An investigation of the alkali metals in the fcc structure using an embedded-atom-method (EAM) model

Marcus Jackman
Utah State University

Follow this and additional works at: https://digitalcommons.usu.edu/phys_capstoneproject

Part of the Physics Commons

Recommended Citation
https://digitalcommons.usu.edu/phys_capstoneproject/61

This Report is brought to you for free and open access by the Physics Student Research at DigitalCommons@USU. It has been accepted for inclusion in Physics Capstone Project by an authorized administrator of DigitalCommons@USU. For more information, please contact rebecca.nelson@usu.edu.
An investigation of the alkali metals in the fcc structure using an embedded-atom-method (EAM) model

Marcus Jackman
(Dated: Dec. 8, 2017)

Embedded-atom-method models have been used in the calculation and prediction of many vibrational and thermal properties of materials. In 2012 Wilson and Riffe constructed a model that predicts dispersion relations and frequency-moment Debye temperatures of the alkali metals with a greater degree of accuracy than previous models. The Wilson-Riffe model was implemented using MATLAB code. Here that model is extended to model alkali metals in the close-packed fcc structure. Code development is discussed, and results are presented for dispersion relations, density of states, Debye temperatures and free energy. The vibrational free energy combined with a suitable constant representing the electronic free energy of these metals is found to be the driving factor in the phase transition to close-packed structures that occurs in Lithium and Sodium at low temperatures.

I. INTRODUCTION

Embedded-atom-method (EAM) models have been used to study many material properties of fcc and bcc metals and have been very good for vibrational dynamics [1]. In 2012 Wilson and Riffe constructed an EAM that predicts phonon dispersion and Debye temperatures in excellent agreement with experimental data for the alkali metals [2]. Although Wilson did some separate calculations on fcc metals, the model was used primarily with the bcc alkalis [3].

There is reason to model the alkali metals in close-packed structures because Li and Na undergo phase transitions to close-packed structures at low temperatures [4, 5]. Also, because of the success of the Wilson-Riffe model there is reason to believe that it will model close-packed structures accurately. Here we explore the alkali metals in the face-centered cubic (fcc) structure. Dispersions curves, density of states, Debye temperatures and vibrational free energy are all calculated and plotted.

II. THE EAM

The EAM model uses the lattice geometry and inherent properties of a material to calculate the total potential energy as a combination of a pair potential interactions between the atoms and an embedding energy. It can be expressed generally as [1]

\[ U = \frac{1}{2} \sum_{ij} \phi(r_{ij}) + \sum_i F(\rho_i), \]  

(1)

where \( i \) and \( j \) label the atoms in the solid, \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( \phi(r_{ij}) \) is the pair potential function, \( F \) is the embedding energy function, and \( \rho_i \) is the electron density at the position of atom \( i \) due to all other atoms in the solid. The density \( \rho_i \) can be written as a sum of individual atomic densities \( f(r_{ij}) \) from the atoms surrounding it,

\[ \rho_i = \sum_j f(r_{ij}). \]  

(2)

A. The dynamical matrix

Here we follow the formulation of Ibach and Luth [6] by expressing the total potential energy \( U \) as a Taylor series expansion in small displacements \( s_{n\alpha i} \) from equilibrium.

\[ U(r_{n\alpha i} + s_{n\alpha i}) = U(r_{n\alpha i}) + \frac{1}{2} \sum_{m\beta j} \frac{\partial^2 U}{\partial r_{n\alpha i} \partial r_{m\beta j}} s_{n\alpha i} s_{m\beta j} \ldots, \]  

(3)

where the indices \( n \) and \( m \) run over all unit cells, \( \alpha \) and \( \beta \) run over the atoms in each cell, and \( i \) and \( j \) run over the three spatial directions. By taking a harmonic approach and ignoring higher order terms this equation represents an extension of the harmonic oscillator potential in the case of many particles. The derivatives of the potential,

\[ \frac{\partial^2 U}{\partial r_{n\alpha i} \partial r_{m\beta j}} = \Phi_{m\beta j}^{n\alpha i}, \]  

(4)

have the dimension of spring constants and are called coupling constants. These can be used somewhat like spring constants in an equation of motion,

\[ M_{\alpha} \ddot{s}_{n\alpha i} + \sum_{m\beta j} \Phi_{n\alpha i}^{m\beta j} s_{m\beta j} = 0. \]  

(5)

Here \( M_\alpha \) is the mass of the atom \( \alpha \). This gives rise to \( 3rN \) differential equations from the \( N \) unit cells each with \( r \) atoms. However with periodic structures significant simplification can be achieved by using a suitable ansatz. This involves writing the displacements \( s_{n\alpha i} \) in terms of a plane wave that is only defined at the lattice points \( r_n \).

\[ s_{n\alpha i} = \frac{1}{\sqrt{M_\alpha}} u_{n\alpha}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_n - \omega t). \]  

(6)

