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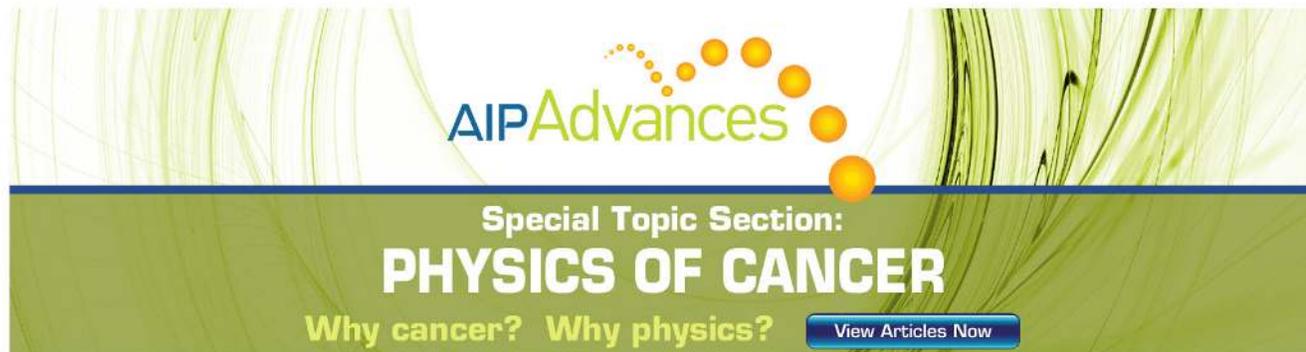
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Correlation induced insulator to metal transition: A systematic density functional study on highly doped *n*-type *trans*-polyacetylene

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Since its discovery in 1977, a number of quantum chemical calculations have been attempted to simulate the metallic state of highly doped *trans*-polyacetylene. These simulations have focused on the possible closure of the band gap at high doping level due to a charge-induced elimination of Peierls distortion; however, conclusive demonstration of a metallic state has not been achieved. The present study presents density functional theory calculations of the band structure of highly doped *trans*-polyacetylene with explicit inclusion of the metal atoms in a one-dimensional periodic structure. The results indicate (i) small lattice dimerization, i.e., remnant of Peierls distortion exists even in the heavily doped *trans*-polyacetylene sample, (ii) charge induced closure of the Peierls gap is not a necessary condition to arrive at a metallic state in such systems, and (iii) electronic correlation, as described at the density functional theory level, with a charge induced small Peierls distortion is sufficient to achieve metallic state of highly doped *n*-type *trans*-polyacetylene even in one dimension. Furthermore, comparison of functionals that include differing degrees of electron correlation suggest that correlation promotes formation of the metallic state. © 2006 American Institute of Physics. [DOI: 10.1063/1.2140694]

I. INTRODUCTION

Electrically conductive conjugated polymers have attracted substantial attention for the last three decades because of their many potential applications and unique optoelectronic properties.¹⁻³ The discovery of conducting polymer not only marked the birth of a new generation of material science but also created a new frontier for low dimensional condensed matter physics.

Of the many conducting polymers identified so far polyacetylene appears first in the family. There are three different geometric forms of polyacetylene, namely *trans*, *cis* transoid, and *trans* cisoid polyacetylene. *Trans*-polyacetylene can be doped by a variety of oxidizing (I₂, Br₂, and ASF₅) and reducing agents (Li, Na and K). As a consequence both *n*-type and *p*-type conduction are possible for doped *trans*-polyacetylene. The experimental Pauli spin susceptibility, the electronic specific heat, high electrical conductivity (up to 10⁶ S/cm), and infrared spectra indicate that doping can increase the electrical conductivity of *trans*-polyacetylene to near metallic regime.⁴⁻⁶ The effect of doping on electronic states, conductivity, and optical properties of polyacetylene has been explored extensively, leading to the proposal that these properties are strongly affected by polaron, bipolaron, or soliton type quasiparticles generated in the neutral quasi-one-dimensional polymer chain.^{7,8} Many of the physical properties of polyacetylene can be explained within the framework of one electron SSH model⁹ in which the electronic state is described according to that of one-dimensional periodic lattice having Peierls distortion. The presence of Peierls distortion in polyacetylene chain is responsible for

strong lattice dimerization and Peierls gap opening at $\pi/2a$ (“*a*” is the lattice constant).

