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EMPIRICAL TIGHT-BINDING PARAMETERS FOR SOLID C_{60}

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ABSTRACT

We present a tight-binding model for the electronic structure of C_{60} using four (1s and 3p) orbitals per carbon atom. The model has been developed by fitting the tight-binding parameters to the ab-initio pseudopotential calculation of Troullier and Martins [Phys. Rev. B46, 1754 (1992)] in the face-centered cubic ($Fm\bar{3}$) phase. Following this, calculations of the energy bands and the density of electronic states have been carried out as a function of the lattice constant. Good agreement has been obtained with the observed lattice-constant dependence of T_c using McMillan's formula. Furthermore, calculations of the electronic structure are presented in the simple cubic ($Pa\bar{3}$) phase.

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1 Introduction

The discovery of C_{60} molecule[1] and a new form of carbon, the solid C_{60} hereafter also referred to as fullerite,[2] and subsequent observation of superconductivity in alkali-doped fullerites[3] (A_3C_{60} where A is an alkali atom) with a moderately high T_c have generated an enormous interest in these systems. Despite the extensive experimental and theoretical studies, many fascinating questions such as the mechanism of superconductivity remain still open. On the experimental side, the electronic spectra for undoped and doped fullerites have been obtained using photoemission[4] and inverse photoemission.[5] Other experimental techniques such as infrared absorption and Raman spectroscopies and neutron scattering[6-8] have been applied to investigate the dynamical properties of the fullerites. The characterization of solid C_{60} has been done at various temperatures using ^{13}C nuclear magnetic resonance[9] (NMR) and neutron[10] and X-ray diffractions.[11] At room temperature solid C_{60} forms a face-centered cubic (fcc) structure. In this phase, the C_{60} molecules reorient rapidly and isotropically and the structure is believed to belong to $Fm\bar{3}$ space group. However, below 260°K, x-ray and neutron diffraction experiments[9-11] have shown that an orientational order develops and ultimately at low temperatures the structure becomes simple cubic (sc) belonging to the space group ($Pa\bar{3}$) with four C_{60} molecules occupying the fcc lattice sites but having different orientations. Evidence has also been reported[12] for a superstructure at low temperatures with a lattice constant which is twice the value of the case of the $Pa\bar{3}$ structure. Upon doping with alkali metals (such as K, Rb and/or Cs), the sample becomes superconducting and the highest T_c (33°K) has been obtained[13] for $RbCs_2C_{60}$. While at low temperatures the C_{60} molecules are not rotating in these doped systems, some orientational disorder of C_{60} molecules is believed to exist.[10]

On the theoretical side, the structural, dynamical and electronic prop-

erties have been calculated extensively by various techniques. Among these techniques, the Car-Parrinello (CP) method[14] has been used to calculate the ground state[15] and finite temperature[16,17] properties of solid C_{60}. However, due to the heavy computational cost of the CP simulations for such systems, a need for simpler approaches is obvious. In fact, recently, a tight-binding molecular dynamics (TBMD) method[18,19] has been developed to study the dynamical properties of fullerenes.[19–21] This method is about hundered times faster[20] than the ab-initio molecular dynamics (CP) simulations (the time step in TBMD is about 10 times larger than that used in CP), and the results obtained for several fullerenes are in good agreement with both experiments and state-of-the-art methods wherever available. Also because of other developments of graphite tubes[22] etc., tight-binding models are attractive to understand the general physics of these and related large systems.

