -3.4196×10$^3$</td>
</tr>
<tr>
<td>$E = -3.8084$</td>
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<td>-</td>
<td>-</td>
<td>$P = -5.0512×10^{-3}$</td>
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### Table B4 : Total Crystal Energy and Pressure for Al_{0.90}Li_{0.10}

<table>
<thead>
<tr>
<th>Energy (Ryd/atom)</th>
<th>Expt. value</th>
<th>Other results</th>
<th>% error</th>
<th>Pressure (Kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ss}(r_i) = -4.6552$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_{ss} = -1.9833 \times 10^3$</td>
</tr>
<tr>
<td>$E_i(r_i) = -0.1039$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_i = 602.9875 \times 10^3$</td>
</tr>
<tr>
<td>$E_i(\Omega) = 3.4214$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_i = 4.3730 \times 10^3$</td>
</tr>
<tr>
<td>$E_2 = -2.1756$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_2 = -2.9926 \times 10^3$</td>
</tr>
<tr>
<td>$E = -3.5133$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P = -2.2952 \times 10^3$</td>
</tr>
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</table>

### Table B5 : Total Crystal Energy and Pressure for Al_{0.85}Li_{0.15}

<table>
<thead>
<tr>
<th>Energy (Ryd/atom)</th>
<th>Expt. value</th>
<th>Other results</th>
<th>% error</th>
<th>Pressure (Kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ss}(r_i) = -4.3099$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_{ss} = -1.8126 \times 10^3$</td>
</tr>
<tr>
<td>$E_i(r_i) = -0.1221$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_i = 546.4629 \times 10^3$</td>
</tr>
<tr>
<td>$E_i(\Omega) = 3.0526$</td>
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<td>-</td>
<td>-</td>
<td>$P_i = 3.8514 \times 10^3$</td>
</tr>
<tr>
<td>$E_2 = -1.8555$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_2 = -2.5852 \times 10^3$</td>
</tr>
<tr>
<td>$E = -3.2349$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P = -6.0219 \times 10^3$</td>
</tr>
</tbody>
</table>

### Table B6 : Total Crystal Energy and Pressure for Al_{0.85}Li_{0.15}

<table>
<thead>
<tr>
<th>Energy (Ryd/atom)</th>
<th>Expt. value</th>
<th>Other results</th>
<th>% error</th>
<th>Pressure (Kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ss}(r_i) = -3.9796$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_{ss} = -1.6524 \times 10^3$</td>
</tr>
<tr>
<td>$E_i(r_i) = -0.1381$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_i = 493.7495 \times 10^3$</td>
</tr>
<tr>
<td>$E_i(\Omega) = 2.6928$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_i = 3.3543 \times 10^3$</td>
</tr>
<tr>
<td>$E_2 = -1.5493$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_2 = -2.1956 \times 10^3$</td>
</tr>
<tr>
<td>$E = -2.9742$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P = -2.5809 \times 10^3$</td>
</tr>
</tbody>
</table>
Table B7: Total Crystal Energy and Pressure for Li

<table>
<thead>
<tr>
<th>Energy (Ryd/atom)</th>
<th>Expt. value</th>
<th>Other results</th>
<th>% Error</th>
<th>Pressure (Kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\alpha}(r_e)$ = -0.5535</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_\alpha = -190.970 \times 10^3$</td>
</tr>
<tr>
<td>$E_1(r_e)$ = -0.1507</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_1 = 37.1909 \times 10^3$</td>
</tr>
<tr>
<td>$E_i(\Omega) = 0.1668$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_i = 172.6613 \times 10^3$</td>
</tr>
<tr>
<td>$E_2 = -0.0179$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$P_2 = -18.8681 \times 10^3$</td>
</tr>
<tr>
<td>$E = -0.5552$</td>
<td>-0.5162 \ ([B23,B24])</td>
<td>-0.5470 \ ([B26]), -0.5429 \ ([B27])</td>
<td>7.5641</td>
<td>$P = -0.0136 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The total pressure predicted using total crystal energy at equilibrium volume and at compressed volume is shown in the Figure 1. It is also observed from the figure that equation of state for Al-Li alloys lies in between the pure components. From the figure it can be seen that the pressure-volume relation for all five combinations shows almost similar trend. Only for Li the pressure for a given value of $\Omega/\Omega_0$ is low. This may be due to the fact that pure Li has been treated as bcc where as all other binary combinations and pure Al as face centered cubic structure. In any case pure Li will be mere compressible because of its bcc structure. It can be referred from the figure that we have to apply very high pressure to compress pure Al and least pressure in case of pure Li. As the concentration of Li in Al is increased the alloy becomes more compressible. This is due to the fact that as we increase the proportion of Li in Al we are moving from a pure fcc structure with less voids towards a structure containing more voids.

