

**CALCULATIONS OF PHONONS AND PHONON DISPERSION IN  
LiFeP Pnictide Superconductor**

A Thesis

Submitted for the Award of

Master of Science Degree in Theoretical Physics

By

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## DEDICATION

Dedicated to the memory of my dear mother and all women who lost their  
lives during child birth

## DECLARATION

I hereby declare that the matter embodied in this report entitled “ CalculationS of Phonon and Phonon Dispersion in LiFeP Pnictide Superconductor“ is the result of investigations carried out by me under the supervision of Dr. O. Akin-Ojo at the International Centre for Theoretical Physics (ICTP) Trieste, Italy and that it has not been submitted elsewhere for the award of any degree or diploma.

In keeping with the general practice in reporting scientific observations, due acknowledgement has been made whenever the work described is based on the findings of other investigators.

.....  
**Salawu Omotayo Akande**

## CERTIFICATION

I hereby certify that the matter embodied in this report entitled ‘Calculations of Phonon and Phonon Dispersion in LiFeP Pnictide Superconductor‘ has been carried out by Salawu Omotayo Akande at the International Centre for Theoretical Physics (ICTP) Trieste, Italy under my supervision and that it has not been submitted elsewhere for the award of any degree or diploma.

.....  
**Dr. O. Akin-Ojo**

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## Abstract

Not too long ago(2008),a new pnictide Superconductor free from arsenic was discovered –LiFeP. It belongs to the family of the so called ‘111’ type iron Superconductor. It has unique characteristics in its normal state which can be useful in understanding the unusual high temperature superconductivity observed in iron pnictide compounds. In this work,we studied LiFeP from first principles. The structure was optimised,electronic structure calculations were performed yielding lattice constants that differed only 2 – 9% from experiment. Band structure was calculated and electronic density of states showing no band gap was found. Calculations on phonon modes was also done. From observing the phonon normal modes,the FeP plane was found to be largely decoupled from the Li atoms.In some modes the P is also decoupled from the Fe plane.A small band gap of about  $25\text{cm}^{-1}$  ( $\equiv 35$ )K was also noticed in the phonon band structure

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# Chapter 1

## 1.1 INTRODUCTION

### 1.1.1 Phonons

Energy is involved in the collective motion of atoms in a material: the atoms vibrate together. This energy occurs in ‘packets’ called phonons. In other words the energy is quantized and a phonon is a quantum of such energy. One can also view phonons as quasi particles which carry the energies of collective vibrations of atoms (much in the same way as the more familiar photons [1] that are also quasi particles which carry electromagnetic energy). Phonons are connected with many properties of materials e.g thermal conductivity-when a solid is heated, its atoms vibrate meaning phonons are being created/destroyed and scattered. Phonons also play an important role in electrical conductivity since the electrons in solids can be scattered [2] by phonons consequently decreasing the electrical conductivity of the material. A strange situation has, however, been found in nature, certain materials demonstrate infinite conductivity; the electrons move without scattering off of phonons despite existence of phonons in such materials. This property of such materials is called superconductivity.

### 1.1.2 Superconductivity

It was discovered in 1911 by the Dutch physicist Karmmerlingh Onnes in the course of his experiment on electrical conductivity of metals at low [3] temperature. It is the complete loss of electrical resistivity; the substance exhibits perfect electrical conductivity. It is also accompanied by expulsion of an applied magnetic field from the material.

Superconductivity is only observed in certain materials and at temperatures below a certain material-dependent temperature known as the the critical temperature,  $T_c$ . It is also dependent on the current density and the applied magnetic field.

The second property of superconductor; the expulsion of an an applied magnetic field from the interior of the superconductors is called the Meissner effect after its discoverer Meissner. Observation showed that when a magnet is brought near a superconductor, the magnet encounters a repulsive force. It can be said that the superconductor completely expel the magnetic field and behave as a perfect diamagnet. This characteristic is important for making high speed, magnetically levitated trains and making powerful, small, superconducting magnets for magnetic resonance imaging. Superconductivity, in materials that exhibit this effect, is reversible and can be destroyed by high temperatures (above  $T_c$ ) or high magnetic fields (above 'critical field'  $B_c$ ). For more than 40 years after its discovery, a microscopic explanation for this phenomenon was absent despite attempts by many scientists.

### **1.1.3 BCS theory of superconductivity and high $T_c$ superconductors**

Finally, in 1957 Bardeen, Cooper and Schriffer [4] put forward a theory of superconductivity. This theory explained the microscopic origin of superconductivity and also predicted properties of superconductors. They proposed that the ground state of a material is unstable with respect to pair of 'bound' electrons. This pair is called Cooper pairs and are caused by the interaction between electrons and phonons. The experimental fact that  $T_c$  depend on masses of atoms in the superconducting material (i.e the isotope effect) was an important clue that the electron interaction with phonons was important in the superconductors found up to that period. In one view, the electron-phonon interaction causes distortion in lattice thereby creating an area of greater positive charge density. Another electron at some distance is then attracted to this region of great positive charge density. Consequently [7] the electrons are indirectly attracted to one another thus forming cooper pairs. Supercurrent is carried by Cooper pairs around the superconductor and the perfect conductivity they experience can be accounted for by the fact that they (Cooper pairs) are more stable than a single electron within

the lattice. The Cooper pairs move through through the lattice relatively unaffected by thermal vibrations (electron-phonon interactions) below the critical temperature. However, with reasonable estimates of certain parameters in BCS theory, a theoretical maximum temperature of about 30K is obtained for critical temperature  $T_c$ . Above this, thermal energy would cause electron-phonon interactions of an energy too high to allow formation of, or sustain, Cooper pairs.

A new discovery in 1986 challenged this theoretical maximum of  $T_c$ . A new material was found by Bednorz and muller [13] to be superconducting with critical temperature of 35K. Since then, many high  $T_c$  (i.e  $T_c > 30K$ ) materials have been found. All of them are characterized by copper oxide ( $CuO$ ) planes. However in February 2008,  $LaO_{1-x}F_xFeAs$  ( $x=0.05 - 0.012$ ) with  $T_c$  26K was discovered by Kamihara [5, 6] and his co-workers. This material has no  $CuO$  plane like the so-called cuprates. Since then, many similar materials with high  $T_c$ , lacking  $CuO$  planes [11] have been discovered. These materials typically called ‘pnictide’ superconductors, contain a pnictogen, i.e an element in group VA of the periodic table namely, P, As or Sb. As it turns out, the BCS theory is not sufficient to explain the mechanism of the high  $T_c$  superconductors (HTSC) although concepts from BCS (e.g Cooper pairs) are widely used in attempts to develop a theory for HTSC. Up till now, there is no consensus on the mechanism of superconducting in HTSCs

#### 1.1.4 Pnictide superconductors

Before the discovery of this class of materials, HTSCs were mostly copper based. The transition temperature of the pnictide material  $LaFeAs(O_{0.89}F_{0.11})$  was 26 K [5] and this temperature increases to 43K under a high pressure of about 4Gpa. This excellent result notwithstanding, the record set over time by copper oxide or cuprates is not challenged. The presence of iron in this material suggest that it would be easier to work with than cuprates which are known to be brittle and require complicated methods in shaping them into desired geometry. Also there are indications that with more research, critical temperature of iron-based superconductors are likely to increase. Typical pnictide material consist of an iron pnictide layer that supports superconducting current interlaced with a charged reservoir which can be alkaline metal (e.g potassium),

fluoride,alkaline earth metal (e.g magnesium) or even earth metal(e.g yttrium)[?].

Despite all these prospects in pnictide materials,one unanswered question is why superconducting in iron pnictide material is not destroyed by the presence of iron since iron is magnetic and its a known fact that superconductivity is inhibited by magnetic field.The discovery of pnictide material will provide a platform for comparison with copper-based superconductors in trying to unravel the cause of high transition temperature and other properties which go beyond the BCS theory in these materials. Therefore it is imperative to search for materials with simpler structure which will help in understanding the physical mechanism of unusual superconductivity observed in pnictides. Note that, recently a superconducting pnictide material lacking Fe was discovered-LiCu<sub>2</sub>P.It is too early to speculate on the mechanism responsible for superconductivity in this material.

Here we study the newly discovered iron pnictide LiFeP. It crystallizes into a Cu<sub>2</sub>Sb structure (crystallographic group P4/nmm) containing an FeP layer. It exhibits superconductivity with  $T_c$  of 6 K. It is the first arsenic-free analog of the family of the so-called 111-type[12] iron pnictides.

This work is inspired by the need to understand the superconducting mechanism of iron pnictide materials. Our main aim is to study the behaviour of phonons in LiFeP from first principles.In the next chapter, we will examine the Hamiltonian for our system and give theoretical background for the methods used in this work. In Chapters 3 and 4 we will analyze and discuss results that were obtained using the techniques. In the final chapter we present the conclusion and some open questions.

# Chapter 2

## 2.1 The Hamiltonian of a solid

### 2.1.1 Splitting the Hamiltonian

To obtain the Hamiltonian for the phonon modes in a system, we start from the complete Hamiltonian of a system of solids which can be written as[14]

$$\hat{H} = \hat{T}_n(R) + \hat{W}_{nn}(R) + \hat{T}_e(r) + \hat{W}_{ee}(R) + \hat{W}_{en}(R, r) \quad (2.1)$$

where

$$\hat{T}_n = -\frac{1}{2} \sum_{\alpha=1}^{N_n} \frac{\nabla^2}{M_\alpha} \quad (2.2)$$

$$\hat{T}_e = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_{r_i}^2 \quad (2.3)$$

$$\hat{W}_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|r_i - r_j|} \quad (2.4)$$

$$\hat{W}_{nn} = \frac{1}{2} \sum_{\alpha \neq \beta}^{N_n} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|} \quad (2.5)$$

$$\hat{W}_{en} = - \sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|r_i - R_\alpha|} \quad (2.6)$$

Where the nuclear and electronic kinetic energy are represented by  $T_n$  and  $T_e$  respectively. Also electron-electron, electron-nuclear and nuclear-nuclear interactions are

represented by the operators  $W_{ee}$ ,  $W_{en}$  and  $W_{nn}$  respectively. The interaction of  $N_e$  electrons and  $N_n$  nuclei with mass  $M_\alpha$  and charge  $Z_\alpha$  are described by the Hamiltonian above. The nuclear and electronic kinetic energy operators are  $T_n$  and  $T_e$  respectively.