Several attempts have also been made recently to study the electronic properties of solid C_{60} using tight-binding (TB) models. Gelfand and Lu[23] have reported a 3-orbital TB model to study orientational disorder in low temperture C_{60} structure. However, their hopping amplitudes were only a few meV and, as a consequence, the resulting bandwidths were smaller by a factor of 15 (10) for pure (doped) C_{60} solid as compared to ab-initio calculations. Satpathy and coworkers[24,25] developed a TB model with a basis consisting of only the 60 radial atomic orbitals per molecule. This one-orbital model was used to study the conduction band structure versus doping. Another model, reported by Xu et al.[21], contains 4 orbitals per carbon atom, however, it was applied to diamond, graphite and carbon microclusters C_n (where $n \leq 10$). In this paper, we report a tight-binding model containing four (1s and 3p) orbitals per carbon atom for solid C_{60}. This model was developed by a fit to a well converged ab-initio pseudopotential calculation of the fcc ($Fm\bar{3}$) phase due to Troullier and Martins.[26] We have applied this model to study the dependence of the electronic structure on lattice constant[27] and used

the results to calculate the lattice-constant dependence of T_c in alkali-doped fullerites (A_3C_{60}). Our results are in good agreement with experimental values.[13]

In the next section, we introduce our tight-binding model and show in details its results for the free C_{60} molecule and for both the hypothetical unidirectional ($Fm\bar{3}$) and the quadridirectional low temperature ($Pa\bar{3}$) structures of solid C_{60}. In section 3, we show briefly our estimations of T_c for alkali-doped fullerites using McMillan's formula. The last section summarizes our results.

2 Electronic structure:

The tight-binding Hamiltonian used in our work can be written as

$$H = \sum_{i,\mu} E_{i,\mu} c^{+}_{i,\mu} c_{i,\mu} + \sum_{<i,\mu;j,\nu>} V_{\mu,\nu}(\vec{r}_{ij}) \left[c^{+}_{i,\mu} c_{j,\nu} + h.c. \right], \qquad (1)$$

where i,j label atomic sites; μ, ν label atomic orbitals (s, p_x, p_y, p_z) and <> indicates that the sum on (ij) is over neighbours which we shall give more explicitly later. $c^{+}_{i,\mu}$ is a creation operator for an electron in the orbital μ at site i. $E_{i,\mu}$ is the on-site energy and $V_{\mu,\nu}(\vec{r}_{ij})$ are the hopping integrals, which decay rapidly with the interatomic distance r_{ij}. The latter are expressed[28] in terms of the two-center integrals $V_{ss\sigma}(r_{ij})$, $V_{sp\sigma}(r_{ij})$, $V_{pp\sigma}(r_{ij})$ and $V_{pp\pi}(r_{ij})$. By fitting to the ab-initio pseudopotential calculations of Troullier and Martins for the fcc phase of solid C_{60}, we obtained the following tight binding parameters corresponding to a distance of d_o = 1.54 Å: E_s = -6.7eV, E_p = 0eV, $V_{ss\sigma}$ = -5.55eV, $V_{sp\sigma}$ = 5.31eV, $V_{pp\sigma}$ = 6.20eV and $V_{pp\pi}$ = -2.30eV. In developing such parameters for solid C_{60} we started with the tight-binding model for tetrahedrally sp^3 bonded carbon material, namely diamond, with a nearest neighbour distance d_o as reported by Wang et al.[29]. For the C_{60} molecule, we have considered the hoping integrals only between the nearest neighbours

and used a distance-dependence of $1/r^2$ as proposed by Harrison.[30] However in the solid phase, the hopping integrals between carbon atoms on neighbouring molecules are truncated[31] after R_c=4.4$\AA$ and their distance-dependence[24] is taken as:

$$V(d) = \left(\frac{d}{d_o}\right) V_o exp\left[\frac{-(d-d_o)}{L}\right], \qquad (2)$$

where V_o denotes the two-center integrals and L = 0.45 $\AA$.