The pressure-volume relations will help to understand how the structure dependent properties change under pressure. In the absence of any experimental data related to the binary combinations in question we feel that presently generated set of data will be much useful for other works in the field. By using this method, we have also established a potential database which has covered pure aluminum and lithium metal and their combination of alloys. In the long run, this database is expected to help design alloys.
Here the atomic properties like total crystal energy, pressure and pressure-volume relations are computed using the reciprocal sum analysis method. The model pseudopotential approach to the total crystal energy calculation is presented. EOS for five concentration Al-Li is calculated. The large and geometry-insensitive core contributions are explicitly projected out by using a pseudopotential formalism. The
proper formalism for the exchange and correlation function is employed in the derivation. Most importantly, a drastic simplification of the EOS is made by formulating the relevant expression in momentum space. The theoretical results are compared with available experimental results. The calculated numerical results of the total energy, pressure and heat of mixing of these compounds are in good agreement with the experimental data and found much better than other such (theoretical) findings. The expression for the total crystal energy in momentum space is particularly designed to be applicable with the pseudopotential method. The present formalism, however, is readily applicable to calculations. Finally, the excellent agreements in the case of metals and their combination of alloys indicate that the reliability and predictability of the present approach is inherent not accidental.

References


[B12] Yi. Wang, D. Chen and Xi. Zhang,
[B13] N.K. Bhatt, P.R. Vyas, A.R. Jani and V.B. Gohel, 

[B14] N.K. Bhatt, A.R. Jani, P.R. Vyas and V.B. Gohel, 
Physica B 357 (2005) 259


[B16] J. P. Perdew, Kieron Burke, Matthias Ernzerhof, 

[B17] P.N. Gajjar, B.Y. Thakore and A.R. Jani, 
Solid State Communications, 100(11), (1996) 785 

[B18] A. R. Jani, P. N. Gajjar, and H.K. Patel, 

[B19] R.S. Avte, P.N.Gajjar, and A. R. Jani, 

[B20] P.S.Vyas, P.N.Gajjar, B.Y.Thakore and A.R.Jani, 

[B21] S. Ichimaru and K. Utsumi, 

[B22] J. Hafner and V. Heine, 

[B23] C. Kittel, 
Introduction to the Solid State Physics, Wiley eastern Ltd., 
New Delhi,1996.

[B24] David R. Lide, 


[B26] D. Sen, S. K. Sarkar, S. Sengupta and D. Roy, 

[B27] D. Sen and S. K. Sarkar, 
Exploding foil simulations based on equation-of-state generation through ab-initio molecular dynamics

Introduction

The exploding foil has been studied for more than four decades, and still it is not very well understood phenomenon. Accurate calculations/experiments are required in order to understand the physical processes taking place in the foil, especially during or near the time of burst. On the theoretical side, earlier computer simulations for exploding foil simulation have either used Ideal Gas [C1] or Gamma-law Equation of State (EOS) [C2] for the pressures generated by the exploding foil. These models have a defect that the results of flyer acceleration for short barrel lengths are not accurate, which means that the early acceleration of the flyer is not simulated properly. Other models [C3] have used temperature as the burst criterion, which may not be true for foils of different materials. For this reason an accurate EOS is required, which will be able to work over a wide range of densities and temperatures. Here we have used an Equation-of-State (EOS) generated using ab-initio Molecular Dynamics, so that accurate calculations of the exploding foil phenomenon can be made. The computer model of the exploding foil is described in next section with the generation of EOS by ab-initio Molecular Dynamics is explained with the results of the simulations.