Apart from the SSH model, a number of quantum chemical techniques¹⁰ ranging from simple Hückel theory to *ab initio* Hartree-Fock method via valence effective Hamiltonian (VEH) technique appear more or less successful to account for the band structure, density of states, mobility of charge carriers of doped and undoped polyacetylene. Although the performance of these methods including the SSH model is quite satisfactory, they fail to account for insulator to metal transition occurring upon doping. The major problem with the SSH model or VEH technique is that both of them are one-electron model without any correlation effect. In the present circumstances electronic correlation effect can be introduced by a number of techniques namely, Peierls Hubbard model, multireference configuration interaction treatment, *ab initio* density functional technique, etc. Recently Bezugly *et al.*¹¹ calculated band structure of undoped *trans*-polyacetylene using multireference configuration interaction method and observed that band gap reduces by 2.31 eV, from 6.42 eV on the Hartree-Fock level down to 4.11 eV when correlation is included. The major limitation of the work is that the band gap is still overestimated by 2.5 eV (approximately) and does not concern the band structure modification of *trans*-polyacetylene due to doping.¹¹

Bredas *et al.*¹² have simulated the band structure of 33% Li-doped *trans*-polyacetylene at restricted Hartree-Fock-Roothan level using christoffersen basis set. The predicted band structure of 33% doped *trans*-polyacetylene does not correspond to the metallic state of the material, since there is a small but finite gap between the upper mid-gap band and the bottom of the conduction band (π^* band). After that several attempts have been made to provide a successful de-

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scription of the metallic state of such a heavily doped system.^{4,5,13}

The focus of the present study involves searching for the metallic state in a doped *trans*-polyacetylene chain of infinite length having finite dimerization amplitude. Peierls theorem, a paradigm of low dimensional physics is strictly valid for one-dimensional (1D) lattice of infinite length. The degree of lattice dimerization, a measure of Peierls distortion, is greatly influenced by static and dynamic electron correlation effect and has been extensively studied for undoped *trans*-polyacetylene system by Choi *et al.*¹⁴ The effect of electron correlation in doped quasi-1D *trans*-polyacetylene chain with finite Peierls distortion is still a fundamental unresolved issue. To provide a better understanding of the band structure and a fundamental insight into the role of electron correlation on metallic state of heavily doped *trans*-polyacetylene, first principle density functional calculations, a traditional method used in condensed matter physics to simulate the electronic properties of infinite periodic lattice is inevitable.

The density functional theory of Hohenberg, Kohn, and Sham has been used extensively in the description of many body quantum mechanical systems over the past few years. The theory provides an exact mapping of the ground state properties of a system of large number of interacting electrons onto a system of noninteracting particles moving under an effective potential.¹⁵ The most important part of effective potential is the exchange-correlation potential. Introduction of electron exchange-correlation term is the improvement over all other previous many body quantum chemical methods.

In practice however, the exchange-correlation part of total energy functional is unknown and replaced by an approximate functional. One such approximation is local-density approximation (LDA) or local spin density approximation (LSDA). Most of the modern electronic structure calculations in solids and in many atomic and molecular systems are based on LDA or LSDA. The LDA and LSDA have been successful in the description of a wide variety of electronic properties of atoms, molecules, and solids.¹⁶ Physical situations involving fluctuation in electron density make use of generalized gradient approximation (GGA). A wide variety of functionals are now available for GGA.

Employing the aforesaid discussion and findings we have initiated a systematic theoretical investigation aimed at simulating the band structure of undoped and heavily doped *trans*-polyacetylene at various density functional theory

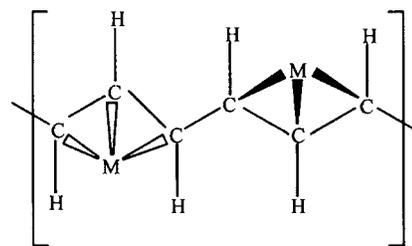


FIG. 1. Unit cell of 33.3% metal doped *trans*-polyacetylene.