As expected by Kroto at al.[1] several years ago, it has been proven that the C_{60} molecule has a truncated icosahedral structure. The sixty carbon atoms of the molecule occupy equivalent sites and span 20 hexagons, and 12 isolated pentagons. These atoms are connected via two kinds of bonds: a double bond of length 1.4$\AA$ shared by two hexagons, and two single bonds of length 1.45$\AA$ shared by a hexagon and a pentagon. The molecule has a diameter of about 7.0$\AA$. In the solid (fullerites), the molecules occupy the sites of the fcc structure where the centers of neighbouring molecules are separated by about 10$\AA$. Ab-initio calculations in the unidirectional fcc phase[15] using the Car-Parrinello method indicate that due to this change in symmetry in the solid phase, the long bond gets three slightly different values (1.449, 1.454 and 1.462 $\AA$) while the short bond is 1.404 $\AA$. Our tight binding calculations on C_{60} molecule show that the effect of this small change in bond lengths on the energy spectrum is negligible. We have used these bond lengths in our calculations. Also as the interactions between the molecules are weak and believed to be predominantly Van der Waals type, we expect only a minor change in bond lengths as a function of the lattice constant and also in going from the fcc to the sc phase. This is neglected in our calculations.

In figure 1, we show the spectrum of a C_{60} molecule and compare it with the spectra obtained from two other methods.[32] The highest occupied molecular orbital (HOMO) is taken to be the zero of energy. Because the

molecule has a high symmetry structure belonging to the icosahedral group I_h, its spectrum show many three-, four- and five-fold degenerate levels. We have shown in figure 1 the irreducible representations[33] which reveal the symmetry and degeneracy of the eigenstates. The subscripts g and u refer respectively to even (gerade) and odd (ungerade) symmetry, which transform distinctly under inversion. Moreover, we discriminate between t_{1g} and t_{2g} (similarly t_{1u} and t_{2u}) by applying the C_5 rotation on the corresponding eigenfunctions (see Appendix). The three-fold (t_{1u} symmetry) state which constitutes the lowest unoccupied molecular orbital (LUMO) is separated by an energy gap of 2.09 eV from the HUMO. The states near the Fermi level have predominantly the π bonding character and are very sensitive to the variation of the hopping parameter $V_{pp\pi}$. In figure 1 we also compare our molecular spectrum with Satpathy's LMTO[32] calculation and with a simple nearest-neighbour tight-binding Hückel calculation,[32] which used only one orbital per atom and a hopping integral t = -2.72eV. The ordering of our molecular orbitals is exactly the same with both the latter methods in the energy range from -5.0eV to 7.5eV. Also the ordering of our molecular spectrum compares well with the ab-initio pseudopotential calculations of Saito and Oshiyama[34] in the range from -5.0eV to 10eV (in our energy scale). In the solid, one expects the interaction between the molecules to play an important role in the formation of the energy bands and in lowering the HUMO-LUMO gap.

In figure 2a, we show the band structure of the unidirectional ($Fm\bar{3}$) structure with the same lattice constant as used by Troullier and Martins a_o = 13.879$\AA$ for the sake of compariso:. This figure shows the band structure of C_{60} along the high symmetry lines in the Brillouin zone for energies close to the fundamental gap, and display the highest group of valence bands and the two lowest groups of conduction bands. The top of the valence band was chosen as the zero of energy. Our bands are also in good agreement with

those obtained by a self-consistent pseudopotential calculations using a Gaussian basis.[34,35] The band gap is 1.58eV (a little wider than that of Ref.26) and direct at the X-point. Figure 2b shows the corresponding density of states (DOS) calculated using the tetrahedron method[36] which included 505 $\vec{k}$-vectors from the irreducible wedge of the Brillouin zone. Our DOS is also in good agreement with the LDA[35] and tight-binding results.[23,24] As compared to reference 26, our valence band is of width 0.59eV (versus 0.58eV), and the two lowest conduction bands have widths of 0.40ev and 0.42eV (versus 0.46eV and 0.53eV respectively).