Computer model

We have used a locally-developed 3-D finite-difference, Lagrangian Hydrodynamic code that follows the formalism of the HEMP-3D code [C4,C5]. The code solves the finite difference approximations of the continuum equations of mass, momentum and energy balance in material coordinates. The code makes use of the artificial viscosity method to handle shocks and non-physical grid distortions. The code yields the variation of material density, specific internal energy, three velocity components and pressure in three space dimensions as well as time. The energy equation for the foil material has a source term representing joule heating, given by \( J \), where \( \rho \) is the electrical resistivity (ohm-m) and \( "J" \) is the current density (A/m²). In general, the current density varies through the foil due to spatial variations in resistivity and the shapes of the land and bridge sections. Hence it is necessary, at each time-step, to calculate the variation of \( "J" \) throughout the foil. A simple calculation shows that, for the time-scales of interest, the skin depth in the foil material is much greater than the foil thickness. Hence magnetic field diffusion through the foil thickness can be neglected,
implying a uniform current density through the thickness. We, therefore, require only to determine the variation of “J” in the plane of the foil. This is done by means of a two-dimensional (2-D) finite element (FEM) code [C6]. The 2-D FEM code is used to determine the current density distribution in the foil, taking into account the spatial variation of electrical resistivity and geometry of the foil, and the surrounding tamping material, if any. The combined code [C7, C8] allows a fairly arbitrary geometry of the foil, and can allow a study of the effectiveness of “foil shaping” in improving the simultaneity of the burst [C3]. The FEM code requires, as input, the variation of _ throughout the foil, and also the total current flowing through the foil. The total current flowing through the foil is obtained, at each time-step, by updating the circuit equations. The current flow is determined, self-consistently, by the instantaneous voltage on the capacitor, the inductance and resistance of the capacitor bank and connections, and the time-varying resistance and inductance of the foil assembly.

Resistivity model

The foil material starts as a solid, and quickly passes through the liquid and vapour phases, eventually becoming a partially-ionized plasma. Hence a multi-phase model for resistivity is required. We have incorporated an electrical resistivity model developed at Sandia National Laboratory [C9] that is valid for different metals. It requires, as input, the temperature and specific volume of the material. The volume- and temperature dependence of the resistivity are determined in four regimes, viz., solid, liquid, partially ionized vapour, and mixed (condensed and vapour). The density-dependent variation of the solid-liquid transition is determined using the Lindemann criterion.

Equation of State

Ideally, we should use a single EOS table that accurately represents the behaviour of the foil material from the solid state, through the liquid and vapour phases, to the partially ionized dense-plasma state. A survey of the literature did not indicate any technique for accurate calculations over such a wide range. Given that the foil material passes through a variety of phases, no single model is applicable. Hence two different EOS tables have been used. The first EOS applies during the time-interval before burst. During this period, the density remains constant at its normal value, while the temperature increases due to joule heating. The electronic contribution to the EOS comes from the Thomas-Fermi model with Quantum and Exchange corrections (TFC) [C10]. The “cold” contribution comes from the Universal EOS for metals [C11] and the
“ion-thermal” contribution from the Chart-JD model [C12]. This EOS has been validated against published Hugoniot data [C10]. The second EOS has been generated using the \textit{ab-initio} Molecular Dynamics method. The generation of this EOS is explained in detailed in the next section. The switchover from the first to the second EOS is done at 5000 K, because data for the second EOS exists from this temperature till 40,000 K. Below 5000 K, equilibration of the MD simulations was a problem and hence the data would be questionable.

