Doping and Defects in the Charge Density Wave of a 1D/3D Model of $BaBiO_3$

Rahul Bhargava

The Wheatley School

Old Westbury, NY 11568

I. INTRODUCTION

The compound $BaBiO_3$ is a three-dimensional lattice cube with distorted perovskite structure. If the ionic charge on bismuth is calculated, with barium as Ba^{+2} and oxygen as O^{-2}, bismuth in an undistorted $BaBiO_3$ structure becomes Bi^{+4}. Due to natural laws, bismuth's five valence electrons are distributed as follows: $6s^2 6p^3$. The removal of four electrons in order to form Bi^{+4} causes the valence shell to simply become $6s^1$. The presence of a lone electron in the valence shell is unstable for an atom. Bismuth would prefer to either rid itself of that lone electron or attract another electron to form a pair. Hence in $BaBiO_3$, an alternating pattern of Bi^{+3} and Bi^{+5} develops, due to a transfer of electrons between neighboring bismuth atoms[1]. The oxygen atoms with a negative two charge are attracted to the Bi^{+5} site. The relationship between the electron transfer and movement of the oxygen atoms, or phonon, is called electron-phonon coupling. In this paper, the strength of this coupling will be referred to as the electron-phonon coupling constant. With half the bismuth sites occupied by electrons and half unoccupied, it is therefore accurate to describe pure $BaBiO_3$ as a three-dimensional cube with simple lattice dimerization.

$BaBiO_3$ can be doped with K on the Ba sites. The K atom has one $4s$ electron in its valence shell, and hence becomes K^+ in the compound. In essence each time K replaces Ba, one electron is removed from the compound. This electron can be removed only from the Bi^{3+} site, which produces a positively charged hole in the compound known as a polaron. It has been shown that if the compound is doped twice, the second electron is removed from the same site[3], forming a hole known as a bipolaron. It is highly reasonable to attribute the formation of polarons and bipolarons to electron-phonon coupling[4]. This project studies the formation of polarons and bipolarons and other similar defects in the lattice structure and the effects of electron-phonon coupling on their formation.
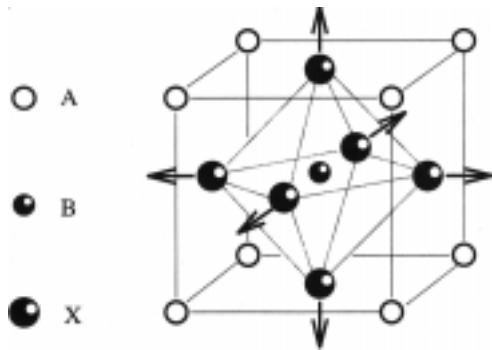
FIG. 1. The structure of a dimerized ABX_3 perovkite. A is a larger cation, B is a smaller cation, and X is an anion. The larger cation A usually has smaller positive charge than cation B.[2]

Although $BaBiO_3$ is a real-world solid, and hence three-dimensional, it behaves in a quasi-one dimensional manner. Therefore an examination of this compound through a one-dimensional model has many considerable benefits. Rice and Sneddon[5] introduced a $d = 3$ model for $BaBiO_3$. The $d = 1, 3$ models that are used in this project are based on the model developed by Rice and Sneddon. Since only the electrons of bismuth and the oxygen atoms in $BaBiO_3$ have any significance, the models consist of alternating bismuth and oxygen atoms. Due to the fact that the atomic mass of bismuth is 13.06 times greater than oxygen's atomic mass, the Bi atoms in the models are in a fixed position and the O atoms are coupled to the Bi atoms by a harmonic spring. Like in the real world, if two atoms in the models move too far apart, the spring is stretched and tries to pull them back; if the atoms move too close, the spring is compressed and tries to push the atoms apart.

On average, the charge on each Bi atom in the lattice is +4. The negatively charged oxygen ions are attracted to the Bi atoms with excess positive charge. The energy gained when the oxygen atoms move towards these Bi atoms is proportional to the excess charge and the displacement, u_n, which measures oxygen movement from the midpoint of two neighboring Bi atoms. The coefficient of proportionality is the electron-phonon coupling constant, g.

The valence shell of Bi in $BaBiO_3$ on average has one $6s$ electron. The wave function

of this electron overlaps with the corresponding wave function on the neighboring Bi atoms. This overlap allows an electron to move to a neighboring Bi site. The energy gained by this hopping is proportional to the overlap integral, defined in the model as t. If the $6s$ valence shell of the Bi atom is doubly occupied, the electrons will repel each other due to Coulomb interactions. Coulomb force is ignored in our models since it is believed Coulomb forces are small in this compound[4].

The Hamiltonian is a matrix operator that describes the energy in quantum mechanics. The Hamiltonian is of the form,

$$\mathcal{H} = \mathcal{H}_0 = \mathcal{H}_t + \mathcal{H}_{e-ph} + \mathcal{H}_{ph} \tag{1}$$

where H_t, H_{e-ph}, and H_{ph}, are the hopping, electron-phonon, and phonon terms, respectively. As explained above,

$$\mathcal{H}_t = -t \sum_{i=1}^{N} \left(c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i \right) \tag{2}$$

$$\mathcal{H}_{e-ph} = -g \sum_{i=1}^{N} \left(u_{i-1} - u_i \right) c_i^\dagger c_i \tag{3}$$

$$\mathcal{H}_{ph} = \sum_{i=1}^{N} \left(\frac{1}{2} k u_i^2 \right) \tag{4}$$

Energy is measured in units of the hopping parameter, t and displacements are measured in units of $\sqrt{t/k}$. Therefore, the Hamiltonian can be rewritten in dimensionless units of $\tilde{u}$ as

$$\mathcal{H} = -1 \sum_{i=1}^{N} \left(c_i^\dagger c_{i+1} + \mathrm{HC} \right) + -\sqrt{\Gamma} \sum_{i=1}^{N} \left(\tilde{u}_{i-1} - \tilde{u}_i \right) c_i^\dagger c_i + \sum_{i=1}^{N} \left(\frac{1}{2} k \tilde{u}_i^2 \right) \tag{5}$$

where, $\Gamma = g^2/kt$.