The low temperature structure of pure C_{60} was solved by David et al.[13]. The molecules are centered on an fcc lattice as in the uni-directional case but they are rotated by an angle of -22.38° along the four different (111) axes[24] such that the space group symmetry is $Pa\bar{3}$. The lattice constant we used for this structure is 14.11$\AA$, which is the same as observed in experiments.[10] We calculated the energy bands along three symmetry lines (ΓR, ΓX and XM). In figure 3, we show the 20 highest valence bands as well as 12 lowest conduction bands. In general agreement with reference 23, the gap is indirect from Γ to R. However, our bandwidths are more realistic. The band gap is 1.669eV and the valence and conduction bands have widths of 0.372eV and 0.344eV respectively. In this low temperature phase, our model can also be used to study the orientational disorder effects. Because C_{60} is not perfectly spherical, this kind of disorder has been shown to presist[10,23] in the low temperature phase, and the investigations of its effects in detailed manner are likely to be important in understanding the physical properties of solid C_{60}.

3 Superconductivity in fullerides:

It has been shown experimentally[13] that changes in T_c could be accounted for by changes in the density of states at the Fermi level, $N(E_F)$, which scales monotonically with lattice constant. Alkali-doped fullerites (A_3C_{60}) have a face-centered cubic structure with the alkali atoms occupying the interstitial tetrahedral and octahedral sites.[37] Theoretical calculations[24,38] of valence charge densities as well as Raman spectra[39] have shown that the valence electrons of the alkali atoms are almost completely transferred to the lowest unoccupied bands of the C_{60} molecular solid. Hence, this latter fact is explored in our TB calculation by treating the dopants simply as sources of electrons for the C_{60} conduction band. Assuming that the intramolecular vibrational modes to be playing the dominant role in the electron-phonon pairing mechanism in fullerides, then the variation in T_c should arise due to changes in the lattice constant which affects $N(E_F)$. (The most direct evidence for phonon-mediated pairing comes from the isotope-effect measurements[40-42].) Thus for a comparative study of the isostructural A_3C_{60} compounds, in another paper[27] we studied the behaviour of the conduction bands of solid C_{60} as a function of the lattice constant. Here, however, we summarize our results in table 1 to show some trends of our model.

In our previous work,[27] we evaluated $N(E_F)$ for different lattice constants corresponding to several fullerides[13] (A_3C_{60}) and estimated T_c using McMillan's formula

$$T_c = \frac{\hbar\omega}{1.2k_B} exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right] \qquad (3)$$

We assume that the averaged phonon frequency ω and the Coulomb-interaction parameter μ^* are independent of the intermolecular separation d. The T_c is then calculated using Eq.(3) and asssuming that $\lambda = N(E_F)V_{e-ph}$ with a d-independent electron-phonon interaction V_{e-ph} and by taking the d dependence of the density of states at the Fermi level from our TB calculations.[27]

We took[43]: $V_{e-ph} = 40$ meV, $\mu^* = 0.19$ and $\frac{\hbar\omega}{k_B} = 1450°$K, and estimated T_c for several lattice constants as shown in table 1. The values of N_F are in the range of 17-20 states/eV-molecule-spin. The resulting T_c (table 1) is in good agreement with the experimental data.[13]

4 Conclusions:

We have developed a full tight-binding model for C_{60} solid by fitting to the well converged ab-initio pseudopotential calculation of Troullier and Martins. Our estimation of the variation of T_c with lattice constant using McMillan's formula is in good agreement with experimental data. Our model can be explored to study the orientational disorder effects in the low temperature phase as well as the dynamical properties of solid C_{60} using the TBMD simulation. We hope also that our TB model will be useful in the study of higher fullerenes as well as graphite tubes. Due to the narrow band widths, it is expected that correlations in solid C_{60} may play an important role and our model can be extended to incorporate these effects.