\textbf{Generation of equation-of-state by \textit{ab-initio} molecular dynamics}

We have employed the VASP (Vienna \textit{ab-initio} Simulation Program) plane-wave pseudo-potential code [C10, C11] for \textit{ab-initio} MD simulations. This code implements the Vanderbilt ultrasoft pseudo-potential scheme [C12] in a form supplied by Kresse and Hafner [C10] and the Perdew-Wang parameterization of the GGA [C13]. The Brillouin Zone was sampled with the Monkhorst-Pack scheme [C14]. We have performed fixed-volume temperature (NVT) molecular dynamics simulations at a large number of density and temperature points, selected to span a range of densities from 1.5 to 2.7 gm/cc and temperatures from 5000 to 40000 K, of interest for exploding conductor simulation. We have used 108 aluminum atoms in the unit cell and fixed the plane-wave cutoff at 128 eV. Integration of the equations of motion proceeded with time steps of 2 fs. Typical simulations ran for 500 time steps with the initial condition derived from a configuration at the same density and lower temperature. We typically let the system equilibrate for 200 time steps and then calculated properties using the final 300 time steps. This procedure proved sufficient to obtain accurate thermodynamic quantities, including pressure and internal energy. The statistical error in the thermodynamical quantities, pressure and internal energy, reported in this work, is of the order of 10\% or less. We employ both micro-canonical and iso-kinetic ensembles for the ions. In the latter, the ion temperature $T_i$ is fixed using velocity scaling. In turn, the assumption of local thermodynamic equilibrium sets the electron temperature $T_e$ to that of the ions $T_i$. In the region of interest to the present study, both ensembles give consistent thermodynamical properties i.e., pressure and internal energy. The generated equation of state for aluminum matches fairly well when compared to recently published data [C15, C16, C17].
Exploding foil simulations

The computer simulations of exploding foils were done for the parameters studied in Logan et al [C3]. We have assumed uniform dimension for the foil without taking into account a transition from the land section. Different dimensions of the foil were used and the data, viz., time to burst, action integral and current density at burst are studied for Aluminum. A comparison of experimental data and results from computer simulations is presented in Table C1.

From Table C1, we observe that the time to burst from computer simulations have a maximum absolute error of about 18% as compared to experimental data for all the cases that have been considered. The time to burst is taken as the time for foil resistance to reach its peak value. The burst current density has a maximum absolute error of about 15% compared to the experimental data. The experimental current density mentioned in Table C1, is computed using the instantaneous current and the original cross-sectional area of the foil. The experimental specific action at burst, given in Table C1, is almost a constant for round wires for a given material [C18, C19]. For foils, the computer simulations generally yield a value < 70% higher than the experimental data. This discrepancy has also been observed in the experiments of Logan et al [C3]. They attribute this to the differences in confinement of foils and wires.

Figure C‐1 shows the temporal profile for the resistance of a foil of dimensions 2.54 cm x 2.54 cm, for different thicknesses. It is observed that the ratio of peak resistance to initial resistance of the foil does not significantly change with foil thickness. The ratio of peak resistance to the initial resistance lies between 141‐149. Figure C‐2 shows the temporal profile of foil resistance for different dimensions, but for same thickness (51 µm). The ratio of peak resistance to the initial resistance is still between 145‐150. We can therefore infer that the ratio of peak resistance to initial resistance of a foil depends only on the firing set and is independent of the foil dimensions. Figure C‐3 shows the temporal profile of foil temperature for a 2.54 cm x 2.54 cm foil, for different thicknesses. The plot clearly shows that the peak temperature attained by foils, ~27,000 K, is independent of foil thickness. It can be seen that the rate of rise of temperature for smaller foil thickness is faster than for thicker foils. Figure C‐4 shows the temporal profile of foil temperature for different dimensions but for the same thickness (51 µm). The peak temperature achieved at any point in the simulation tends to decrease as foil dimensions are increased. For a given thickness, smaller foils seem to have a faster rate of temperature rise. Figures C‐5 and C‐6 show the temporal profile of specific action for the foils of various dimensions and thicknesses. The marks on the graphs show the burst
specific action. Figure C-7 shows the temporal profile of foil current for a similar dimension but for different foil thicknesses. The burst current and time to burst increase as the foil thickness is increased. Figure C-8 shows the temporal profile of foil current for different dimensions but same foil thickness. The marks on graphs of both figures show the burst current. We see restrike occurring in all cases, except for the foil thickness of 152 µm. As there is no tamping and the resistance also has dropped off fast, the current would therefore rise and re-strike. Figure C-9 shows the temporal profile of hydrodynamic pressure for a similar dimension but for different foil thicknesses. The peak pressure increases as the foil thickness in increased from 25 µm to 102 µm but decreases for 152 µm. The Full Width at Half Maximum (FHWM) of the pressure also increases as the foil thickness is increased. The FHWM for 25 µm, 51 µm, 102 µm and 152 µm foils are 0.12 µs, 0.18 µs, 0.28 µs and 0.47 µs respectively. Figure C-10 shows the temporal profile of hydrodynamic pressure for different dimensions and foil thickness of 51 µm. The peak hydrodynamic pressure decreases as the foil dimensions are increased. The FHWM of the pressure curves also increase as the foil dimensions are increased. For 0.95 cm x 0.95 cm, 1.91 cm x 1.91 cm and 3.56 cm x 3.56 cm, the FWHM are 0.076 µs, 0.13 µs and 0.27 µs respectively. After attaining peak, the pressure falls off rapidly mainly due to large expansion of the foil.