The Schrödinger equation for the system is

$$\hat{H}\Phi_m(r, R) = \mathcal{E}_m\Phi_m(r, R), \quad (2.7)$$

with  $\Phi_m(r, R)$  being the eigenfunction for the system and  $\mathcal{E}_m$  the corresponding eigenvalue in the  $m$ th state. To solve this equation, one first makes the Born-Oppenheimer approximation, i.e., neglect the nuclei kinetic energy term which is small since  $M \gg 1$ . One then solves the equation with the resulting Hamiltonian, called the electronic Hamiltonian  $\hat{H}_{el}$ , at fixed values of the nuclei positions  $R_0$ . Explicitly,

$$\hat{H}_{el} = \hat{T}_e + \hat{W}_{ee} + \hat{W}_{en} \quad (2.8)$$

and

$$\hat{H}_{el}\psi_k(r; R_0) = \epsilon_k\psi_k(r; R_0) \quad (2.9)$$

where  $\psi_k(r; R_0)$  is the ‘‘electronic’’ wavefunction and  $\epsilon_k$  the corresponding eigenvalue in the electronic state  $k$  for a given  $R_0$ . To solve the electronic problem above, many approaches are available. In this work we used the popular density-functional theory (DFT) described in Subsection 2.1.2.

With a solution of the electronic part, we can now solve the original equation by expanding  $\Phi_m(r, R)$  as follows:

$$\Phi_m(r, R) = \sum_l \chi_{ml}(R)\psi_l(r; R) \quad (2.10)$$

where  $\chi_{ml}(R)$  are ‘expansion’ coefficients to be determined. These coefficients are determined by minimizing  $\int \Phi_m(r, R)^* \hat{H} \Phi_m(r, R) d^{3N_n} R d^{3N_e} r$  with respect to  $\chi_{ml}(R)^*$  subject to the condition that both  $\chi_{ml}(R)$  and  $\psi_l(r; R_0)$  are orthonormal. This yields:

$$\left[ \hat{T}_n + V_{\text{BO}}(R) \right] \chi_{km}(R) + \sum_l [T_n]_{kl} \chi_{lm}(R) = E \chi_{km}(R) \quad (2.11)$$

where,  $[T_n]_{kl} = \int \psi_k^*(r; R) \hat{T}_n \psi_l(r; R) d^{3N_e} r$  and  $V_{\text{BO}}(R) = \epsilon_k(R) + \hat{W}_{nn}(R)$ . In the BO approximation, [16, 18] one neglects the coupling between different electronic states

in Eq. 2.11. Furthermore, we could assume that the ground electronic state is well separated from the other electronic states so that, unless the system is given an exceptionally high energy, we need only consider the ground electronic state. The remaining term  $[T_n]_{00}$  is typically negligible.

To see how the phonons arise, one only needs to Taylor-expand  $V_{\text{BO}}(R)$  about the equilibrium position of the system  $R_e$  in powers of ' $R - R_e$ ' and then express ' $R - R_e$ ' in normal coordinates  $Q$ , thus making the transformation:

$$\hat{T}_n + V_{\text{BO}}(R) \rightarrow \sum_i \left[ -\frac{1}{2} \nabla_{Q_i}^2 + \frac{1}{2} \omega_i^2 Q_i^2 + \dots \right] \quad (2.12)$$

with  $\omega_i^2$  coming from an appropriate combination of the atomic masses and the second derivatives of  $V_{\text{BO}}(R)$ . This is the phonon Hamiltonian. The dots indicate terms in higher powers of  $Q$ . Without these higher terms, the Hamiltonian above is that of independent simple-harmonic oscillators (SHOs) showing that the phonons can be treated as quasiparticles which are independent SHOs.

Before discussing the method used in this work to solve the electronic problem, let us examine how the electron-phonon (e-ph) term arises. This term is important in superconductivity as, in the original BCS theory, it causes the electron-electron pairing (Cooper pairing). The electron-phonon terms in BCS comes by Taylor-expanding the electron-nuclei interaction term  $\hat{W}_{en}(r, R)$  about the equilibrium position of the nuclei  $R_e$ , expressing ' $R - R_e$ ' in normal coordinates  $Q$  as before, and considering only the term in the first derivative of  $\hat{W}_{en}$ . In Frohlich's explanation,[14] this e-ph interaction causes ions to be attracted and move towards an electron, thus creating a region of higher positive charge. This region of higher positive charge then attracts another electron. Hence, the attraction between the two electrons is mediated by the motion of the nuclei, i.e., by phonons – interacting with electrons.

### 2.1.2 The electronic Hamiltonian

In the Born-Oppenheimer approximation,[15] the Schrodinger equation for the electronic part of the total Hamiltonian  $H_{el}$  is given by

$$\hat{H}_{el} \psi(r_1, r_2, \dots, r_N) = E \psi(r_1, r_2, \dots, r_N) \quad (2.13)$$

where  $\psi$  is the many-body wavefunction for  $N$  electrons with coordinates  $(r_1, \dots, r_N)$ . The Hamiltonian operator consists of three terms, the kinetic energy of electrons, the interaction of the electrons with the external potential ( $V_{ext}$ ) and the electron-electron interaction ( $V_{ee}$ ) i.e

$$H_{el} = T_{el} + V_{ext} + V_{ee} \quad (2.14)$$

The kinetic energy operator is given by

$$T_{el} = -\frac{1}{2} \sum_{i=1}^N \nabla_{r_i}^2 \quad (2.15)$$

two electrons at  $r_i$  and  $r_j$  repel one another and produce a potential energy term  $|r_i - r_j|^{-1}$  so that the total electron-electron interaction is

$$V_{ee} = -\frac{1}{2} \sum_{i \neq j}^N \frac{1}{|r_i - r_j|} \quad (2.16)$$

Due to the presence of ions, the electrons experience a potential given by

$$V_{ext} = -\sum_{I,J} \frac{Z_I}{|R_I - r_i|} \quad (2.17)$$

Also two ions at positions  $R_I, R_J$  repel one another so that the total ion-ion interaction is

$$\sum_{I,J} \frac{Z_I Z_J}{|R_I - R_J|} \quad (2.18)$$

Explicitly the electronic Hamiltonian is

$$H_{el} = -\frac{1}{2} \sum_{i=1}^N \nabla_{r_i}^2 - \sum_{I,J} \frac{Z_I}{|R_I - r_i|} + \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|r_i - r_j|} + \sum_{I,J} \frac{Z_I Z_J}{|R_I - R_J|} \quad (2.19)$$

The average total energy for a state specified by a particular  $\psi$ , not necessarily one of the eigenfunctions of the previous equation is the expectation value of  $H$ , that is,

$$E[\psi] = \int \psi^* \hat{H} \psi d^{3N}r = \langle \psi | \hat{H} | \psi \rangle \quad (2.20)$$

The notation  $E[\psi]$  specifies that the energy is a functional of the wave function,  $\psi$  assumed normalized i.e  $\langle \psi | \psi \rangle = 1$ . This energy is greater than that of the ground state ( $E_0$ ) unless  $\psi$  is exactly  $\psi$  and this implies variational theorem

$$E[\psi] \geq E_0 \quad (2.21)$$



By inspecting all possible wavefunctions for the one that minimizes the total energy under the constraint that  $\psi$  is antisymmetric, we can obtain the energy and ground state wavefunction

The structure of  $\psi$  is contained in Hartree-Fock theory is assumed to be an antisymmetric product of function  $\phi_i$  each of which depends on the coordinates of a single electron, that is[20]

$$\psi_{HF} = \frac{1}{\sqrt{N!}} \det \phi_1 \phi_2 \phi_3 \dots \phi_N \quad (2.22)$$

Where, det implies a matrix determinant. Substituting this ansatz for  $\psi$  into the Schrödinger equation results in an expression for the Hartree-Fock energy,

$$E_{HF} = \sum_i \langle \phi_i | -\frac{1}{2} \nabla^2 + \hat{V}_{ion}(r) | \Phi_i \rangle + \frac{1}{2} \sum_{i,j(i \neq j)} \langle \Phi_i \Phi_j | \frac{1}{|r-r'|} | \Phi_i \Phi_j \rangle - \frac{1}{2} \sum_{i,j(i \neq j)} \langle \Phi_i \Phi_j | \frac{1}{|r-r'|} | \Phi_j \Phi_i \rangle \quad (2.23)$$

The ground state orbitals are determined by applying the variation theorem to this energy expression under the constraint that the orbitals are orthonormal. This leads to the self consistent functional equations,

$$\left[ -\frac{1}{2} \sum_i^N \nabla^2 + \hat{V}_{ext}(r) + \int \frac{\rho(r')}{|r-r'|} dr' \right] \phi_i(r) + \int V_x(r, r') \phi_i(r') dr' = \epsilon_i \phi_i(r) \quad (2.24)$$

where  $\rho(r) = \sum_i^N \phi_i^*(r) \phi_i(r)$  the non-local exchange potential  $V_x$  is defined such that

$$\int V_x(r, r') \phi_i(r') dr' = \sum_j^N \int \frac{\phi_j(r) \phi_j^*(r')}{|r-r'|} \phi_i(r') dr' \quad (2.25)$$

Non-interacting electron which are bound by the mean field potential are described by the Hartree-Fock equations from where we can obtain better approximation for  $\psi$  and  $E_0$  though doing this computationally expensive and the expense increases as the number of electrons increases.

DFT suggests that it is not necessary to solve the Schrödinger equation and determine the  $3N$  dimensional wavefunction in order to compute the ground state energy.

### 2.1.3 Density Functional Theory: The Hohenberg and Kohn Theorem

The most successful approach for computing the total energy and electronic structure of matter is the Density Functional theory(DFT)[21]. It is based on Hohenberg and

Kohn's theorem-Here the basic variable used is the ground state electronic charge density rather than the many electrons wave functions. Using this approach help to avoid solving large number of Slater determinants for a many body system[17]. In 1964 Hohenberg and Kohn[19] put forward two theorems that provide an exact theory for many body systems. The two theorems are:

**Theorem 1** For any system of interacting particles in an external potential  $V_{ext}$ , the total energy are unique functional of the electron density  $n(\mathbf{r})$ .

**Theorem 2** The functional for the ground state energy is minimized by the ground state electron density, in other words, the density that minimizes the total energy is the exact ground state density.