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Appendix

Let us assume that the eigenvalue E_n is g_n-fold degenerate (excluding any accidental degeneracies). Then we may choose a set of g_n orthonormal eigenfunctions, $\Psi_n^{(j)}$, j=1,..,g_n belonging to E_n, to form a basis for a g_n-dimensional space. This space is a subspace of the entire Hilbert space of eigenfunctions of the Hamiltonian H; a subspace invariant under all the operations P_R of the group of Schrödinger equation: $P_R H \Psi_n^{(j)} = H P_R \Psi_n^{(j)} = E_n P_R \Psi_n^{(j)}$. (Here P_R is a symmetry operation corresponding to the rotation R.) Thus $P_R \Psi_n^{(j)}$ is also an eigenfunction with an eigenvalue E_n and can be expressed as a linear combination of the g_n degenerate eigenfunctions:

$$P_R \Psi_n^{(j)} = \sum_{i=1}^{g_n} \Psi_n^{(i)} \Gamma^n(R)_{ij} \qquad (A)$$

where $\Gamma^n(R)$ is the irreducible representation corresponding to the point group operation R. Expressing the eigenfunction $\Psi_n^{(j)}$ in the tight-binding basis, we have

$$\Psi_n^{(j)}(\vec{r}) = \sum_{\alpha=1}^{N} C_\alpha^{n,j} \Phi_\alpha(\vec{r}) \qquad (B)$$

Here α denotes an (s, p_x, p_y, or p_z) orbital centered at one of the sixty carbon atoms and N=240. Then Eq.(A) becomes:

$$P_R \Psi_n^{(j)} = \sum_{\alpha=1}^{N} \Phi_\alpha(\vec{r}) \left[\sum_{i=1}^{g_n} C_\alpha^{n,i} \Gamma^n(R)_{ij} \right] \qquad (C)$$

We consider now the operation

$$P_R \Psi_n^{(j)}(\vec{r}) = \Psi_n^{(j)}(R^{-1}\vec{r}) \qquad (D)$$

and using Eq.(B) to find:

$$P_R \Psi_n^{(j)}(\vec{r}) = \sum_{\alpha=1}^{N} C_{R^{-1}\alpha}^{n,j} \Phi_\alpha(\vec{r}) \qquad (E)$$

Comparing Eqs.(C) and (E), one can extract the relation governing the transformation of the g_n-degenerate eigenfunctions' components

$$C_{R^{-1}\alpha}^{n,j} = \sum_{i=1}^{g_n} C_\alpha^{n,i} \Gamma^n(R)_{ij} \qquad (F)$$

We have practically used this relation to study the symmetry of the eigenstates of the C_{60}-spectrum shown in figure 1, and especifically to discreminate between t_{1g} and t_{2g} (similarly t_{1u} and t_{2u}) symmetries using the C_5 rotation.

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Table 1: The superconducting transition temperatures and structural data for A_3C_{60}. (1) Experimental data,[13] and (2) Our theoretical results.[27]

A_3	$a_o^{(1)}(\AA)$	$T_c^{(1)}(^oK)$	$T_c^{(2)}(^oK)$
K_3	14.253	19.28	20.65
K_2Rb	14.299	21.80	21.85
Rb_2K	14.364	26.40	23.82
Rb_3	14.436	29.40	26.42
Rb_2Cs	14.493	31.30	28.50

Figure Captions

Figure 1: Spectra of C_{60} molecule, using various methods, are presented in the energy range from -5 to 10 eV. The HOMO is taken to be the zero of energy. The results are from the following methods: the LMTO calculation,[32] the Hückel calculation with one orbital per carbon atom,[32] and our TB calculation described in the text.

Figure 2: (a) The band structure of fcc ($Fm\bar{3}$) phase with a lattice constant a_o= 13.879$\mathring{A}$ for comparison with Ref.26. (b) Density of states (DOS), per molecule for combiued spins, calculated using the tetrahedron method with 505 $\vec{k}$-vectors from the irreducible wedge of the Brillouin zone. The zero of energy is at the top of the valence band for both (a) and (b).

Figure 3: The band structure of sc ($Pa\bar{3}$) phase with a lattice constant a_o= 14.11$\mathring{A}$. The zero of energy is at the top of valence band.