The definition of the Hamiltonian operator allows for the use of the Shroedinger Equation of the form

$$\mathcal{H} |\lambda\rangle = \varepsilon_\lambda |\lambda\rangle \tag{6}$$

in order to find all the eigenvectors and eigenvalues of the system.

If the oxygen atoms were forced to be undisplaced (this occurs naturally when $\Gamma = 0$), then the density of states would be similar to the diagram in Figure 2. Each eigenvalue in the eigenvalue spectrum would have double degeneracy. However if the oxygen atoms were allowed to be displaced, the degenerate eigenvalues would separate into two states, with one of the two states having lower energy than the degenerate eigenstate, as shown by Jahn-Teller. The density of states diagram of the ground state of $BaBiO_3$ thus develops a gap, Δ, between the valence band and the conduction band. (See Figure 2.) The presence of this gap causes $BaBiO_3$ to be a prototype $d = 3$ Peierls insulator.
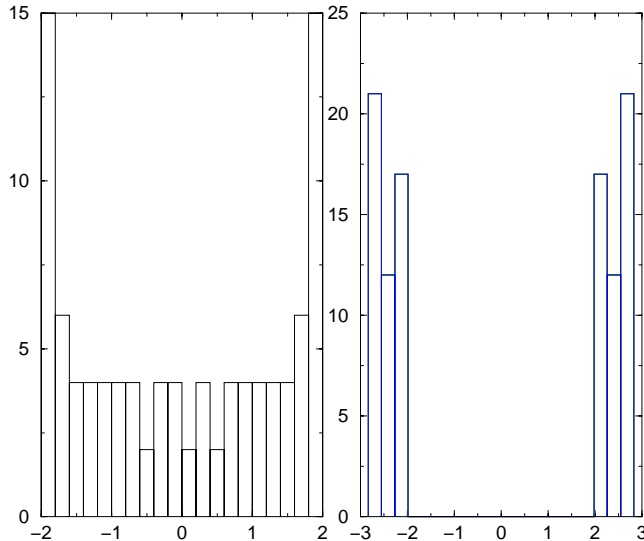

FIG. 2.

$Ba_{1-x}K_xBiO_3$ remains insulating up to $x = 30\%$ doping concentration. At this level, a metal-insulator transition occurs and $BaBiO_3$ becomes superconducting at temperatures below $30K$, the highest superconductor transition temperature for any oxide superconductor not containing copper[6-9]. Any K concentration less than 30% is not enough for the carriers donated by the dopants to escape being trapped into localized polaron or bi-polaron states at or near the Fermi Level.

II. METHODOLOGY

A. 1D Model

The model of $BaBiO_3$ was created using computer simulation. An entire simulation was written in the MICROSOFT VISUAL C++ language to model the solid. With bismuth atoms assigned a fixed position, only the oxygen atoms are allowed to move in the model. Thus, the system is fully solved when the optimum positions of the oxygen atoms are determined. The optimum positions of the oxygen atoms are the positions for which the solid has the lowest energy.

To facilitate analyzing of the data and speed computer calculations, the oxygen displacements are measured in dimensionless units $\tilde{u}$ and the spring constant k and hopping term t are set to 1 and -1 respectively. The model has three input parameters: the number of Bi atoms (equivalent to the number of O atoms), N, the number of electrons, N_x, and the electron-phonon coupling constant, Γ. The number of holes is defined to be $N - N_x$. Hence, when $N = N_x$, the system is said to have no holes, or half filled.

After the value of each parameter is assigned, the initial positions of the oxygen atoms are determined. This can be done in several ways. One way would be to have the oxygen atoms undisplaced, lying at the midpoints between neighboring bismuth atoms. Random displacements could be used, moving the oxygen atoms random amounts in random directions. Also, two-fold or four-fold periodic initial positions can be used. These types of initial positions would be more similar to the oxygen positions found in the real-world. In this project, all four initial positions were used in simulations. With the oxygen positions determined, the $N \times N$ Hamiltonian was constructed. Using algorithms from $Numerical\ Recipes\ for\ C$[10], the Hamiltonian matrix is diagonalized and the eigenvalues, denoted by ε_λ, and eigenvectors, denoted by $|\lambda\rangle$, of the system are determined using the Shroedinger Equation (6). An eigenvector can be written as a linear combination of the form, $|\lambda\rangle = \alpha|\lambda_1\rangle + \beta|\lambda_2\rangle$ By convention, α and β are chosen such that $\alpha^2 + \beta^2 = 1$. This relationship means that

$\langle \lambda | \lambda \rangle = \alpha^2 + \beta^2 = 1$ When this is true, the eigenvectors are said to be normalized. One of the important properties of normalized eigenvectors is

$$\sum_{n=1}^{N} |\langle n | \lambda \rangle|^2 = 1 \tag{7}$$

The energy of the solid can then be calculated as follows:

$$E = 2 \sum_{\lambda=1}^{\left[\frac{N_x}{2}\right]} \varepsilon_\lambda + \sum_{i=1}^{N} \frac{\tilde{u}_i^2}{2} \tag{8}$$

where $[x]$ is the greatest integer less than or equal to function. A third term, $\varepsilon_{[N_x/2]+1}$ has to be added on if $[N_x/2]$ does not equal $N_x/2$. Note that there is no coefficient of two in front of this term since this state is only occupied by one electron, and not two.