Here \( u \) is the amplitude of a given wave vector \( \mathbf{q} \), and \( \omega^2 \) is the associated frequency. Substituting this form into (5) we get the following,

\[ -\omega^2 u_{n\alpha}(\mathbf{q}) + \sum_{\beta j} \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{n\alpha i}^{m\beta j} e^{i\mathbf{a} \cdot (\mathbf{r}_m - \mathbf{r}_n)} u_{\beta j}(\mathbf{q}) = 0. \]  

(7)
Then due to discrete translational invariance the terms of the sum over $m$ are independent of $n$. The dynamical matrix $D_{\alpha i}^{\beta j}$ is obtained as
\[ D_{\alpha i}^{\beta j} = \sum_{m} \frac{1}{\sqrt{M_{\alpha}M_{\beta}}} \Phi_{m\beta}^{*} \Phi_{n\alpha} e^{i\mathbf{q} \cdot (\mathbf{r}_{m} - \mathbf{r}_{n})}. \] (8)
The linear homogeneous system of equations is then written as follows,
\[ -\omega^2 u_{\alpha i}(\mathbf{q}) + \sum_{\beta j} D_{\alpha i}^{\beta j}(\mathbf{q}) u_{\beta j}(\mathbf{q}) = 0. \] (9)
These elements of the dynamical matrix describe the allowed atomic motions. Using the system of equations, finding the frequencies of vibration for a given wave vector can be simplified into an eigenvalue problem on the dynamical matrix. With the solutions, material properties can be deduced.

B. Wilson-Riffe EAM model

In the Wilson-Riffe EAM previously introduced forms of the pair potential, embedding energy, and atomic density are used. The pair potential model is taken from Wang and Boercker [7],
\[ \phi(r) = \sum_{n=0}^{6} K_n \left(\frac{r}{r_1} - 1\right)^n \exp\left(-\alpha \left(\frac{r}{r_1} - 1\right)^2\right), \] (10)
and the embedding energy and atomic density are taken from Johnson and Oh [8],
\[ F(\rho) = -(E_{coh} - E_{1w}^{(F)}) \left[1 - \lambda \ln\left(\frac{\rho}{\rho_c}\right)\right] \left(\frac{\rho}{\rho_3}\right)^{\lambda} \] (11)
and
\[ f(r) = f_1 \exp\left(-\beta \left(\frac{r}{r_1} - 1\right)\right). \] (12)
This EAM produces such accurate results because of the appropriate selection of these formulations and the precise values used in their parameters. The results obtained by the Wilson-Riffe model are generally in better agreement with experiment than previous models for bcc alkali metals, as is illustrated for sodium in Fig. 1.

III. CODE DEVELOPMENT

Due to the complex and time consuming nature of the calculations involved in the model, Wilson implemented everything in MATLAB code. Originally the code was meant to simply be a means of calculation with no intentions of being reused or added upon, and as such was written in a way that wasn’t conducive to other programmers working with it. Luckily however, a few years later Joseph Richardson was able to consolidate and update the code to be reusable and easier to read and work with, which made expanding the application to close-packed structures much easier [9].

A. Alkali fcc lattice constant

One of the reasons the Wilson-Riffe model is so successful is because of the use of accurate input parameters. So naturally the first step to expanding the model was to find those input parameters for the fcc structure. One parameter that is used in every equation relating to the lattice energy is the lattice constant $a_0$. To calculate this, a function was written to calculate and plot the total potential energy of the lattice vs the volume per atom, then using the minimum energy volume, the lattice constant was easily extracted by dividing by the number of atoms per unit cell. To calculate the potential energy in the fcc structure primitive vectors were needed to generate vectors to all nearest neighbors. These primitive vectors can be written as
\[ v_1 = \left[\frac{a}{2}, \frac{a}{2}, 0\right], v_2 = \left[0, \frac{a}{2}, \frac{a}{2}\right], v_3 = \left[\frac{a}{2}, 0, \frac{a}{2}\right]. \] (13)
The function also calculated the cohesive energy $E_{coh}$ associated with the minimum potential energy. Wilson had made some of these calculations previously so everything was checked to be in accordance with those earlier calculations [3]. Fig. 2 shows the calculated values.

<table>
<thead>
<tr>
<th></th>
<th>FCC</th>
<th>$a_0 (\lambda)$</th>
<th>$a_0^3 (\lambda^3)$</th>
<th>$E_{coh}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>4.335</td>
<td>20.3661</td>
<td>-1.626</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>5.295</td>
<td>37.114</td>
<td>-1.1042</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>6.558</td>
<td>70.5106</td>
<td>-0.9287</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>7.03</td>
<td>86.8572</td>
<td>-0.8518</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>7.618</td>
<td>110.5256</td>
<td>-0.8038</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 2. Table of calculated values.
B. Dispersion curves

With accurate input parameters for the fcc structure it naturally follows to generate dispersion relation plots. Calculating the dispersion data was fairly easy as the function to do so with a bcc structure was already written and it simply needed fcc inputs. After generating the data, plotting it correctly was slightly more difficult because the fcc brillouin zone is quite different than the bcc. However, after altering the code to model the fcc directional data, plots were generated. Note in the first plot of Fig. 3, the dispersion curves of fcc lithium, there are some irregularities near \( \Gamma \) where the curve drops to 0. This is a spurious result of the model and doesn’t reflect any physical property of the material. It is worth mentioning that due to this shortcoming of the model with lithium the density of states near \( \Gamma \) is affected which causes the sharp downward slope of the fcc Debye -3, and -2 temperatures (shown below).