(DFT) levels. In the present work we propose the simulation of heavily doped *trans*-polyacetylene chain of infinite length using Li, Na, and K as doping agents. In order to take care of dynamical electron correlation effect BLYP exchange-correlation functional is used in addition to LDA functional.

II. COMPUTATIONAL DETAILS

All the calculations have been implemented in the Amsterdam density functional package (ADF 2004.01).¹⁷ The geometry of the unit cell for the doped case is presented in Fig. 1. The geometry of the unit cell is optimized using BLYP type exchange-correlation functional and TZ2P basis set. Different bond lengths and bond angles considered for the calculation are tabulated in Table I. The density functional technique used here involves spin restricted calculations under LDA and GGA. The exchange-correlation functional of Vosko-Wilk and Nusair (VWN)¹⁸ is used in LDA and its counterpart in GGA is Becke-Lee-Yang and Parr (BLYP).¹⁹ The basis set chosen is TZ2P NAO+STO basis (basis V in the band program), which consists of a triple zeta basis augmented with two polarization functions. For integration in the real space the accuracy parameter is set to three. The reciprocal space integration accuracy is set to five, resulting in five symmetry unique k points in the first Brillouin zone. Self-consistent field (SCF) convergence is reached by introducing the Tails Basis Key. According to the program, Tails Basis is associated with the nonorthogonal SCF basis. The Tails Basis is set to $1E-2$. The fit functions (also obtained from the basis V in the band program) in “Atoms type” key of the input is taking care of the Coulomb interaction. The dependency basis for the fit functions is set to $1E-10$, because of the use of the dependency key word the calculation should continue even if the basis is nearly linearly dependent. The band structures are generated using ORIGIN 6.0 package.

TABLE I. Geometric parameters of doped and undoped *trans*-polyacetylene unit cells.^a

Name of the sample	C—C double bond length (Å)	C—C single bond length (Å)	CCC angle (°)	CCH angle (double bonded CC) (°)	C—M distance (M=metal) (Å)	C—H distance (Å)
Sample A	1.34	1.42	124.5	119.2	Infinite	1.109
Sample B	1.38	1.41	124.5	119.2	2.00	1.109
Sample C	1.38	1.40	124.5	119.2	2.52	1.109
Sample D	1.391	1.401	124.5	119.2	2.71	1.109

^aSample A: undoped *trans*-polyacetylene. Sample B: Li-doped *trans*-polyacetylene. Sample C: Na-doped *trans*-polyacetylene. Sample D: K-doped *trans*-polyacetylene.

III. RESULTS AND DISCUSSIONS

The dimerization amplitude of pristine *trans*-polyacetylene as evident from the experimental results should lie in between 0.08 and 0.09 Å.^{20,21} Nutation nuclear magnetic resonance data predict the CC single and double bond lengths as 1.44 and 1.36 Å, respectively, while Kahlert *et al.*,²² on the basis of x-ray powder data, have reported the CC single and double bond lengths as 1.45 and 1.36 Å, respectively. Since there is a discrepancy in the experimental results of these bond lengths, the geometry of the unit cell of the pristine *trans*-polyacetylene and its doped analog are optimized through DFT calculations. Earlier Choi *et al.*¹⁴ investigated the effect of electronic correlation on bond length alternation at various levels of quantum chemical calculations. They have explored the explicit influence of dynamic and nondynamic correlation energy on bond length alternation. The results of Choi *et al.*¹⁴ suggest that the dimerization amplitude obtained with nondynamical correlation effect is significantly smaller (0.05 Å) than that of the experimentally observed values (0.08 and 0.09 Å). Therefore, to overcome the underestimation problem of dimerization amplitude, geometry of the unit cell should be optimized using dynamic correlation functional. Interestingly, theoretical works of Mok *et al.*²³ suggest that LYP correlation functional is dynamical in nature. In the present study, the use of BLYP exchange-correlation functional with TZ2P basis produces dimerization amplitude of 0.08 Å. Moreover the CC single (1.42 Å) and CC double (1.34 Å) bond lengths of pristine *trans*-polyacetylene obtained with BLYP exchange-correlation functional are also very close to the experimentally observed values (1.36 and 1.44 Å). Since the optimized structure with BLYP exchange-correlation functional corroborates experimental findings, geometry optimization of the unit cells of the doped samples has also been performed using the same exchange-correlation functional. The detail geometric parameters of all the samples are displayed in Table I.