For an electronic system with a given Hamiltonian, it implies that since the number of electrons are determined by the ground state electronic density then the wavefunction is determined by the density and consequently all ground state properties of the system- the ground state kinetic energy, the total energy and the electron interaction energies are all functions of the density  $n(\mathbf{r})$ . We can therefore write the total energy Functional in the second H-K theorem in terms of the given external potential  $V_{ext}$  as

$$E[n(\mathbf{r})] = \int V_{ext}(\mathbf{r})n(\mathbf{r}) + F[n(\mathbf{r})] \quad (2.26)$$

where the functional  $F[n(\mathbf{r})]$  is the electronic part of the Hamiltonian, consisting of the kinetic energy  $T[n(\mathbf{r})]$  of the electrons and the electron-electron interaction  $V_{ee}$ . Hence we can write  $F[n(\mathbf{r})]$  as

$$F[n(\mathbf{r})] = \langle \Psi | T + V_{ee} | \Psi \rangle \quad (2.27)$$

From the two theorems above reducing the  $3N$  dimensional minimization problem of determining the ground state electronic density can be justified. This achievement notwithstanding, the theorems does not offer a way of computing  $F[n(\mathbf{r})]$  and hence there is no easy way for determining the ground state density of the system. A method to tackle this problem was offered by Kohn and Sham a year after Hohenberg and Kohn's paper

### 2.1.4 The Energy Functional

In their work, Kohn and Sham [22] put forward a new structure for the energy functional in order to find an analytic solution for it. The functional is split into 3 parts

$$E[n(r)] = T_o[n(r)] + E_H[n] + E_{xc}[n] \quad (2.28)$$

$T_o[n]$ , is the kinetic energy functional for a fictitious system of non-interacting electrons producing the same density as  $n(r)$ .  $E_H[n]$ , is the so called Hartree energy, arising classically from the mutual Coulomb repulsion of all electrons and is given by

$$E_H[n] = \frac{1}{2} \int \int \frac{n(r)n(r')}{|r - r'|} \quad (2.29)$$

and  $E_{xc}$  is the exchange-correlation functional. The first and second terms in the functional equation are known hence we need to approximate the third term (exchange-correlation functional). The applications of the Hohenberg and Kohn's theorem are grouped according to the approximation used for the exchange-correlation functional  $E_{xc}$ . A number of approximations to  $E_{xc}$  have been derived by researchers. These include LDA which expresses  $E_{xc}$  in terms of density of uniform electron gas and GGA which takes into account  $n(r)$  in addition to its gradient.

### 2.1.5 Local density Approximation

One of the commonest approximations used for  $E_{xc}[\rho]$  is the local density approximation LDA written as

$$E_{xc}^{LDA} = \int n(r)\varepsilon_{xc}[n(r)]dr \quad (2.30)$$

where  $\varepsilon_{xc}(n)$  is the exchange and correlation energy per particle of a uniform electron gas whose density is  $n(r)=\text{constant}$ . In this system the electrons are subjected to a constant external potential and thus the charge density is constant. Hence the system is specified by the value of the electron density  $n(r)$   $\varepsilon$  is a function of local density only and no longer a function of the whole density and its form is well known.

We can choose the auxiliary Hamiltonian so that it contains the kinetic energy operator and effective Sham-Kohn local potential acting on the electron at point  $r$ . The

many body equation can be mapped onto a system of single particles that are not interacting. The kinetic energy can be described by defining an orthogonal and normalized single particle orbital which are related to the real density of the system as follows:

$$n(r) = \sum_{i=1} n(i) |\Phi_i(r)|^2 \quad (2.31)$$

$$\langle \Phi_i | \phi_i \rangle = \int |\Phi(r)|^2 dr = 1 \quad (2.32)$$

$n_i$  is the occupation number of these orbitals which are streamlined to a certain set of values usually integers or real numbers. This follows Fermi-Dirac distribution in case of small excitation. We can therefore write the kinetic energy as

$$T_o[\Phi_i(r)] = \sum_i n_i \int \Phi_i^*(r) \left( \frac{-\nabla^2}{2} \right) \Phi_i(r) dr \quad (2.33)$$

We can now write  $E[n(r)]$  in terms the new orbitals. The minimum of the energy of the energy function becomes a variation with respect to the orbitals, with constraint that the orbital is orthogonal and normalized

$$\frac{\delta}{\delta \Phi_i^*} \{ E[N(r)] + \sum \varepsilon_i [1 - \int |\phi_i(r)|^2] \} = 0 \quad (2.34)$$

where  $\varepsilon_i$  is the multiplier and solving the equation, a schrodinger-like equation is obtained.

$$\left[ -\frac{\nabla^2}{2} + V_{ext}(r) + V_H([n(r), r]) + V_{xc}([n(r), r]) \right] \phi_i = \varepsilon_i \phi_i(r) \quad (2.35)$$

### 2.1.6 The generalized Gradient Approximation

This approximation offers a natural means to correcting homogeneous electron gas results. Here the energy functional depends on both the density and its gradient i.e the first order gradient term will be used. The GGA functional is of the form:

$$E_{xc} = \int \rho(r) \varepsilon_{xc}(\rho, \nabla \rho) dr \quad (2.36)$$

This type of approximation is useful for molecules

### 2.1.7 Plane waves pseudo potentials

The works of Hohenberg ,Kohn and Sham notwithstanding,solution to the many body problem is still not easy to come by this is because to obtain an accurate result, we have to consider the motion of all the electrons .This approach is cumbersome as it involves solving for too many particles.Furthermore, obtaining a potential that satisfies the kohn-sham electron density conditions and minimizing the energy is not easy. To this end,some researchers defined a periodic boundary condition which simplifies the computation and those not loose the physics of the problem in the process of doing so The plane wave basis set is employed,it has the form

$$u_{mk} = \sum_G e^{iG \cdot r} c_{mk}(G) \quad (2.37)$$

where  $G$  is the reciprocal lattice vector and  $c_{mk}$  is the Fourier component of the atomic orbitals.

The number of plane wave needed even when doing a simple calculation is large,this is due to rapid oscillation in the core region of the wavefunction which describes the valence electrons. A first attempt to avoid this difficulty will be to disregard the core electrons since they do not participate in the chemical properties of matter. It can be frozen around the nuclei and we can redefine the system to consist of valence electrons and ions. Another problem is how to deal with the oscillation in the core region of the valence wavefunction.This can be tackled by introducing pseudo potentials which take the place of the ionic Coulomb potential such that the valence pseudo eigenvalue values is equivalent to the all electron ones and the pseudo wavefunction also match with that of the all electron ones from a fixed core radius and are smooth below the core radius with the only constraint to be normalized(norm-conserving pseudo potentials).Many attempts have been made to illustrate pseudo wave function,ionic potential and valence wavefunction. From this attempts it was noted that the pseudo wavefunction and the all electron wavefunction and their corresponding pseudo potential and ionic potential are alike outside the cutoff radius  $r_c$ .There exist rapid oscillation of the all electron wavefunction near the core region while pseudo wavefunction is smooth In order to satisfy this condition,it is imperative that the pseudo wavefunction corresponding to different angular momenta are eigenfunction functions of different potentials.Also the long range behaviour of these different potentials must conform with the true ones.

In constructing pseudo potentials, we have the freedom to choose how many electrons to consider the core ones and how many to be in the valence region though it is recommended that one use those that have been tested and that can be accessed from the INTERNET in the site [www.pwscf.org](http://www.pwscf.org)

### **2.1.8 Density of states**

The density of state can be described as the number of allowed energy levels of that system per unit energy interval. The importance of density of states in many physical situations are enormous . This is because when we look at the states of a system that are occupied, the controlling factor is the energy of the states. This allows properties such as total energies to be derived from a knowledge of the density of states, as may changes of energy with temperature. It is also worthy of note that many properties in a Fermi system are specified by the number of electrons within a small energy of the Fermi surface-this fact is responsible for determining the density of state at the Fermi energy. The density of state at Fermi level also help in classifying materials-for instance, insulators have a zero density of state at Fermi energy while conductors have a non-zero one. We can estimate the density of states by calculating the energies of all the allowed states in the system. This is the case in liquids and crystalline and amorphous solids. It suffice to say the density of state at the Fermi level is an important parameter in the free electron model because only electrons in these state can participate in dynamic process such as electronic conduction.

### **2.1.9 The PWSCF program**

The study of vibrational properties and structure of matter can be done convincingly using Ab-initio methods of Density Functional Theory (DFT). Approximations such as LDA and GGA provides a platform which is accurate in describing structure of systems. DFT also has applications in calculation of phonon and other electronic and dynamic characteristics of a system. It is imperative to describe the computer program used in this work, it is PWSCF (plane -wave self-consistent field) and is a modular tool it is in modules and every module have a specific task it performs. For instance, the ground state energy minimization is handled by the pw.x program, it does this by obtaining

the best possible ground state electronic density  $n_o(\mathbf{r})$ . Also applying the ground state set of wave functions gotten from after the pw.x exercise, we can use the same program to obtain the electronic energies for an arbitrary set of kpoints. The ph.x takes care of phonon calculations.

# Chapter 3

## 3.1 Details of Computation

### 3.1.1 Methodology

The ground state electronic structure was calculated using the Density Functional Theory (DFT). The program Quantum Espresso [24] was used for all calculations. The single particle wavefunction were expanded using plane waves [27]. Exchange correlation effects were treated Generalized Gradient Approximation (GGA) [25] with the popular functional proposed by Perdew-Burke-Einzerhof. The electronic wavefunction was described using plane waves with kinetic energy cutoff of 30Ry and kinetic energy cutoff of 300Ry for charge density. Integration over the Brillouin zone was carried out using a  $10 \times 10 \times 8$  mesh of k points. The ultra soft pseudo potential [26] is employed in this work. Atomic positions in the structure were optimized to obtain equilibrium geometry. Convergence of the structure was achieved when the difference in total energy is less than  $10^{-6}$ eV and maximum force allowed on each atom is less than  $10^{-4}$ eV. Figure 3.1 shows the crystal structure of LiFeP. It has a tetragonal structure with space group  $P4/nmm$ , it comprises of alternating  $[Fe_2P_2]$  blocks which surrounds the Li atoms.