As stated previously, the system has been solved when the energy is at the global minimum. The problem of global minimization has been one that has drawn the attention of mathematicians and physicists alike. While there is no one single algorithm that works perfectly, several algorithms have been developed that find accurate local minima which are believed to be the global minimum. The algorithm that was used in this project used the concepts of calculus. Let $(\tilde{u}_1, \tilde{u}_2, ..., \tilde{u}_N) = |\tilde{u}\rangle$ and a function $F(|\tilde{u}\rangle) = E$, where E is the energy. The goal is to minimize F. It is not known for what oxygen displacements F attains its minimum value. Let $(\tilde{u}_1^0, \tilde{u}_2^0, ..., \tilde{u}_N^0) = |\tilde{u}^0\rangle$ be the optimum oxygen displacements. Using the Taylor Formula for multi-dimensional variables,

$$\begin{aligned} F(|\tilde{u}\rangle) = {} & F\left(|\tilde{u}^0\rangle\right) + \frac{\partial F}{\partial \tilde{u}_1}\left(\tilde{u}_1 - \tilde{u}_1^0\right) + \frac{\partial F}{\partial \tilde{u}_2}\left(\tilde{u}_2 - \tilde{u}_2^0\right) + \frac{\partial F}{\partial \tilde{u}_N}\left(\tilde{u}_N - \tilde{u}_N^0\right) \\ & + \frac{1}{2!}\left[\left(\tilde{u}_1 - \tilde{u}_1^0\right)\frac{\partial^2 F}{\partial \tilde{u}_1 \tilde{u}_1}\left(\tilde{u}_1 - \tilde{u}_1^0\right) + \left(\tilde{u}_1 - \tilde{u}_1^0\right)\frac{\partial^2 F}{\partial \tilde{u}_1 \tilde{u}_2}\left(\tilde{u}_2 - \tilde{u}_2^0\right) + \cdots \right. \\ & + \left(\tilde{u}_1 - \tilde{u}_1^0\right)\frac{\partial^2 F}{\partial \tilde{u}_1 \tilde{u}_N}\left(\tilde{u}_N - \tilde{u}_N^0\right) + \left(\tilde{u}_2 - \tilde{u}_2^0\right)\frac{\partial^2 F}{\partial \tilde{u}_2 \tilde{u}_1}\left(\tilde{u}_1 - \tilde{u}_1^0\right) + \cdots \\ & \left. + \left(\tilde{u}_N - \tilde{u}_N^0\right)\frac{\partial^2 F}{\partial \tilde{u}_N \tilde{u}_N}\left(\tilde{u}_N - \tilde{u}_N^0\right) \right. \end{aligned}$$

Let,

$$\begin{aligned} \overrightarrow{\nabla F} &= \left(-\frac{\partial F}{\partial \tilde{u}_1}, -\frac{\partial F}{\partial \tilde{u}_2}, \cdots, -\frac{\partial F}{\partial \tilde{u}_N}\right) \\ \overrightarrow{\Delta u} &= \left(\tilde{u}_1^0 - \tilde{u}_1, \tilde{u}_2^0 - \tilde{u}_2, \cdots, \tilde{u}_N^0 - \tilde{u}_N\right) \\ A_{ij} &= \frac{\partial^2 F}{\partial \tilde{u}_i \partial \tilde{u}_j} \end{aligned}$$

where, $\overrightarrow{\nabla F}$ is defined as the force on the oxygen atoms and $\overrightarrow{\Delta u}$ is defined as the difference between successive oxygen displacements. Then,

$$F\left(|\tilde{u}\rangle\right) = F\left(|\tilde{u}^0\rangle\right) + \left(\overrightarrow{\nabla F}\,\overrightarrow{\Delta u}\right) + \frac{1}{2!}\overrightarrow{\Delta u}A\overrightarrow{\Delta u}$$

If the partial derivative of F with respect to $\overrightarrow{\Delta u}$ equals zero, then $|\tilde{u}\rangle = |\tilde{u}^0\rangle$ and the optimum solution has been found. Thus,

$$\begin{aligned}
\frac{\partial F}{\partial \overrightarrow{\Delta u}} &= 0 \\
\frac{\partial F}{\partial \overrightarrow{\Delta u}} &= \overrightarrow{\nabla F} + A\overrightarrow{\Delta u} = 0 \\
A\overrightarrow{\Delta u} &= \overrightarrow{\nabla F} \\
\overrightarrow{\Delta u} &= A^{-1}\overrightarrow{\nabla F}
\end{aligned} \tag{9}$$