The energy band structure of undoped *trans*-polyacetylene comprised of three monomer units in a unit cell is presented in Fig. 2. The band gap for the trimer unit cell is calculated as 0.73 eV and the gap for a lattice consisting of two monomer acetylene units is found to be ~ 1.0 eV. The underestimation of band gap is due to the inherent nature of DFT calculation.

Energy band structure of doped *trans*-polyacetylene is investigated through a series of calculations with different types of metallic dopants (Li, Na, and K). The metals are the *n*-type dopants to the conducting polymer chain. Density functional band structure calculation is performed for a chain experiencing a 33.3% doping per monomer. The electronic band structures obtained due to Li doping are presented in Figs. 3 and 4. The results of both LDA and GGA calculations indicate the appearance of two distinct energy bands in the gap between the valence band (π band) and conduction band (π^* band). Results also indicate appreciable charge transfer from the Li atom to the polymer chain in both the calculations. This feature is reflected in Table II. The position of Fermi energy level is also described in Table II. The energy

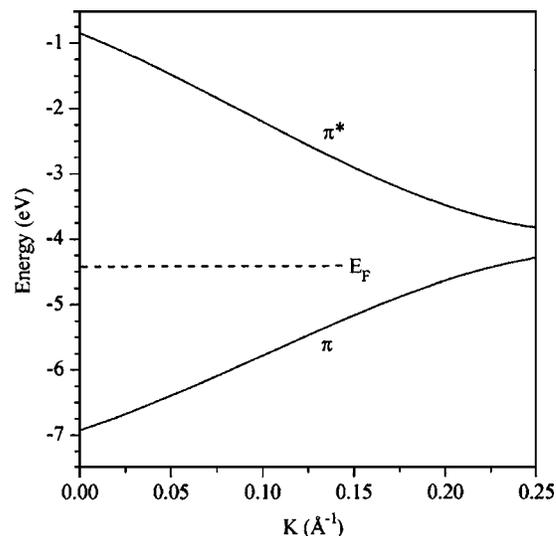


FIG. 2. Band structure of undoped *trans*-polyacetylene.

band structure (Fig. 3) obtained in LDA calculation reveals that the midgap states and π , π^* have started crossing each other. The crossing of energy bands establishes the fact that the metallic situation has been achieved. The metallic situation is more pronounced in the energy band structure (Fig. 4) obtained from GGA calculation. There is a wider smearing of mid-gap states and it provides a description of better metallic situation.

Similar results are obtained when sodium and potassium are used as dopants. In the case of LDA calculation with sodium the charge transfer from sodium to the polymer chain is appreciable. This is also true in the case of GGA calculation. The relevant data along with the position of Fermi energy level are available in Table II. The energy band structure obtained with LDA calculation is depicted in the Fig. 5. Similar to the case of Li doping two distinct energy bands have appeared in the gap between the π band and π^* band. A near metallic situation is introduced due to the closure of the gap states. The introduction of near metallic situation due to

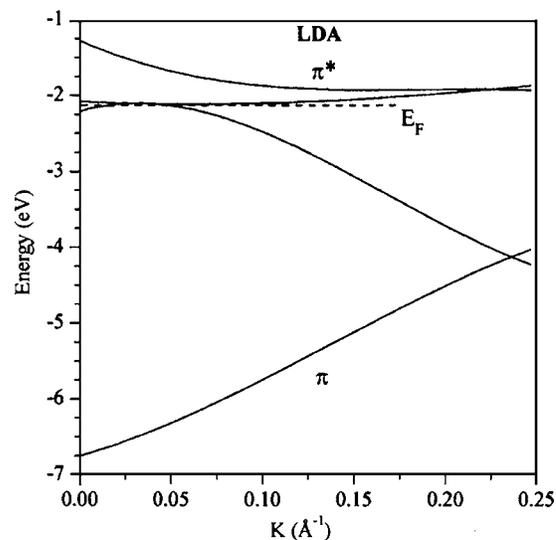


FIG. 3. Band structure of 33.3% Li doped *trans*-polyacetylene in LDA scheme.