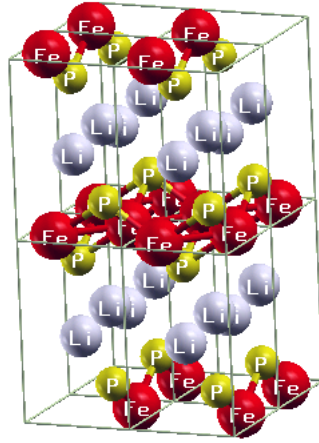


Figure 3.1: crystal structure of LiFeP

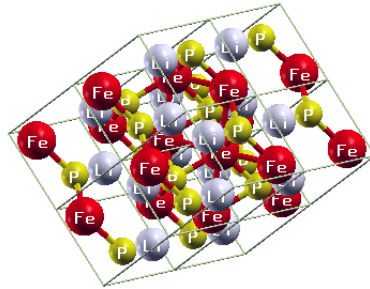


Figure 3.2: crystal structure of LiFeP

## 3.2 Results:Electronic properties

The LiFeP adopts the tetragonal crystal structure (space group). The experimentally obtained lattice constants are  $a=3.692\text{\AA}$  and  $c=6.031\text{\AA}$ . Values  $a=3.75$  and  $c=6.58$  were obtained from our minimization. This is not too far from the experimentally obtained values-Our value of ' $a$ ' is only 2% larger than the experimental one while ' $c$ ' is about 9% larger. The band structure of LiFeP with optimized geometry as calculated along the k points is as shown in figure 3.3. The total density of states and partial densities are as shown in figures 3.4, 3.5 and 3.6

From Fig.3.2,the first two bands (around  $-11\text{eV}$ ),the density of state(DOS) is almost completely contributed by P 3s orbitals.The gap between the near Fermi valence band and the two lowest band is about 4 eV.In the interval between 6 and 1.2eV the DOS is made by contributions from almost all atoms of LiFeP.

The electrons near the Fermi surface are responsible for the formation of superconducting state.The region near the Fermi level are formed by the states of  $[Fe_2P_2]$ .The quasi-core pnictogen s band was found to be about 2.5 eV in this work and 2.3eV in the work by I.Shein and A.Ivanovskii while the gap between the end of pnictogen s band to the band near Fermi level is about 6eV and the whole band occupy about 12.5eV which was about 12.4 eV in [12],The gap between the Fermi level to start of the edge of the pnictogen s band is about 6.0 in this work and 5.8 was obtained in see ref[12]

The electronic band structure was calculated along the direction  $\Gamma \rightarrow Z \rightarrow R \rightarrow X \rightarrow M \rightarrow A \rightarrow \Gamma$  where  $\Gamma = (0, 0, 0)$ ,  $Z = (0, 0, 0)$ ,  $R = (0, \frac{1}{2}, \frac{1}{2})$ ,  $X = (0, \frac{1}{2}, 0)$ ,  $M = (\frac{1}{2}, \frac{1}{2}, 0)$ ,  $A = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and  $\Gamma = (0, 0, 0)$ .The Fermi is at  $E=0\text{eV}$ . Clearly the material is a conductor—there is no band gap between the occupied  $(E<0)$  and  $(E>0)$  states.

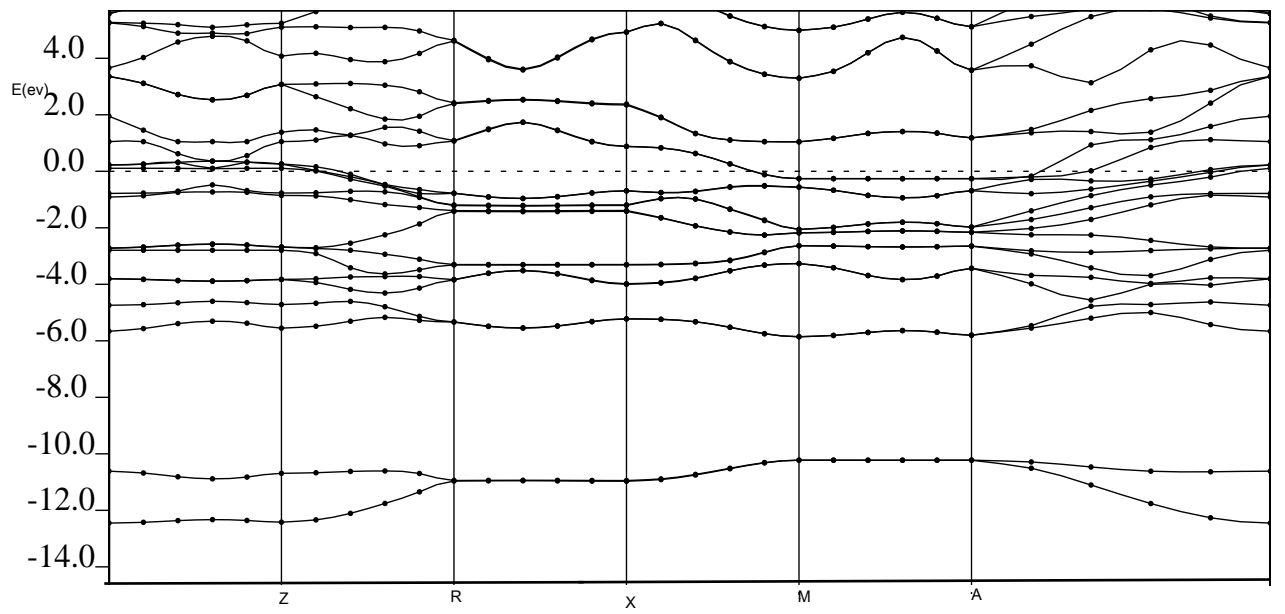


Figure 3.3: Electronic band structure of LiFeP

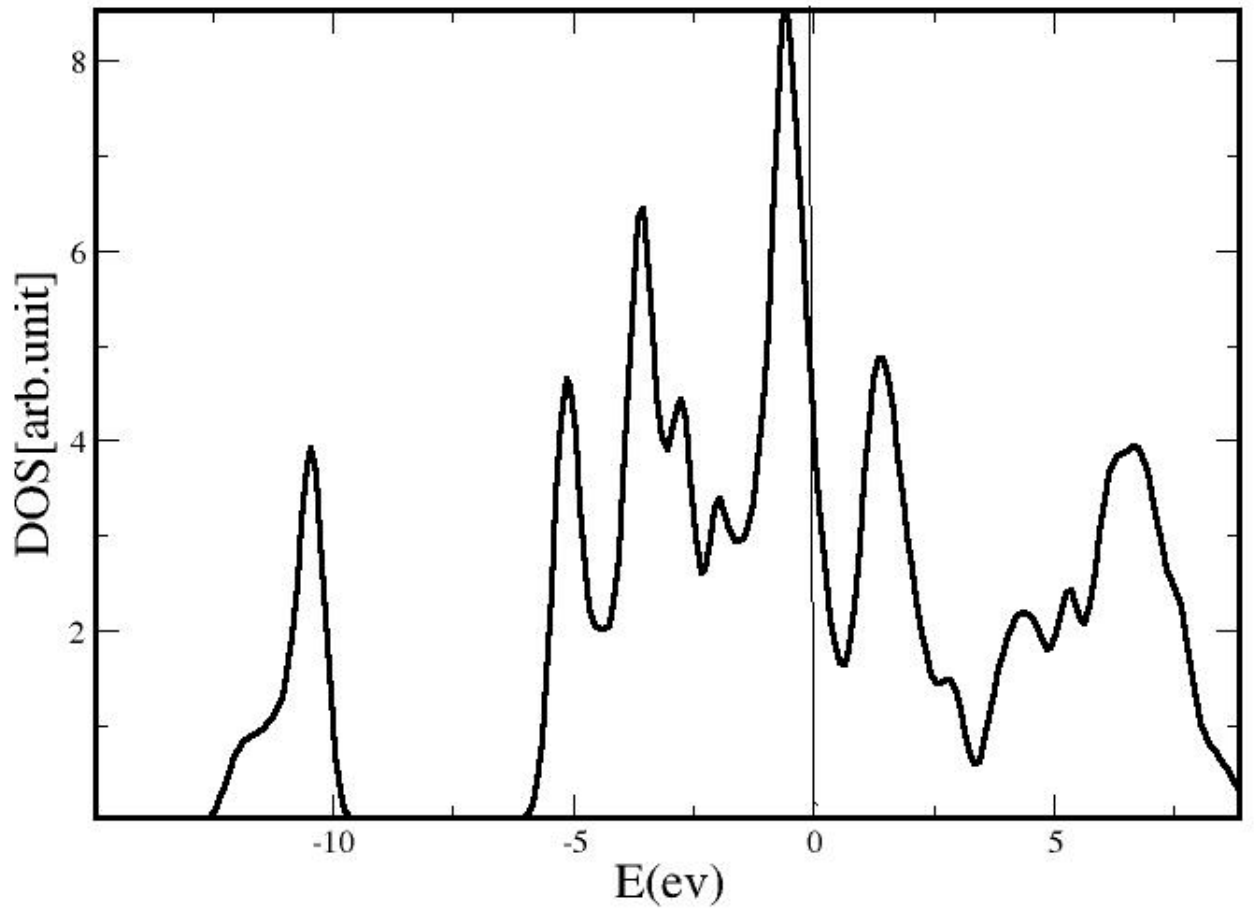


Figure 3.4: Total density of states of LiFeP

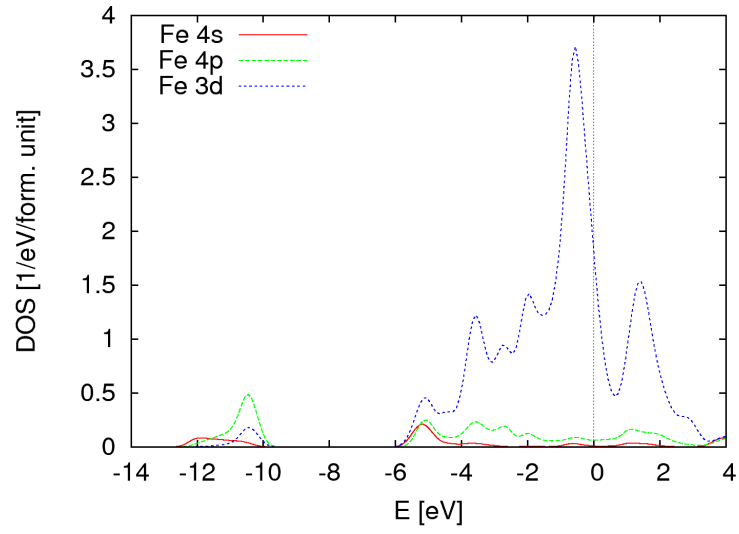


Figure 3.5: Partial density of states of LiFeP(Fe)