The A matrix is proportional to the unit matrix when the oxygen atoms are still at the initial positions. After the first displacement, the Broyden-Fletcher-Goldtarb-Shanno (BFGS) algorithm is used to calculate the A matrix. This algorithm can be found in $Numerical$ $Recipes\ for\ C$. The force, as defined previously, is the negative derivative of the energy. Thus, the force on the ith oxygen atom is equal to (when N_x is even):

$$\begin{aligned}
\overrightarrow{\nabla F_i} &= -\frac{d}{d\tilde{u}_i}\left[2\sum_{\lambda}^{\frac{N_x}{2}}\varepsilon_\lambda + \sum_{j}^{N}\frac{\tilde{u}_j^2}{2}\right] \\
&= -\left[2\sum_{\lambda}^{\frac{N_x}{2}}\frac{d\varepsilon_\lambda}{d\tilde{u}_i} + \tilde{u}_i\right]
\end{aligned}$$

It is now necessary to find the derivative of an eigenvalue with respect to the ith oxygen displacement. Due to the symmetry of the Hamiltonian matrix, the principle of ortho-normality can be used to find the required derivative. This principle states that $\langle\lambda'|\lambda\rangle = \delta$, where $\delta = 1$ when $\lambda' = \lambda$ and $\delta = 0$ otherwise. Using the Shroedinger Eq. (6),

$$\begin{aligned}
\langle\lambda|H|\lambda\rangle &= \varepsilon_\lambda\langle\lambda|\lambda\rangle = \varepsilon_\lambda \\
\frac{d\varepsilon_\lambda}{d\tilde{u}_i} &= \frac{d}{d\tilde{u}_i}\langle\lambda|H|\lambda\rangle
\end{aligned}$$

Applying the chain rule for derivatives gives $d\varepsilon_\lambda/d\tilde{u}_i = \langle\lambda|dH/d\tilde{u}_i|\lambda\rangle+$ two other terms, which by the Feynman Theorem are known to equal zero. Since the term $\tilde{u}_i$ appears only twice in the Hamiltonian,

$$\frac{dH}{d\tilde{u}_i} = \begin{vmatrix} 0 & \cdots & & 0 \\ & -\sqrt{\Gamma} & & \cdots \\ 0 & & \sqrt{\Gamma} & \cdots \\ & \cdots & & 0 \end{vmatrix}$$

Let,

$$|\lambda\rangle = (\phi_1, \phi_2, \cdots, \phi_N)$$

Then,

$$\left\langle \lambda \left| \frac{dH}{d\tilde{u}_i} \right| \lambda \right\rangle = -\sqrt{\Gamma}\left(\phi_i^2 - \phi_{i+1}^2\right)$$

Thus $\overrightarrow{\nabla F_i} = -\sqrt{\Gamma}\left(\rho_i - \rho_{i+1}\right)$, where

$$\rho_i = 2\sum_{j=1}^{[\frac{N_x}{2}]} \left(\langle i|\lambda_j\rangle\right)^2 \tag{10}$$

If the number of electrons is odd, then an additional term, $\langle i|\lambda_{[N_x/2]+1}\rangle^2$ must be added.

Thus knowing the force, $\overrightarrow{\nabla F_i}$ and matrix A, the displacement vector, $\overrightarrow{\Delta u}$, can be calculated using Equation (9). The Hamiltonian is then reconstructed and the whole procedure is repeated. The procedure is stopped once the scalar product of the force vector is equal to zero, meaning the final oxygen atom positions have been found.

The determination of the oxygen positions allows for several interesting calculations to be made regarding the system. The charge density describes the probability of finding a certain number of electrons on a particular bismuth atom. The charge, ρ, or electron occupation on the ith bismuth atom is the sum of the squares of the occupied wave functions for that particular site (10). The charge density wave (CDW) is repeated periodically charge distribution on Bi atoms.

Another useful and interesting calculation that can be made is the inverse participation ratio (IPR). Given the eigenvector $|a\rangle$, $\langle n|a\rangle$ is the amplitude of the ath wave function on the nth atom. Hence, $|\langle n|a\rangle|^2$ is the probability that an electron in the ath state is located on the nth atom. By, taking the sum of $|\langle n|a\rangle|^4$ for all values of n from 1 to N, the inverse participation ratio of each eigenstate is found. A graph of inverse participation ratio versus eigenvalue describes the eigenvalues spectrum as well as how localized or delocalized a state is. For example, if every eigenstate is equally present on each site (delocalized), the IPR would equal $N \cdot |\langle n|a\rangle|^4 = 1/N$. This is a fairly small value for large values of N. On the other hand, if an eigenstate was very localized on one Bi atom n', the IPR would be approximately 1.

Two primary doping level cases are examined: half-filled, and two holes. The value of Γ in each case ranges from 0.0 to 1.0. For the half-filled case, the relationship between Δ and Γ is carefully studied, as well as the energy landscape of the compound. For the two hole case, defects in the CDW and localized states in the IPR vs. Energy graph are closely analyzed.

B. 3D Model

The primary input parameters are three translational vectors that define the shape, size, and symmetry of the lattice. The translational vectors are of the form

$$\bar{A} = (m_1, m_2, m_3)$$
$$\bar{B} = (l_1, l_2, l_3)$$
$$\bar{C} = (n_1, n_2, n_3)$$

Hence,

$$N = abs \begin{vmatrix} m_1 & m_2 & m_3 \\ l_1 & l_2 & l_3 \\ n_1 & n_2 & n_3 \end{vmatrix}$$

The eight vertices of the cubic lattice are the linear combinations of the three translational vectors. Since a plane is determined by three points, choosing three vertices, (x_1, y_1, z_1), (x_2, y_2, z_2), and (x_3, y_3, z_3), the equation of each of the six planes can be found by

$$
\begin{vmatrix} y_1 & z_1 & 1 \\ y_2 & z_2 & 1 \\ y_3 & z_3 & 1 \end{vmatrix} x +
\begin{vmatrix} z_1 & x_1 & 1 \\ z_2 & x_2 & 1 \\ z_3 & x_3 & 1 \end{vmatrix} y +
\begin{vmatrix} x_1 & y_1 & 1 \\ x_2 & y_2 & 1 \\ x_3 & y_3 & 1 \end{vmatrix} z -
\begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = 0
$$

By constructing a cube that completely encompasses the unit cell, and testing each point inside the larger cell to determine whether it is inside the unit cell, the positions of the N atoms are found. A point is said to be inside the unit cell if the value of the equation of the planes, front, left, and bottom faces, is non-negative, and the value of the equation of the planes, back, right, top faces, is negative.