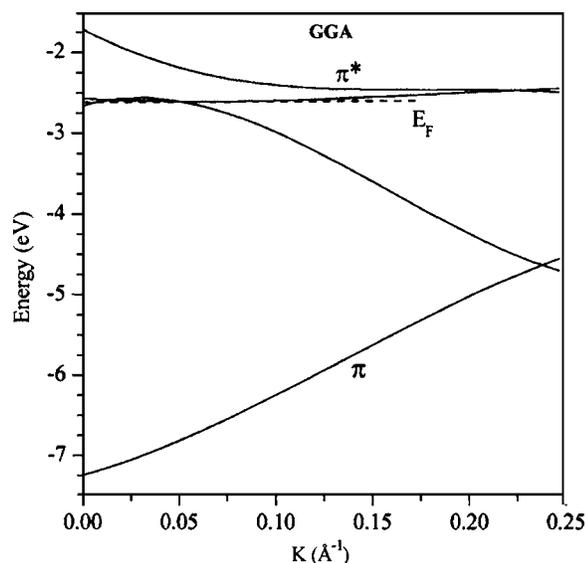


FIG. 4. Band structure of 33.3% Li doped *trans*-polyacetylene in GGA scheme.

heavy doping of sodium is more prominent in the energy band structure obtained in GGA calculation. The relevant band structure is depicted in Fig. 6. In this case two mid-gap states are closer to each other, which is clearly an indication of better metallic situation compared to the results of LDA calculation.

LDA and GGA calculations performed with potassium as dopant reveal that the overall charge transfer from potassium to the polymer chain has been increased in comparison to the Li and Na doped samples. The supporting information as well as the position of Fermi energy level is described in Table II. The energy band structure obtained in LDA and GGA calculations is described in Figs. 7 and 8, respectively. Similar to the cases of Li and Na doping two distinct gap states are created in the gap between the π band and π^* band. The closure of mid-gap states increases from LDA to GGA. The fact that the gap states are getting closer to each

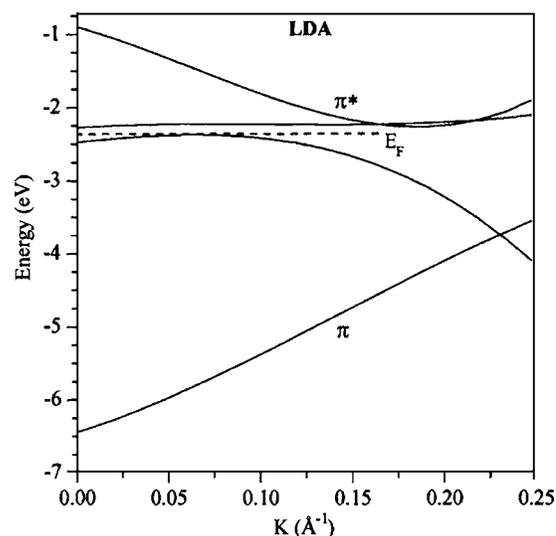


FIG. 5. Band structure of 33.3% Na doped *trans*-polyacetylene in LDA scheme.

other, as theoretically stronger correlation effect is introduced, establishes the role of electron correlation on the metallic state.

The results of energy band structure calculations indicate an upward shift of Fermi energy level of the doped samples in comparison to its undoped analog. This is expected in case of metallic dopants as they introduce an *n*-type situation where Fermi energy level is nearer to the conduction band. Results of LDA and GGA calculation in all the cases yield comparable valence and conduction band width. The valence band edge and the lower gap state cross each other at the end of first Brillouin zone in each type of doping. Significant overlap of upper gap state and the conduction band edge has been observed in every doped sample and it represents near metallic situation. These observations are supported by the results of Table II. However, the true metallic situation can only be achieved if upper and lower gap states merge together apart from the overlap of lower and upper gap states

TABLE II. Results of electronic band structure calculations of doped and undoped *trans*-polyacetylene.^a