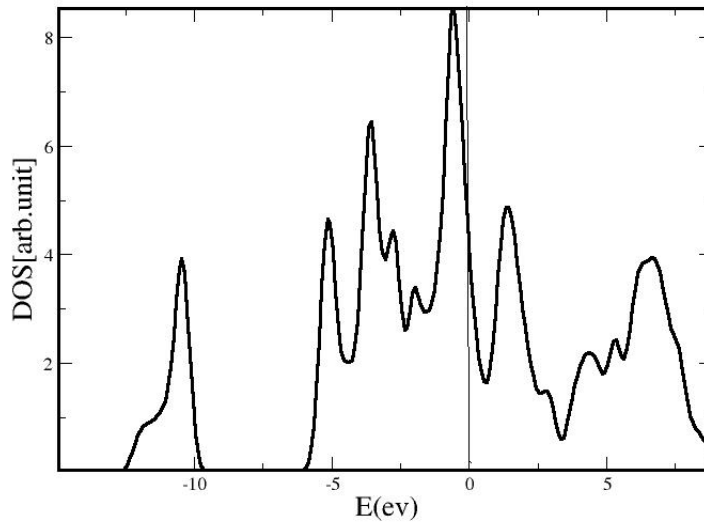


Figure 3.6: Total density of states of LiFeP

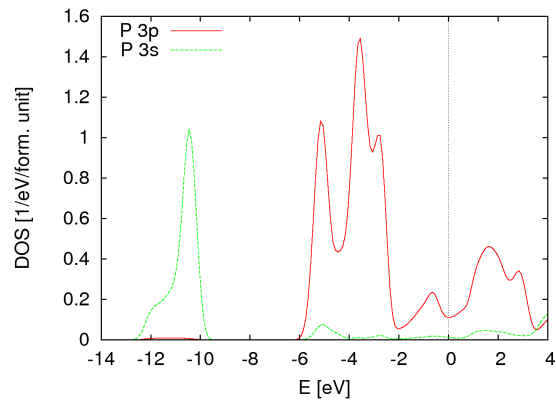


Figure 3.7: Partial density of states of LiFeP(P)

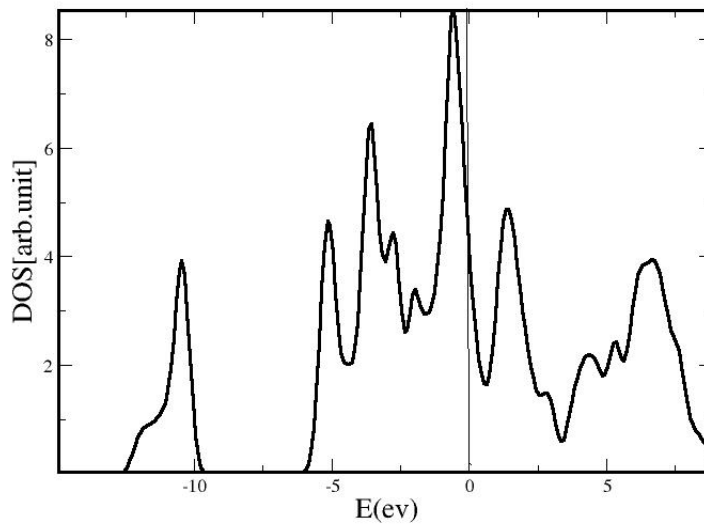


Figure 3.8: Total density of states of LiFeP

# Chapter 4

## 4.1 Phonons calculation

### 4.1.1 Normal vibrational modes

As earlier stated, phonons play a very important role in many physical properties of solids. The Born approximation (B-O) enables us to split the vibrational and electronic degrees of freedom. Treating the nuclei classically, the problem reduces to coupled classical equations of motion for each nuclear position  $R_I(T)$ ,

$$M_I \frac{\partial R_I}{\partial t^2} = F_I(R) = -\frac{\partial E(R)}{\partial R_I} \quad (4.1)$$

where  $M_I$  is the mass of the  $I^{\text{th}}$  nucleus and  $R_I$  is the coordinate.  $R$  indicates the set of all nuclear coordinates and  $E(R)$  is the B-O energy surface. At equilibrium  $R_I = R_I^o$ , this is determined by zero-force condition on each nuclei, i.e.  $F_I = 0$ . Within the harmonic oscillator approximation, the displacement  $U_I(t)$  can be described in terms of vibrational modes of frequency  $\omega$  as follows

$$U_I(t) = R_I(t) - R_I^o \equiv U_I e^{i\omega t} \quad (4.2)$$

Hence equation 4.1 can be written as

$$-\omega^2 M_I U_{I\alpha} = -\sum_{J\beta} C_{I,\alpha;J,\beta} \quad (4.3)$$

where  $\alpha, \beta$  indicates the Cartesian components and  $C_{I,\alpha;J,\beta}$  are elements of inter atomic force constant matrix given by

$$C_{I,\alpha;J,\beta} = \frac{\partial^2 E(R)}{\partial R_{I,\alpha} \partial R_{J,\beta}} \quad (4.4)$$

equations 4.3 and 4.4 combined gives vibrational frequency determined by

$$\det \left| \frac{1}{\sqrt{M_I M_J}} C_{I,\alpha;j,\beta} - \omega^2 \right| = 0 \quad (4.5)$$

## 4.2 Inter atomic force constants

Storing information contained in dynamical matrices can be achieved with the help of inter-atomic force constant (in real space). The real space force constants are powerful tools used for interpolating dynamical matrices through out the Brillouin zone. They are conveniently calculated by Fourier analyzing their reciprocal space counterpart which are being calculated on a finite grid. The number of q points in the finite grid is equivalent to the number of force constant obtained. Obtaining real space constant this way, reciprocal space dynamical matrices can be obtained by inverse Fourier transform.

## 4.3 Results

Calculation of dynamical matrix and inter atomic force constant was done and eigen values were calculated along the direction  $\Gamma \rightarrow Z \rightarrow R \rightarrow X \rightarrow M \rightarrow A \rightarrow \Gamma$  points. These points are defined in section 3.2. Figures 4.1 shows a plot of the phonon dispersions along symmetry lines. Figure 4.2 shows a plot of the phonon density of states. We noticed that the existence of a small gap of about  $25\text{cm}^{-1}$  which is equivalent to about 35 K in the phonon band structure, there also exist degeneracy in some states. Also from the DOS, there are more modes at higher frequency. The normal modes are shown in from Figures 4.3 – 4.21.

In Figures 4.3 – 4.21 showing the phonon modes, displacement of the three types of atoms (Li, Fe, p) occur in the first three modes hence translation is said to take place in this modes. All the other modes do not have all the atoms vibrating except mode 11. In mode 11 the Fe atoms move opposite to the direction of movement of the other atom types. This direction is reversed as we move from the top of the crystal to the bottom.



All atoms except Li atoms are at rest in modes 6,7 and 8 but while the Li atom in mode 8 is displaced in the same direction and exerting pressure on the planes beneath it,those in modes 6 and 7 change direction as we go down the plane and are directed horizontally,thereby causing the iron pnictogen plane to be at rest.

Fe and P atoms are displaced in modes 9 and 10 though with lesser displacement of the P atoms,the Fe atoms move in alternating direction as we proceed downwards.In modes 12 and 13,high displacement of the Li atoms occur but while only Li is displaced in 12,13 saw P atoms experiencing high displacement,with its Li atoms moving against each other. In modes 4 and 5,displacement of only the Li atoms in the same direction occur.

P atoms are displaced in the downward direction in 14 thereby exerting pressure on the Li atoms,and displacement of the Fe atoms also noticed.With greater displacement of the P atoms,modes 15 and 16 saw P and Fe moving in opposite direction while Li is at rest. In mode 18 Li atoms are at rest here with the pnictogen planes moving,though their direction of movement is alternating as we go downwards.

In summary,the Li appears to be largely decoupled from the iron pnictogen plane even though we observed that the P atoms are also decoupled from the Fe plane in some modes.

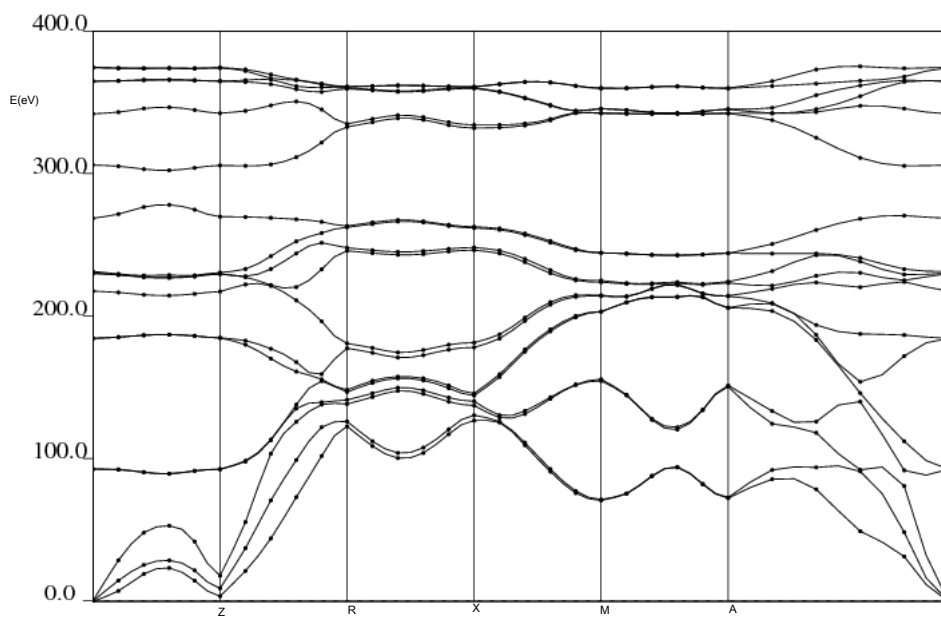


Figure 4.1:

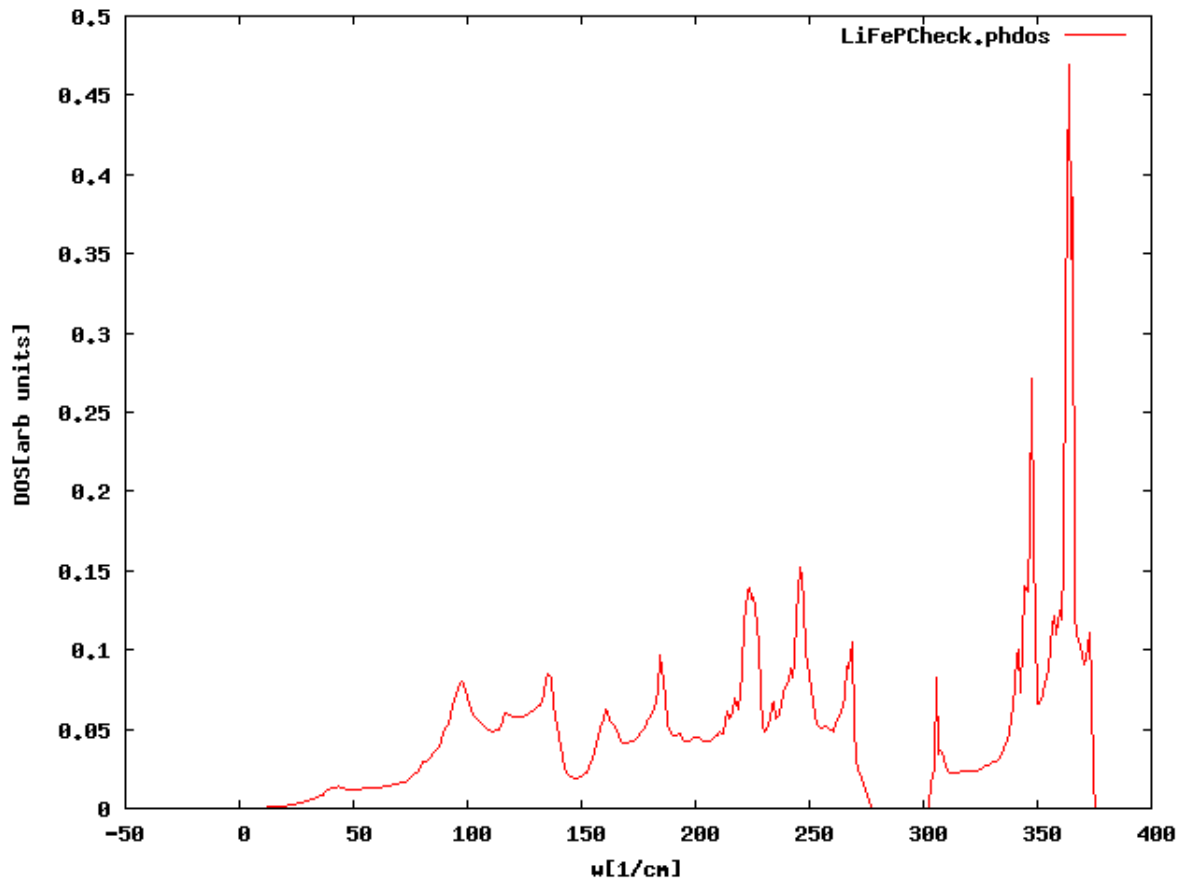


Figure 4.2: Phonon dispersion in LiFeP

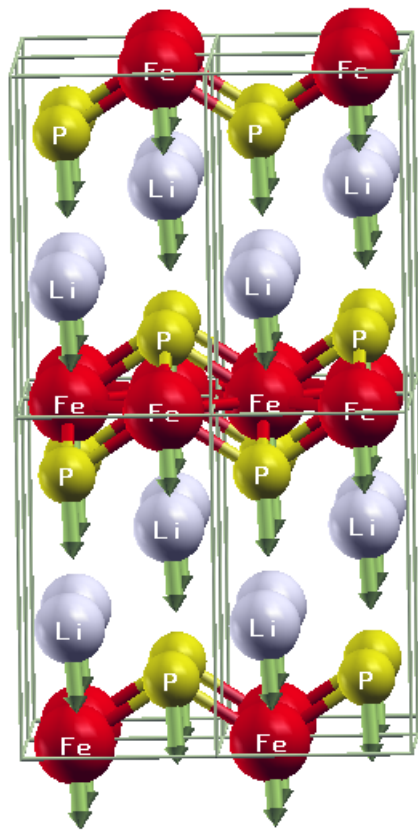


Figure 4.3: Phonon model

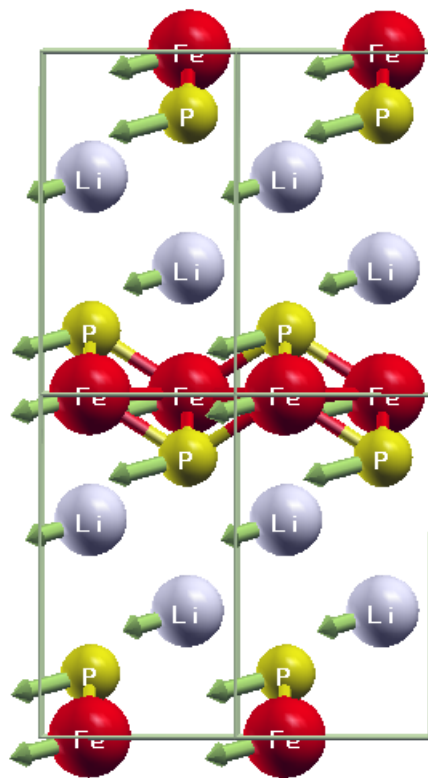


Figure 4.4: Phonon mode 2

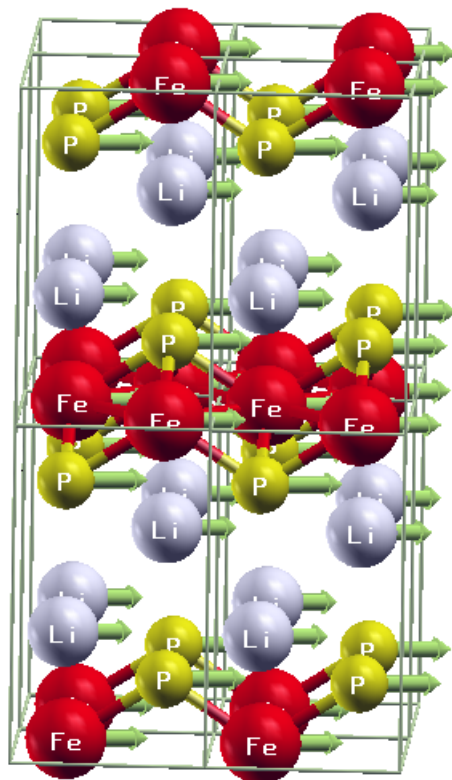


Figure 4.5: phonon mode3

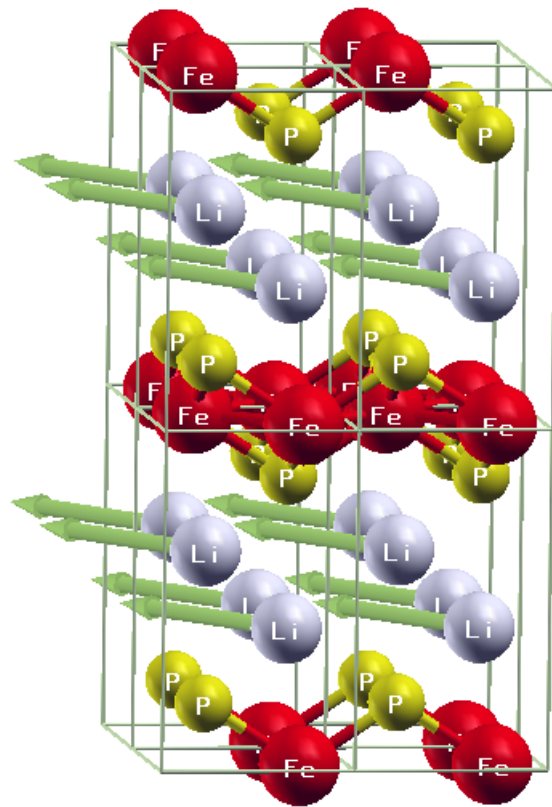


Figure 4.6: Phonon mode4

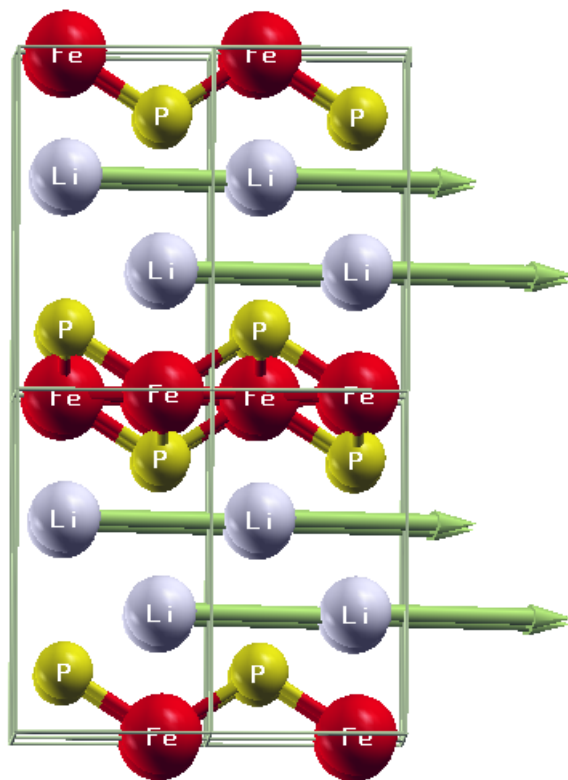


Figure 4.7: Phonon mode 5



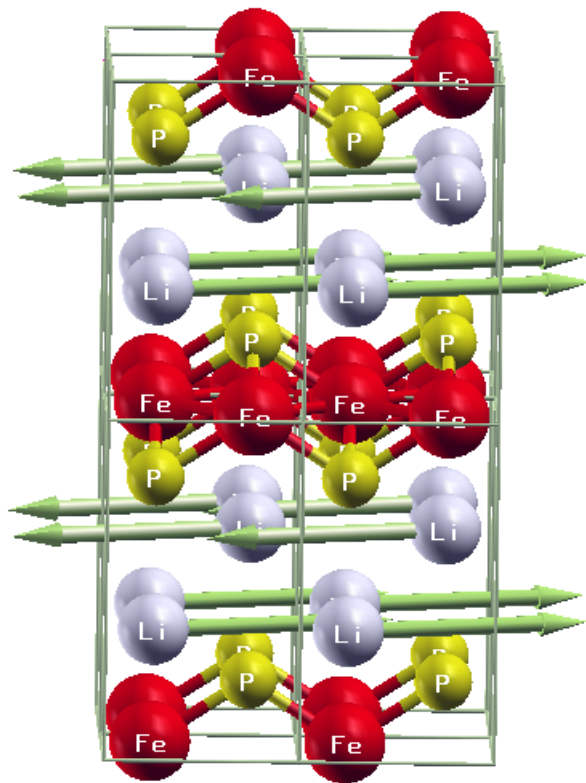


Figure 4.8: Phonon mode 6

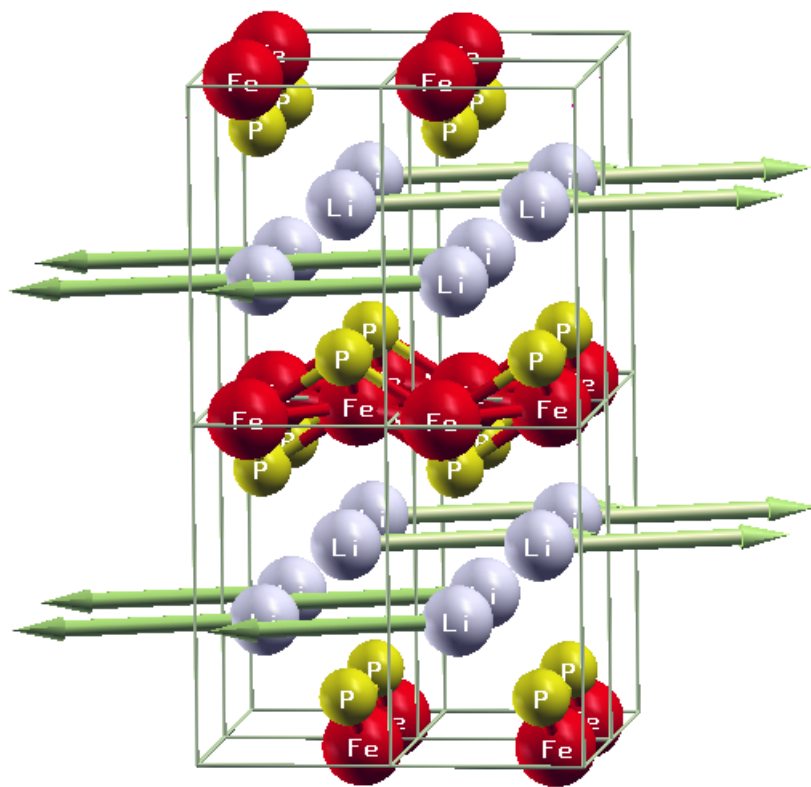


Figure 4.9: Phonon mode 7

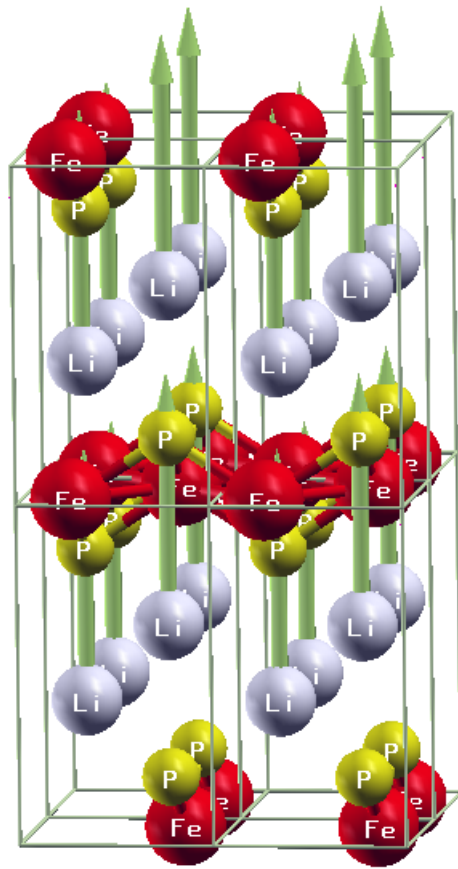


Figure 4.10: Phonon mode 8

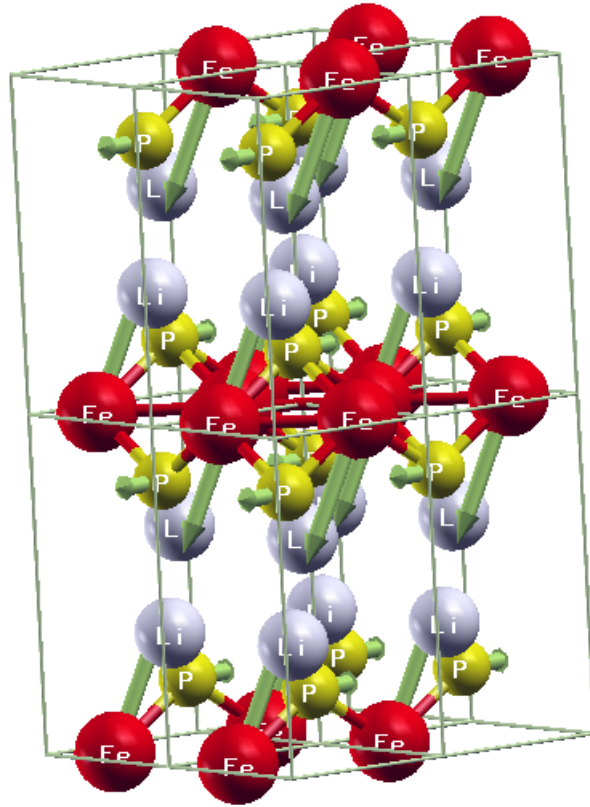


Figure 4.11: Phonon mode 9

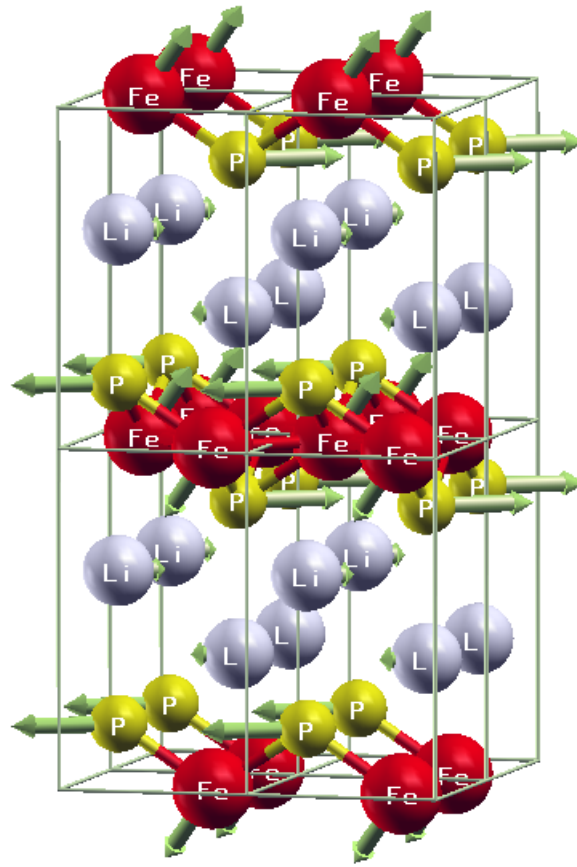


Figure 4.12: Phonon mode 10