To account for the hopping integral term in the Hamiltonian , the position of the neighbors of each Bi atom are determined. There are a total of six neighbors; three in the positive x, y, and z direction and three in the negative x, y, and z direction. By taking an atom and adding/subtracting one from its x (and likewise y and z) coordinate, the neighbor of that atom in the positive and negative x direction is found by searching for the ith Bi atom with that coordinate. In the case of a Bi atom located on the edge of the cell, the translational vectors were added/subtraced from the coordinate of the Bi atom. With the position of the neighbors determined, the Hamiltonian can thus be constructed.

III. RESULTS

A. Half-Filled Case

The gap in the density of states diagram, referred to as Δ, is significant with regard to the compound's superconductivity since an electron has to travel across this gap to reach the conduction band. Figure 3 is the graph of Δ versus Γ.
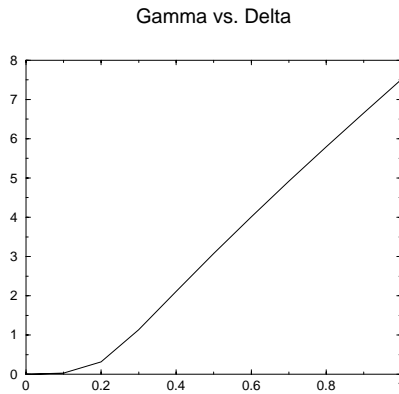
FIG. 3.

Much of the energy landscape of $BaBiO_3$ is not known. While Figure 3 shows the energy of the compound in its ground state for different values of Γ, there are several meta-stable states that have interesting defects in the CDW. By assigning oxygen atoms random initial positions, the model produced many of these higher energy states. The defects always came in pairs; there was a positively charged defect and a negatively charged defect which counterbalanced it. For each pair of defects, the energy the compound gained was approximately 2.52.

B. Two Hole Case

Due to the absence of two electrons, defects or adjustments in the CDW of the compound were forced. Every initial oxygen atom displacement vector was used and several meta-stable states were found. The polaron state was not found at values of Γ less than .56. Instead, the apparent state with the lowest energy was a two-fold periodic solution with the difference between two consecutive bismuth sites less than the difference found in the half-filled case for the corresponding values of Γ. At $\Gamma = 0.6$, the use of random initial positions led to the finding of a polaron state divided in the middle by a single high charged bismuth site. The energy of this state was lower than that of the polaron. The two positively charged pieces of the polaron, are called phase slips[11]. By using the final oxygen atom displacements for one value of Γ as the initial displacements for the next value of Γ, the phase slip solution

was found for values of $\Gamma \geq 0.6$). It was found that as Γ increased, the difference between the energy of the polaron and phase slip solutions also increased.
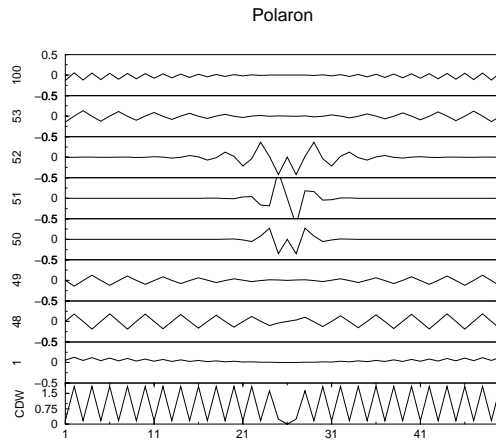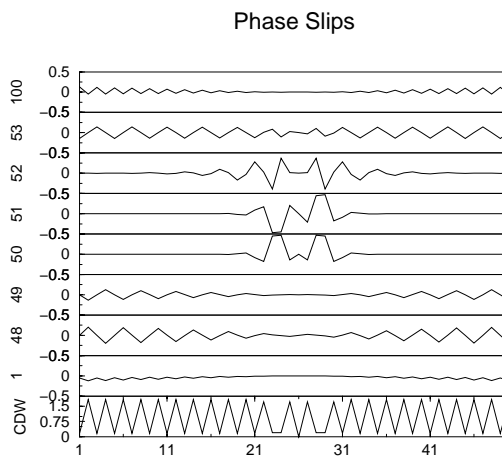
Polaron

FIG. 4.

Phase Slips

FIG. 5.