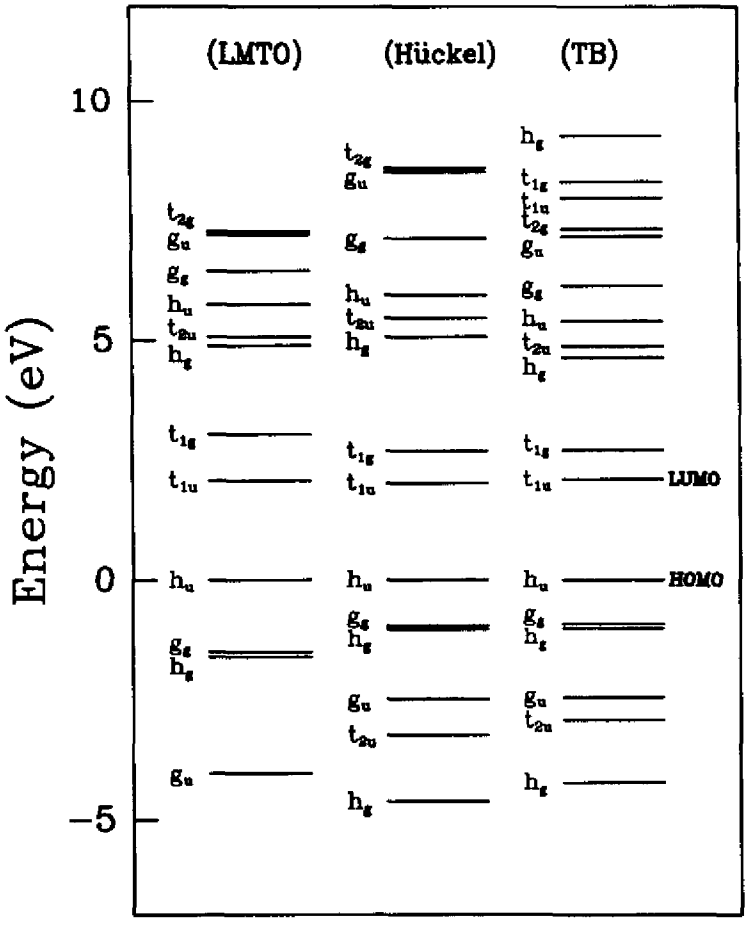

Figure 1

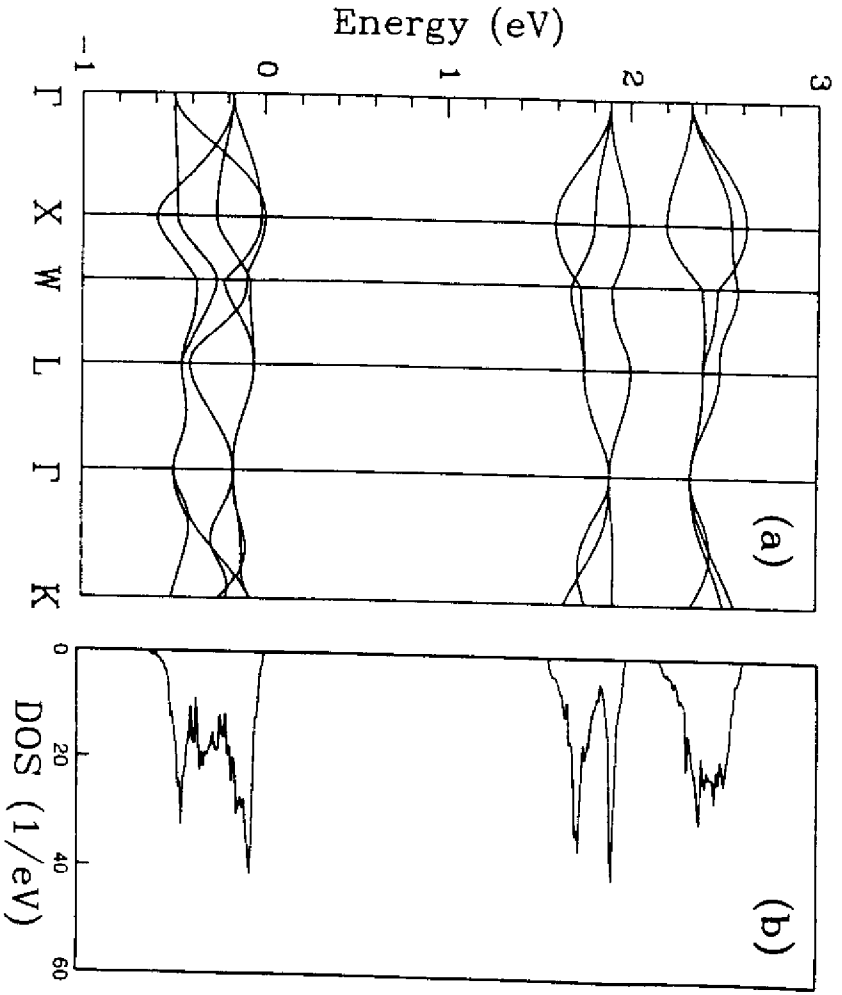