**Table C1: comparison of experimental data and results from computer simulation.**

*(Figures in parenthesis shows a relative error compared to experimental data)*

<table>
<thead>
<tr>
<th>Foil Dimension (in cm)</th>
<th>Experimental data</th>
<th>Simulation data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Burst time $t_b$ (µs)</td>
<td>Burst current density $J_b$ (TA/m²)</td>
</tr>
<tr>
<td>2.54×2.54×0.0025</td>
<td>0.65</td>
<td>0.70</td>
</tr>
<tr>
<td>2.54×2.54×0.0051</td>
<td>1.00</td>
<td>0.54</td>
</tr>
<tr>
<td>2.54×2.54×0.0102</td>
<td>1.50</td>
<td>0.39</td>
</tr>
<tr>
<td>2.54×2.54×0.0152</td>
<td>1.99</td>
<td>0.28</td>
</tr>
<tr>
<td>0.95×0.95×0.0051</td>
<td>0.56</td>
<td>0.65</td>
</tr>
<tr>
<td>1.91×1.91×0.0051</td>
<td>0.85</td>
<td>0.62</td>
</tr>
<tr>
<td>3.56×3.56×0.0051</td>
<td>1.32</td>
<td>0.41</td>
</tr>
</tbody>
</table>
Conclusions

We have successfully simulated exploding foil systems by making use of an \textit{ab-initio} Molecular Dynamics generated Equation-of-State (EOS) data. The generation of the EOS has been done from the first principles method and therefore gives a fairly accurate calculations of the foil expansion. The results match fairly well with experimental data.

![Figure C-1: Temporal profile of foil resistance for different thickness of a similar dimension (2.54 cm \times 2.54 cm)](image1)

![Figure C-2: Temporal profile of foil resistance for different foil dimensions (foil thickness =51 \mu m )](image2)
Figure C-3: Temporal profile of foil temperature for different foil thicknesses of a similar dimension (2.54 cm x 2.54 cm).

Figure C-4: Temporal profile of foil temperature for different dimensions (foil thickness = 51 µm).
Figure C-5: Temporal profile of specific action for different foil thicknesses of a similar dimension (2.54 cm x 2.54 cm). (Burst points are marked with symbols.)

Figure C-6: Temporal profile of specific action for different dimensions (foil thickness = 51µm). (Burst points are marked with symbols.)
Figure C-7: Temporal profile of foil current for different thicknesses of a similar dimension (2.54 cm x 2.54 cm).  
(Burst points are marked with symbols.)

Figure C-8: Temporal profile of foil current for different dimensions (foil thickness = 51µm).  
(Burst points are marked with symbols.)
Figure C-9: Temporal profile of hydrodynamic pressure for different thicknesses of a similar dimension (2.54 cm x 2.54 cm).

Figure C-10: Temporal profile of hydrodynamic pressure for different foil dimensions (foil thickness = 51 µm).
Appendix

References


[C11]  G. Kresse and J. Furthmuller,  

[C12]  D. Vanderbilt,  

[C13]  J. P. Perdew and Y. Wang,  

[C14]  H. Monkhorst & J. Pack,  


[C17]  G. Faussurier, C. Blancard, P. Renaudin, and P.L. Silvestrelli,  

[C18]  T.J. Tucker and R.P. Toth,  

[C19]  T.J. Tucker and R.P. Toth,  