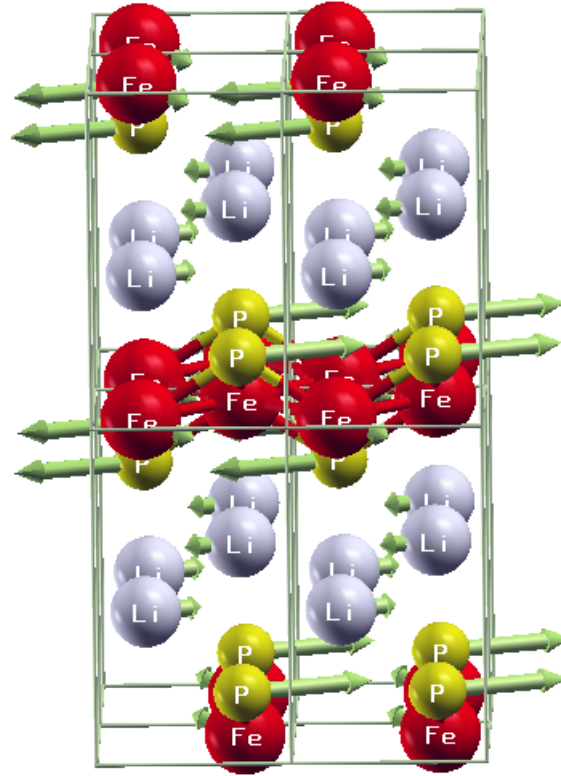


Figure 4.13: Phonon mode 11

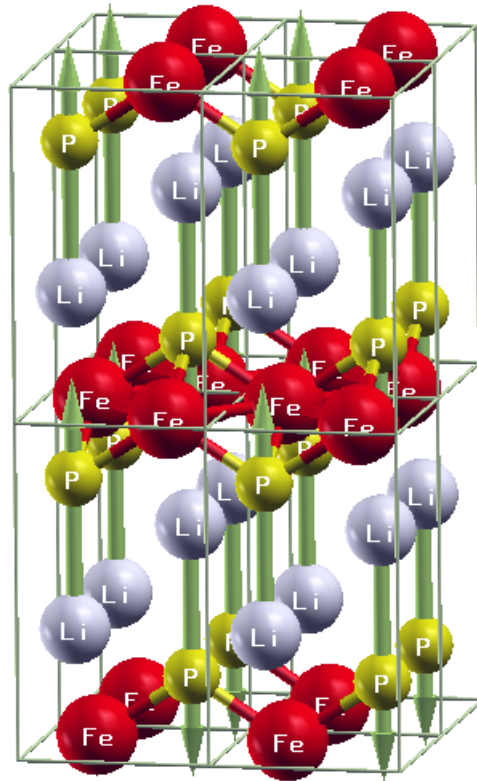


Figure 4.14: Phonon mode 12

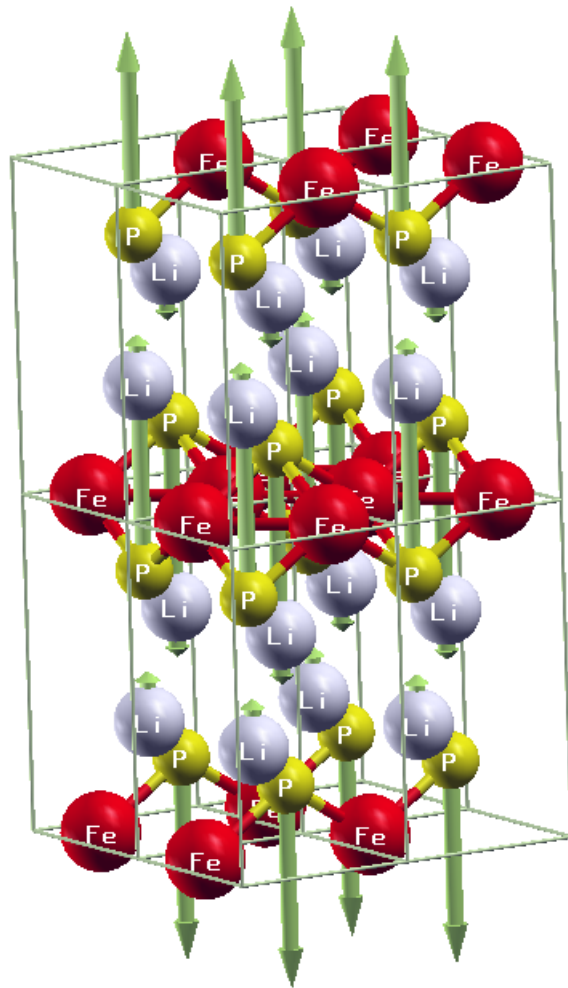


Figure 4.15: Phonon mode 13



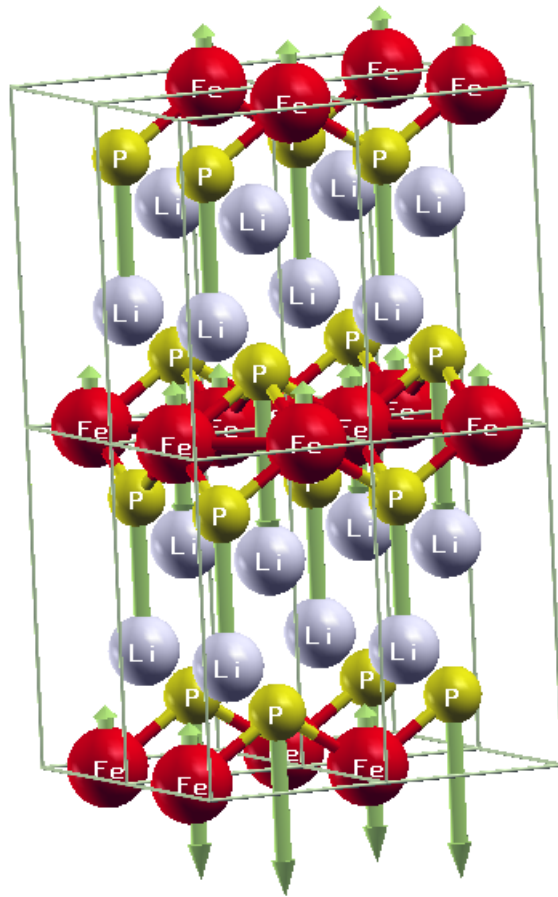


Figure 4.16: Phonon mode 14

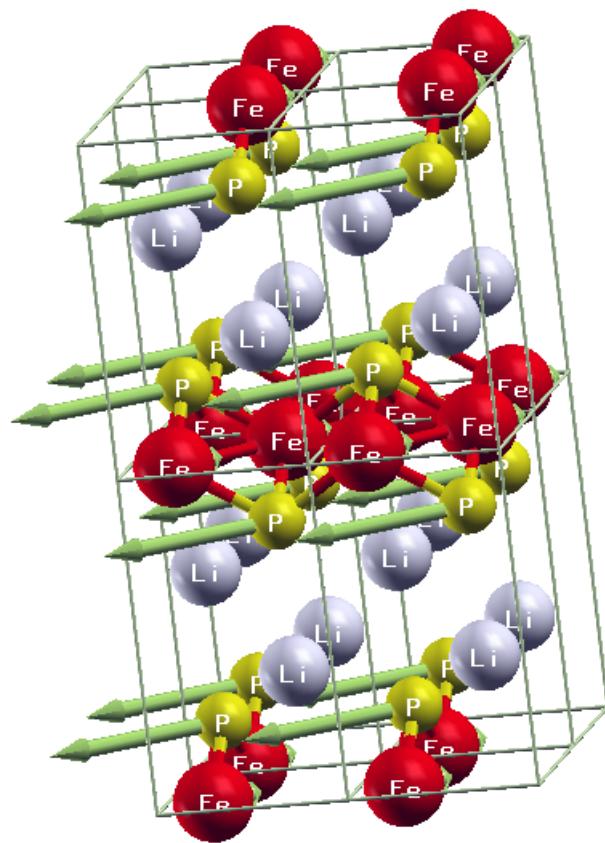


Figure 4.17: Phonon mode 15

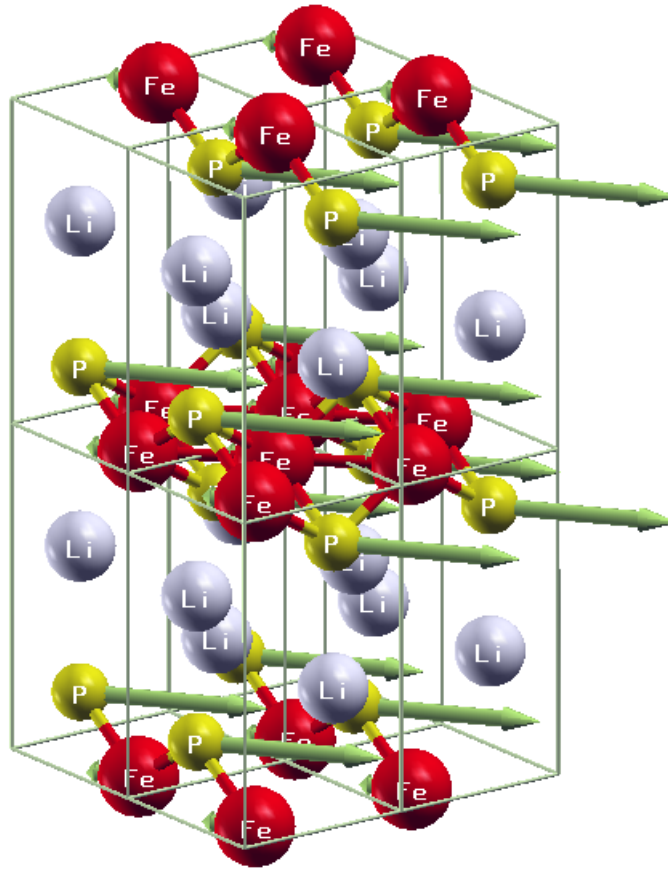


Figure 4.18: Phonon mode 16

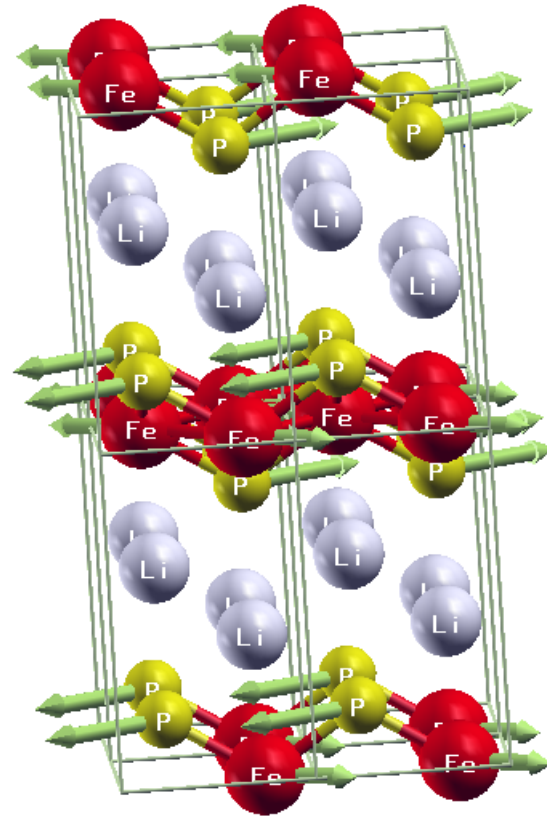


Figure 4.19: Phonon mode 17

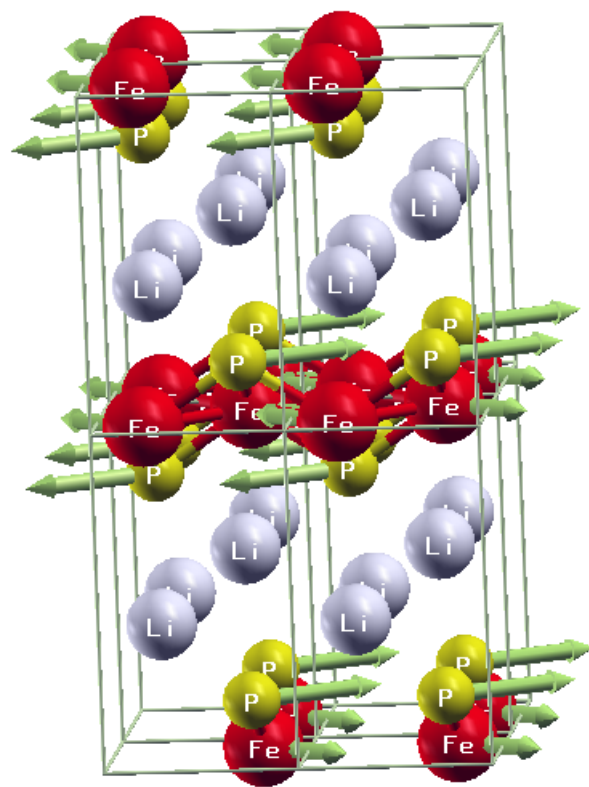


Figure 4.20: Phonon mode 18

# Chapter 5

## Conclusion

In conclusion, we have presented our studies on the electronic properties and phonons of the iron pnictide LiFeP. We obtained the density of state and band structure along high symmetry points. Phonon dispersion and phonon modes of the material were also examined. We also described the displacement and direction of movement for each phonon mode.

The values obtained from the electronic band calculations were found to conform with those from previous work cited in this work. Further work is necessary to examine the effect of electron-phonon coupling and its effect on superconductivity in LiFeP—for the electron-phonon coupling was found to be too weak to produce the relatively large  $T_c$  in other materials. Thus, other mechanisms may be responsible for superconductivity in these materials. Whether this is also the case for LiFeP or not is yet to be determined.

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