Sample	Charge transferred per carbon (<i>e/C</i>)	Fermi level (eV)	π and π^* bandwidth (eV)	Lower and upper gap state crossing (\AA^{-1})	Upper gap state and π^* band crossing (\AA^{-1})
Sample A	N.A.	-4.4222	2.6553 and 2.9984	N.A.	N.A.
Sample B (LDA)	0.0773	-2.1378	2.704 and 0.618	$K=0.0303$ and 0.0390	$K=0.2252$
Sample B (GGA)	0.0823	-2.6011	2.686 and 0.744	$K=0.0162$ and 0.0510	$K=0.2255$
Sample C (LDA)	0.0736	-2.3557	2.8896 and 0.9891	Energy gap of 0.1365 eV	$K=0.1648$ and 0.2181
Sample C (GGA)	0.0733	-2.8759	2.8355 and 1.1483	Energy gap of 0.0845 eV	$K=0.1647$ and 0.2153
Sample D (LDA)	0.0816	-2.0445	2.958 and 0.53	Energy gap of 0.0197 eV	$K=0.1875$ and 0.2099
Sample D (GGA)	0.0933	-2.4151	2.966 and 0.808	Energy gap of 0.0045 eV	$K=0.1731$ and 0.2151

^aSample A: undoped *trans*-polyacetylene. Sample B: Li-doped *trans*-polyacetylene. Sample C: Na-doped *trans*-polyacetylene. Sample D: K-doped *trans*-polyacetylene.

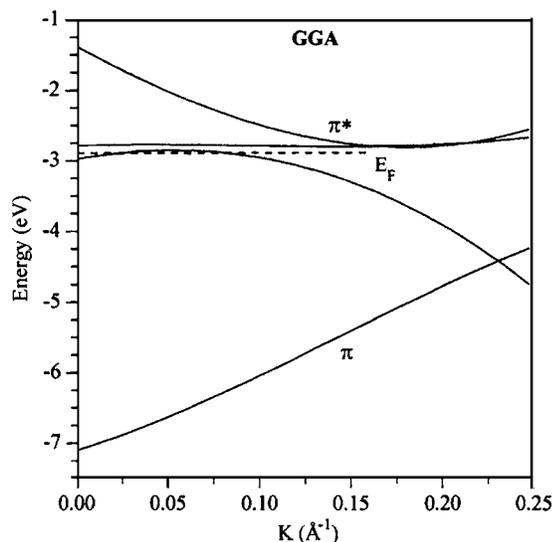


FIG. 6. Band structure of 33.3% Na doped *trans*-polyacetylene in GGA scheme.

with valence and conduction band, respectively. The smearing of gap states and hence realization of the insulator to metal transition is quite prominent in Li doped *trans*-polyacetylene. The upper and lower gap states are in close proximity in case of doping with Na; the better the correlation (comparison of LDA and GGA results) the closer the gap states are. The closeness of the gap states is increased in the calculation with potassium as dopants. In case of GGA results with K doping, the energy gap between the gap states is as low as 0.0045 eV.

The metallic situation demonstrated here is significantly different from the earlier works. Paloheimo *et al.*⁵ in their LDA calculation with *trans*-polyacetylene chain considered two holes per unit cell of $C_{10}H_{10}$, which is an attempt to introduce strongly interacting polarons or solitons in *trans*-polyacetylene chain. In their band structure calculation either of polaron lattice or soliton lattice, band gap depends on dimerization amplitude and as a consequence their result

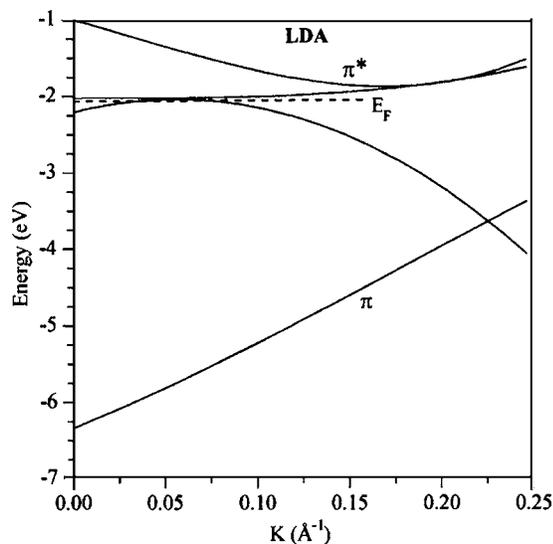


FIG. 7. Band structure of 33.3% K doped *trans*-polyacetylene in LDA scheme.