C. Density of states

The directional dispersion curves were a good building block to then calculate and plot the density of states. To do this, frequencies associated with k-space points within the irreducible brillouin zone (IBZ) were generated and then the number of recurrences of these frequencies were plotted. The process of generating these frequencies was the most time consuming task in the code because of the inefficient way of obtaining k-space points within the IBZ. Because the code was already written to do this with a bcc structure efficiency didn’t take a priority and it was just expanded to work with fcc structures. Essentially, the code generated millions of k-space points then ran them through a screening function to determine which were in the IBZ with a series of IF statements. By using this same process the code was changed to make sure points were in the fcc IBZ. Some geometric calculations were made to obtain numerical boundaries to the IBZ.
and were found to be:

\[
\begin{align*}
\Gamma &= (0, 0, 0) \\
X &= (0, 0.5, 0) \\
L &= (0.25, 0.25, 0.25) \\
U &= (0.125, 0.5, 0.125) \\
W &= (0.25, 0.5, 0) \\
K &= (0.375, 0.375, 0)
\end{align*}
\]

Here these coordinates are in the standard \((x, y, z)\) cartesian system and correspond to the IBZ illustrated in Fig. 5. After generating these frequencies each was weighted because the IBZ is only a fraction of the total BZ (in the case of the fcc structure, the IBZ is one-forty eighth of the BZ). These weighted frequencies were then used to generate the density of states plot. The frequencies were grouped into bins and for each bin a gaussian was plotted with an amplitude equal to the number of frequencies within the bin. Then by altering the number of bins, and the width of each gaussian smooth plots were generated in Fig. 6 and Fig. 7.

![FIG. 5. fcc brillouin zone](image)

![FIG. 6. fcc density of states for Li](image)

![FIG. 7. fcc alkali density of states for Na, K, Rb and Cs](image)
D. Debye Temperatures

Following Wilson and Riffe, the Debye temperatures could now be calculated to demonstrate the accuracy of the model throughout the BZ. The Debye temperature given by [11]

\[ \Theta_D(n) = \frac{\hbar}{k_B} \left( n + 3 \frac{\int \omega^2 g(\omega) d\omega}{\int g(\omega)} \right)^{\frac{1}{2}} \] (15)

is fairly straightforward to implement as it simply used the frequencies and weights generated from the density of states. By using frequencies and weights from bcc, and fcc structures the following plots were generated for Debye temperatures from -3 to 6. There was some irregularity in the -3 and -2 Debye temperatures in Li; this was due to the anomaly near \( \Gamma \) seen in the dispersion plot.

![Debye Temperatures](image1)

FIG. 8. fcc and bcc Debye temperatures for Li and Na

E. Helmholtz free energy

One of the main initial motivations for this investigation was the phase transition of Lithium and Sodium at low temperatures to close-packed structures. The calculation of the total Helmholtz free energy \( F \) showed that it is the driving factor in this phase transition. The formulation for \( F \) from [12] was used,

\[ F = \sum_q \frac{\hbar \omega^2(q)}{2} + k_B T \ln \left[ 1 - \exp \left( -\frac{\hbar \omega^2(q)}{k_B T} \right) \right]. \] (16)

Here \( q \) is a wave vector, \( \omega^2(q) \) is the associated frequency, \( T \) is temperature, and \( k_B \) and \( \hbar \) are constants. Using this formulation \( F \) is expressed as a function of temperature, which is plotted in Fig. 10. This formulation however, is only of the vibrational part of the free energy which is why the bcc free energy is lower at all temperatures than that of the fcc. Because the temperature of the phase transition is known a formulation of the total free energy
FIG. 10. Lithium and Sodium free energy in bcc and fcc can be generated. The electronic piece of the free energy can be added as a constant such that the fcc total free energy dips below the bcc total free energy at the temperature at which the phase transition occurs. This addition yields a more accurate formulation and understanding of the phase transition. Riffe has done some separate calculations with the total free energy [13], but here only the vibrational part is presented.

IV. CONCLUSION

As suspected, the Wilson and Riffe model was successful in calculating and modeling properties in the close-packed fcc structure. This success is again attributed to accurate input parameters, and precise formulations for the pieces of the EAM model. Accurate models like this give us a better understanding of fundamental vibrational and thermal properties of these metals, and this understanding can be useful in future scientific or engineering work. While this paper only explores a few fundamental material properties, others can be deduced such as entropy and specific heat. Future work with this model will be to extend it to the bulk hcp structure, and then to extend surface calculations to both fcc and hcp structures.