The unexpected discovery of a solution with lower energy than the polaron led to an examination of the wave functions on the bismuth sites near the defects of both solutions. (See Figure 4 and Figure 5) Many interesting observations were made from these graphs. First, the value of all the wave functions at the polaron site, or in midgap of the phase slip solution was zero. Second, the wave functions were either odd or even. Consecutive wave functions alternated between odd and even. The only exceptions were the $N/2$ and the $N/2 - 1$ wave functions. However, these observations did not lead to a definite answer as to why the phase slip solution was of lower energy. Thus, the IPR of both the solutions

13

were calculated. (See Figure 6) The intriguing aspect of this graph is the presence of several localized states near the valence and conduction bands. It was thought that these localized states were size defects that would disappear for a larger value of N or Γ. However when this hypothesis was tested, the localized state directly to the left of the conduction band remained.
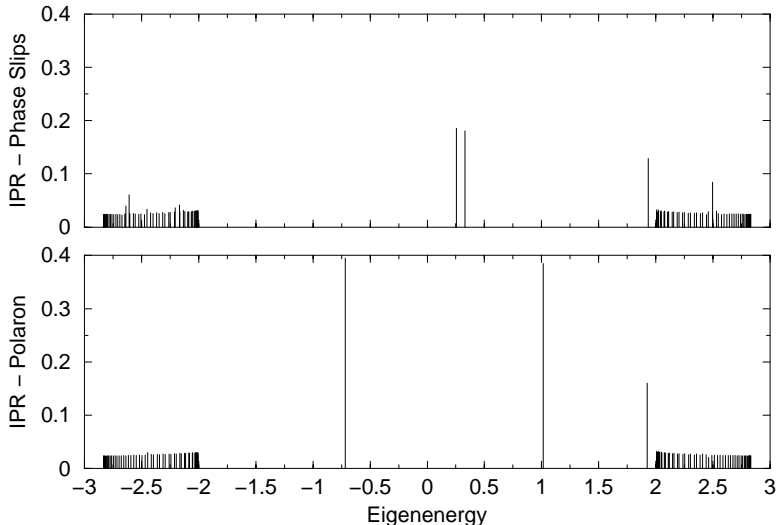

FIG. 6.

The need to know whether certain charge distributions, which were not being found by the model, were meta-stable, made it necessary to manually input the site occupations and convert the charges into initial oxygen displacements. Since, $\overline{\nabla F_n} = -\tilde{u}_n - \sqrt{\Gamma}\left(\varrho_{n+1} - \varrho_n\right)$ and the force on each atom is equal to zero when the compound is minimized, $\tilde{u}_n = -\sqrt{\Gamma}\left(\varrho_{n+1} - \varrho_n\right)$. The phase slips were forced to collapse into the polaron state, and were also allowed to move further apart. The table below shows the number of atoms between the phase slips and the corresponding energy, for $\Gamma = 0.6$. As can be seen, the like charged phase slips apparently repelled each other. Hence, the polaron solution was of higher energy since the force of repulsion had to be overcome.

Figure 7 is a graph of an exponential regression of the above data. It is known that,

$$\frac{dlog(E - E_0)}{dr} = m = -1.651$$

where r is the number of atoms between the phase slips and E_0 is the energy of the compound when the phase slips are infinitely separated. In this particular case, $E_0 = -157.390514310$. Then, $E - E_0 = ve^{-1.651}$, $\ln(1000v) = b = 4.12$, $v = 4.12$, which implies $E(r) = E_0 + 0.0616e^{-1.651r}$.
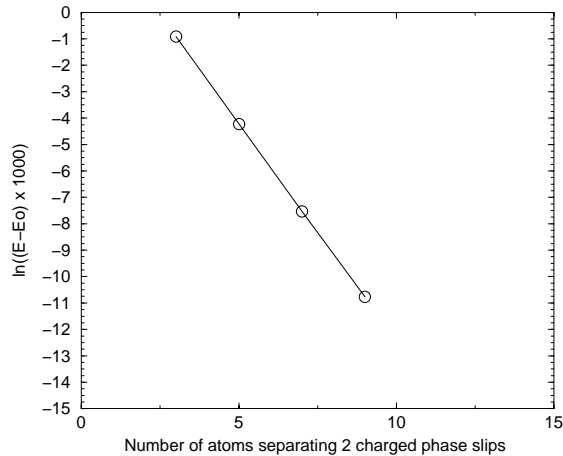

FIG. 7.

IV. DISCUSSION AND CONCLUSION

The half-filled case is devoid of any complications such as missing electrons. It can be fully solved analytically using the laws of Newton and mathematical methods. To insure the soundness of the model therefore, it is reasonable to solve the system mathematically and compare the result to the answer generated by the model. This can be done by comparing eigenvalues found analytically to those found numerically. If the eigenvalues are the same, then the corresponding eigenvectors will be equal and the system is solved. Making the assumption, $\tilde{u}_n = (-1)^n \tilde{u}_0$ and substituting into the Hamiltonian,

$$\mathcal{H} = \sum_{i=1}^{N} 2g\tilde{u}_0(-1)^i c_i^\dagger c_i + \sum_{i=1}^{N} \left(c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i \right) + \frac{N\tilde{u}_0^2}{2}$$

As discussed previously, $BaBiO_3$ is naturally dimerized at half-filling. Half the bismuth atoms in the compound have excess charge relative to the charge of the other bismuth atoms.

