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Thermophysical properties of B1-LiF

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Abstract. Lithium fluoride (LiF) is an important technological material. It is chemically stable, thermal insulator, having found application in the field of high pressure as a pressure transmitting medium. In the present paper, we report various thermophysical properties of rock salt structured LiF using plane wave pseudopotential density functional theory within local density approximation in conjunction with quasi harmonic Debye model. Ground state properties are studied using density functional theory. To include effect to ionic motion at finite temperatures, quasi harmonic Debye model is used. Calculated ground state and finite temperature/pressure thermophysical properties are found to be in good agreement with experimental and other theoretical results.

1. Introduction

Among all alkali halides and ionic crystals, LiF has found much attraction due to its interesting physical properties. It is a material with low absorption, low scattering factor for sample measurement through Diamond Anvil Cell (DAC). As a result, it has found application as pressure transmitting medium as well as pressure sensor. Structural stability of LiF up to about one mega bar pressure also makes it an important material [1]. Previously, experimental and theoretical work on LiF is performed mostly at ambient conditions [2]. Studies on thermophysical properties of LiF are reported in limited range of temperature and pressure [3]. Liu et al [1] have studied thermophysical properties up to 37 GPa pressure and ~1000 K temperature. Most recently, Smirnov [4] has studied various ground state properties of LiF using full potential linear muffin tin orbital method as implemented in LMTART code with few modifications. Further, he has studied pressure dependence of elastic constants and structural stability under pressure. In his work, thermal contribution at finite temperature was taken into account using modified Debye model. In the present work, we describe ground state and finite temperature/pressure thermophysical properties of rock salt structured (B1) LiF using plane wave pseudopotential density functional theory as implemented in Quantum ESPRESSO package [5] in conjunction with quasi harmonic Debye model [6]. The paper is prepared as follows. The next section 2 describes the theoretical method used in the present study. The section 3 describes the results and discussion. The last section 4 describes the conclusions.

2. Method of Calculation

In the present work, ground state properties of LiF are calculated using plane wave pseudopotential density functional theory within local density approximation (LDA) as implemented
in Quantum ESPRESSO code [5]. It is known that LiF crystallizes in rock salt (B1) structure and remain stable up to very high pressure. Total energy calculation of B1-LiF was performed at various values of lattice constants in the step of 0.1 au. Before that, a convergence test was performed and it gave an 8x8x8 Monkhorst-Pack [7] $k$-point grid for Brillouin zone integration along with an energy cut-off of 100 Ry. Norm conserving pseudopotentials were used for the calculation of total energy. The calculated total energies were fitted to Murnaghan equation of state [8], in order to estimate equilibrium lattice constant, isothermal bulk modulus and its pressure derivative. Full phonon dispersion along major symmetry directions in B1-LiF are calculated using density functional perturbation theory [5]. A 2x2x2 grid of $q$ point was used for the computation of force constants, which were further interpolated to calculate phonon frequencies. Further, elastic stiffness constants are calculated from the long wavelength limit of phonon frequencies along [100] and [110] planes [9]. Once the ground state properties are obtained, free energy at elevated temperature can be obtained using quasi harmonic Debye model [6]. In this approach, non equilibrium GIBBS function is given by,

$$G^*(V; p, T) = E(V) + PV + A_{\text{ionic}}(\Theta(V), T) \tag{1}$$

Here, the first term on right side is the optimized energy. Second represents the corresponding pressure. Third term corresponds to the thermal ionic contribution at finite temperature. Thermal electronic contribution is not included, as LiF is a wide band gap material. More details about quasi harmonic Debye model can be found out in Ref. [6]. The important input is the Poisson’s ratio of LiF, which in the present work is calculated from the presently calculated elastic constants.