Figure 2

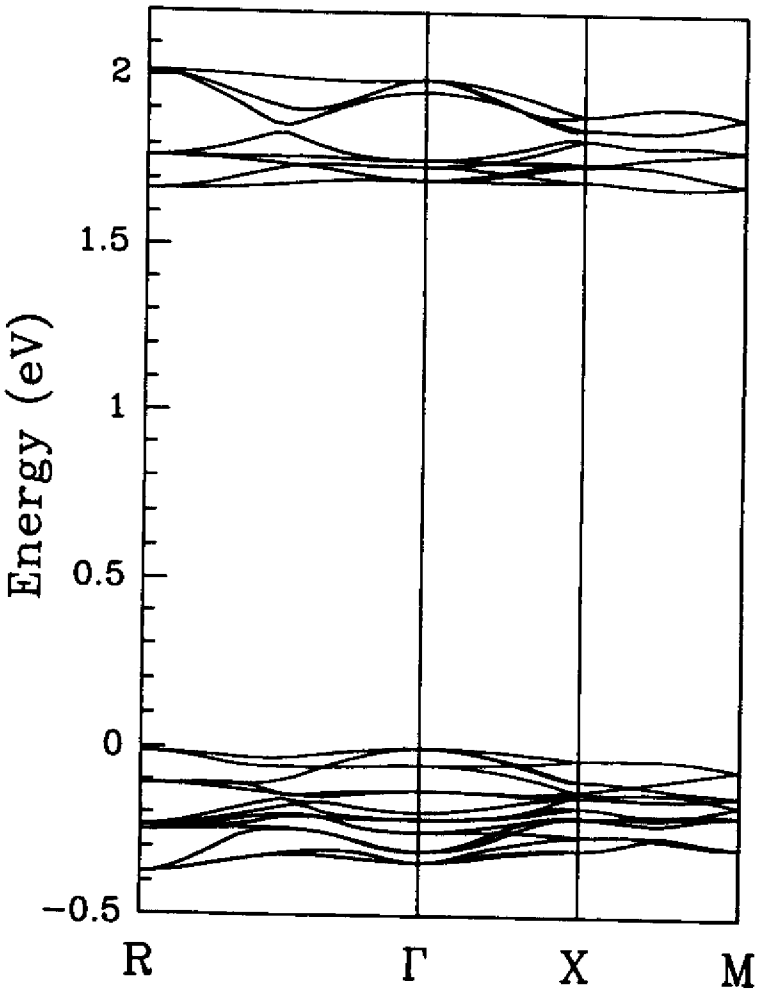

Figure 3