15

Let the bismuth atoms with excess charge be in sub-lattice A. Let the other bismuth atoms be in sub-lattice B. Since type A atoms and type B atoms are alternating, let the A type atoms be odd numbered. Then the Hamiltonian can be rewritten as,

$$\mathcal{H} = \sum_{i \in A} -2g\tilde{u}_0 c_i^{A\dagger} c_i^A + \sum_{i \in B} 2g\tilde{u}_0 c_i^{B\dagger} c_i^B + \sum_{i \in A} \left(c_i^{A\dagger} c_{i+1}^B + c_{i+1}^{B\dagger} c_i^A \right) + \sum_{i \in B} \left(c_i^{B\dagger} c_{i+1}^A + c_{i+1}^{A\dagger} c_i^B \right)$$

Substitute n as the counter variable for i. Let $c_n^\dagger$ and c_n undergo Fourier Transformations:

$$c_n^\dagger = \frac{1}{\sqrt{N}} \sum_{k=1}^{N} c_k^\dagger e^{ikn}$$

$$c_n = \frac{1}{\sqrt{N}} \sum_{k=1}^{N} c_k e^{-ikn}$$

Then,

$$c_n^\dagger c_{n+1} = \frac{1}{\sqrt{N}} \sum_{k_1=1}^{N} c_{k_1}^\dagger e^{ik_1 n} \cdot \frac{1}{\sqrt{N}} \sum_{k_2=1}^{N} c_{k_2} e^{-ik_2(n+1)}$$

$$\sum_{n=1}^{N} c_n^\dagger c_{n+1} = \sum_{k_1=1}^{N} \sum_{k_2=1}^{N} \frac{1}{N} c_{k_1}^\dagger c_{k_2} e^{-ik_2} \cdot \sum_{m=1}^{N} e^{ik_1 m} \cdot e^{-ik_2 m}$$

It is known that,

$$\sum_{n=1}^{N} e^{i\alpha n} = \begin{cases} N & \text{if } \alpha = 0 \\ 0 & \text{otherwise} \end{cases}$$

Hence, let

$$\sum_{m=1}^{N} e^{i(k_1 - k_2)m} = N\delta_{k_1, k_2}$$

where δ_{k_1, k_2} is a function that takes on two values, 0 or 1. Then,

$$\sum_{n=1}^{N} c_n^\dagger c_{n+1} = \sum_{k_1=1}^{N} \sum_{k_2=1}^{N} \frac{1}{N} c_{k_1}^\dagger c_{k_2} e^{-ik_2} \cdot N\delta_{k_1, k_2}$$

$$= \sum_{k_1=1}^{N} c_{k_1}^\dagger c_{k_1} e^{-ik_1}$$

$$= \sum_{k=1}^{N} c_k^\dagger c_k e^{-ik}$$

Thus,

$$\sum_{n=1}^{N} c_{n+1}^\dagger c_n = \sum_{k=1}^{N} c_k^\dagger c_k e^{ik}$$

and,

$$\mathcal{H}_{el-ph} = \sum_{k=1}^{N} c_k^\dagger c_k \left(e^{ik} + e^{-ik} \right)$$

$$= \sum_{k=1}^{N} 2 \cos k c_k^\dagger c_k$$

By definition, the eigenvalue, $\lambda_k = 2 \cos k$. Returning to the dimerized, A and B Hamiltonian,

$$\mathcal{H} = \sum_{k=1}^{N} \left[-2g\tilde{u}_0 c_k^{\dagger A} c_k^A + 2g\tilde{u}_0 c_k^{\dagger B} c_k^B + 2 \cos k c_k^{\dagger A} c_k^B + 2 \cos k c_k^{\dagger B} c_k^A \right]$$

From this two equations are derived,

$$-2g\tilde{u}_0 c_k^A + 2 \cos k c_k^b = \lambda c_k^A$$

$$2 \cos k c_k^A + 2g\tilde{u}_0 c_k^B = \lambda c_k^B$$

Solving using techniques of linear algebra,

$$\lambda = \pm\sqrt{(2 \cos k)^2 + (2g\tilde{u}_0)^2} \tag{11}$$

where $k = 2\pi n/N$, $n = 1, 2, \cdots, N - 1$.

Examination of the graph of Δ versus Γ (See Figure 3.) reveals a possibility for expressing Δ as a function of Γ. Taking the dimensionless Hamiltonian, and Eq.(10),

$$E = -4 \sum_{k}^{|k|<\pi/2} \sqrt{\cos^2 k + \Gamma \tilde{u}_0^2} + \frac{N}{2} \tilde{u}_0^2$$

$$\frac{\partial E}{\partial \tilde{u}_0} = 0 = -4 \sum_{k}^{|k|<\pi/2} \frac{\Gamma \tilde{u}_0}{\sqrt{\cos^2 k + \Gamma \tilde{u}_0^2}} + N\tilde{u}_0$$

$$\frac{1}{\Gamma} = \frac{4}{N} \sum_{k} \frac{1}{\sqrt{\cos^2 k + \Gamma \tilde{u}_0^2}}$$

Let $\delta = \Delta/2 = \tilde{u}_0 \sqrt{\Gamma}$. Also let $\Delta k = 2\pi/N$. Then,

$$\frac{1}{\Gamma} = \frac{4}{2\pi} \sum_{k} \frac{\Delta k}{\sqrt{\cos^2 k + \delta^2}}$$

$$= \frac{4}{\pi} \int_0^{\pi/2} dk \frac{1}{\sqrt{\cos^2 k + \delta^2}}$$

$$= \frac{4}{\pi} \int_0^{\pi/2} dk \frac{1}{\sqrt{\sin^2 k + \delta^2}}$$

17

This will first be solved for small values of Γ and hence δ.