3. Results and Discussion

In the present work, we have calculated various ground state and finite temperature thermophysical properties of B1-LiF. Calculated cohesive energy is shown in Figure 1. The calculated energy is fitted to Murnaghan equation of state in order to predict structural properties viz; equilibrium lattice constants, isothermal bulk modulus and its pressure derivative. The calculated data is shown in Table 1 along with corresponding experimental and theoretical findings. A good agreement is observed. Equilibrium lattice constant is slightly underestimated compared to experimental results, which may be attributed to LDA as exchange-correlation functional. Further, full phonon dispersion is calculated using density functional perturbation theory. Calculated phonon frequencies along major symmetry directions show good agreement with experimental values [2]. We have also calculated phonon frequencies at high pressure (P = 85 GPa). We observe that at such high pressure, phonons along $\Gamma \rightarrow X$ and $\Gamma \rightarrow L$ directions are greatly affected. Also, longitudinal phonon frequencies along [100] plane shows maximum near 0.7 Å$^{-1}$ and drops at zone boundary. This feature is generally observed in the heavy elements like lead [10], but not in the light compounds like LiF. Such feature in lead was explained in terms of spin-orbit coupling by Verstraete et al [10]. Thus we predict that spin-orbit coupling might be playing important role at high pressures. Also, LO-TO splitting is found to decrease with pressure along $\Gamma \rightarrow X$ direction. From the long wavelength limit of phonon frequencies along [100] and [110] direction, we have calculated elastic stiffness constants and the results are shown in Table 1. Again a good agreement is observed, except that $C'$ is slightly overestimated.

We have calculated various thermodynamic properties using GIBBS program. Calculated room temperature thermal equation of state is shown in Figure 3 along with experimental data [1]. Here also, a good agreement is observed. Isothermal bulk modulus and Debye temperature are calculated at different temperatures and the results are shown in Figure 4 and Figure 5, respectively along with experimental results [12]. The trend of variation of bulk modulus and Debye temperature with temperature matches with the experimental results. The presently calculated temperature coefficient of bulk modulus is -0.033 GPa/K, while the experimental value is -0.0218 GPa/K. Similarly, the temperature coefficient of Debye temperature with temperature is -0.133, while the experimental value is -0.15. We have also calculated temperature variation of specific heat. Figure 6 shows the calculated data with the experimental value [13]. The value of room temperature specific heat agrees well with the experimental values. No other values of specific heats at constant pressure or at constant volume were found for comparison.
Figure 1. Cohesive energy of LiF as a function of atomic volume.

Figure 2. Phonon dispersion in LiF in ground state and at high pressure, along with experimental data.

Table 1. Calculated structural and elastic properties of B1-LiF.

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<td>$a_0$ (Å)</td>
<td>3.944</td>
<td>4.026 [11]</td>
<td>4.022</td>
</tr>
<tr>
<td>$B_o$ (GPa)</td>
<td>76.4</td>
<td>73.0 [1]</td>
<td>73.8</td>
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<tr>
<td>$B'_o$</td>
<td>3.36</td>
<td>3.90 [1]</td>
<td>3.76</td>
</tr>
<tr>
<td>$C'$ (GPa)</td>
<td>53.775</td>
<td>41.1 [12]</td>
<td>41.3</td>
</tr>
<tr>
<td>$C_{44}$ (GPa)</td>
<td>68.36</td>
<td>64.9 [12]</td>
<td>66.0</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.216</td>
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Figure 3. Room temperature thermal equation of state of LiF.

Figure 4. Isothermal bulk modulus at different temperatures along with experimental results.
In conclusion, we conclude that present work reports various ground state and finite temperature thermophysical properties of rock salt structured LiF. Our presently calculated structural and lattice mechanical properties agree well with experimental values. Phonon frequencies at high pressures show features, generally not observed in light elements or compounds. To the best of our knowledge, phonons in LiF are reported first time using density functional perturbation theory. Calculated thermodynamic properties namely room temperature equation of state, temperature variation of bulk modulus, Debye temperature and specific heat show good agreement with corresponding experimental values, confirming present approach in determining finite temperature thermophysical properties of LiF. Present results form a useful set of data of finite temperature/pressure thermophysical properties of LiF, which may be useful for further research in this field.

4. References