$$\frac{\pi/4}{\Gamma} = \int_0^{\pi/2} \frac{dk}{\sqrt{\delta^2 + k^2}} + \int_0^{\pi/2} \left(\frac{1}{\sqrt{\delta^2 + \sin^2 k}} - \frac{1}{\sqrt{\delta^2 + k^2}} \right) dk$$

$$\frac{\pi/4}{\Gamma} \approx \int_0^{\pi/2} \frac{dk}{\sqrt{\delta^2 + k^2}} + \int_0^{\pi/2} \left(\frac{1}{\sin k} - \frac{1}{k} \right) dk$$

$$\frac{\pi}{4\Gamma} = \log \left(k + \sqrt{k^2 + \delta^2} \right) \Big|_0^{\pi/2} + \left[\log |\tan k/2| - \log k \right] \Big|_0^{\pi/2}$$

Evaluating this expression gives,

$$8 e^{-\frac{\pi}{4\Gamma}} = \Delta \tag{12}$$

For large values of Γ, $\delta^2 \gg \cos^2 k$. Hence,

$$\frac{1}{\Gamma} = \frac{4}{N} \sum_k \left(\frac{1}{\delta} \right)$$

$$\Delta = 4\Gamma \tag{13}$$

A. Further Research - Experiments with the 3D Model

The presence of slightly localized states directly to the left of the conduction band prompted the question whether these bounded states were size defects, defects of the 1D model, or if these states actually did exist. As previously noted, these states were not size defects. The bipolaron trial was conducted using the 3D model, and once again these bound states were seen in the graph of Eigenenergy v. IPR. In solving a system such as the H_2^+ molecule for the charge distribution of the electron in the system, several states or solution to the problem are obtained. However, these states differ in energy. There is the bonding s-state, which has only positive signs in the wave function. In order to find the probability of the location of an electron, the wave function is squared. In the bonding case, there is a non-zero probability of finding the electron between the two H^+ ions; hence this is the bonding state. For the anti-bonding state in which the wave function changes signs, there is zero probability of finding the electron in between the ions; the electron is either at the left or right ion. This system is analogous to the bipolaron case. By solving the system using Shroedinger's Equation (6), the binding state as well as excited solutions are found. The

ground state is the removal of two electrons from a Bi atom (the central atom). However there are excited states, e.g. the hole is distributed half on the atom to the right of the central atom, and half on the atom to the left. This is the p-state, where the wave function has a change of sign, and hence the electron has zero probability of being located on the central atom. Figure 8 shows a closer view of these bound states. Note that the three states to the left, and two to the right appear to be grouped. The three states are the three p orbitals, while the two states are two of the five d orbitals. The absence of three d orbitals is not perplexing since in solid state physics, the atom is viewed as a cube and not as a sphere. When this cube is rotated, is quite likely that certain characteristics (i.e. three d orbitals) cannot be seen.
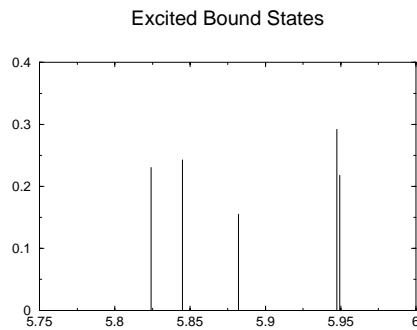

FIG. 8.

An experiment is currently being conducted using the 3D model in which an electron is removed from the lattice and then placed back again in the lattice. It is hoped that this experiment will reveal a great deal of information with respect to how the oxygen atoms (particularly the atoms surrounding the polaron) react when a defect occurs in the lattice. It is hypothesized that either the polaron will be 'filled,' or defects in the lattice structure known as excitons will form. This experiment is an important step towards the ultimate objective of this research: to determine the doping concentration that will cause a striped lattice solution to form.

REFERENCES

[1] G. Thornton, and A.J. Jacobson: Mater. Res. Bull **11**, 837 (1976).

[2] Vladamir N. Kostur and Philip B. Allen: Phys. Rev. B **56** 3105 (1997).

[3] J. Yu, X.Y. Chen, and W.P. Su: Phys. Rev. B **41** 344 (1990).

[4] Philip B. Allen and Vladamir N. Kostur: Zeitschrift Fur Physik B **104** 613 (1997).

[5] T.M. Rice and L.Sneddon: Phys. Rev. Lett **47**, 689 (1982).

[6] Shiyou Pei, J.D. Jorgensen, B. Dabrowshi, D.G. Hinks, D.R. Richards, A.W. Mitchell, J.M. Newsam, S.K. Sinha, D. Vaknin, and A.J. Jacobson: Phys. Rev. B **41**, 4126 (1990).

[7] L.F. Mattheis, E.M. Gyorgy, and D.W. Johnson, Jr.: Phys. Rev. B **37**, 3745 (1988).

[8] R.J. Cava, A.E. White, K.T. Short, W.F. Peck, Jr., and T.Y. Kometani: Nature **332**, 814 (1988).

[9] D.G. Hinks, B.Dabrowski, J.D. Jorgensen, A.W. Mitchell, D.R. Richards, Shiyou Pei, and Donglu Shi: Nature **333**, 836 (1988).

[10] Numerical Recipes in C: the art of of scientific computing. New York: Cambridge University Press, (1992).

[11] Graciela B. Blanchet, C.R. Fincher, and A.J. Heeger: Phys. Rev. Lett: **51** 2132 (1983).

Charles Kittel: Introduction to Solid State Physics. New York: John Wiley Sons, Inc., (1996).

A.S. Alexandrov, N.F. Mott:Polarons and bipolarons. Singapore: World Scientific (1995).