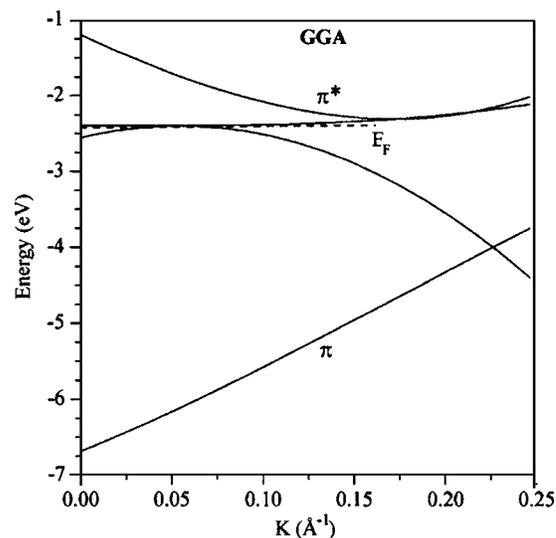


FIG. 8. Band structure of 33.3% K doped *trans*-polyacetylene in GGA scheme.

fails to account for a metallic situation with finite dimerization amplitude. Moreover the dopants are not included explicitly. Conwell *et al.*⁴ described the metallic state of potassium doped *trans*-polyacetylene considering more than one *trans*-polyacetylene chain and in their calculation electron correlation effect is not taken into account. They have also neglected the role of the dopants explicitly in the band structure calculations. Sun *et al.*¹³ have considered $K(C_6H_6)$ as a unit cell for calculating the band structure which actually resembles metallic state but they have also presumed elimination of Peierls distortion in their model calculations. In the present study band structure calculations have been performed on quasi-one-dimensional *trans*-polyacetylene chain of infinite length, both doped and undoped form and bands from the dopants have been considered explicitly. The present investigation suggests that the true metallic or near metallic state of doped *trans*-polyacetylene chain of infinite length is possible even if Peierls distortion exists. The presence of subtle but discernible lattice dimerization and simultaneous metallic state is quite remarkable and in this regard the role of charge transfer is very important.

The transfer of charge from the dopant to the polymer chain will affect the electron-electron ($e-e$) interaction and electronic correlation to a significant extent. The effect of electronic correlation and electron-electron interaction for pristine *trans*-polyacetylene has been thoroughly investigated over the past two decades.²⁴ The results of the combining effect of $e-e$ interaction and electron correlation indicate that for short range $e-e$ repulsion the bond alternation actually decreases with the enhancement of $e-e$ interaction strength and the magnitude of bond alternation will increase if long range $e-e$ repulsion is being considered.²⁵ Although contradictory arguments exist, nevertheless it appears decisive that electron correlation effect always tends to decrease lattice dimerization.²⁵ The quenching of lattice dimerization in heavily doped *trans*-polyacetylene in comparison to its pristine analog is possibly due to the greater electron correlation effect.

The possibility of geometric change upon charge injection has been a matter of great debate among many investigators;^{15,26} the belief about the existence of soliton in doped $(\text{CH})_x$ predicts a vanishing of bond alternation and the introduction of a near metallic regime while others have the opinion that bond alternation still persists although it is greatly reduced in comparison to the undoped chain.²⁷ The results of the present study reveal that albeit appreciable charge injection occurs to the chain still there exists bond alternation by a margin of 0.03–0.01 Å. Therefore in view of the above discussion one may surmise that the closure of Peierls gap, a reflection of the metallic state, should not appear.

Surprisingly, the crossing or smearing of energy bands of highly doped *trans*-polyacetylene has been observed even in the presence of this small Peierls distortion. It indicates that closure of Peierls gap is not at all necessary to arrive at the metallic state of *trans*-polyacetylene. The most striking feature of DFT calculation is that it includes electron correlation effect even in one electron Kohn-Sham equation. The smearing of energy bands as evident from the analysis indicates that electronic correlation effect plays the dominant role in the creation of such metallic state. Choi *et al.*¹⁴ studied the effect of electronic correlation on reduction of the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap of undoped oligoenes through an alternative density functional approach. They have investigated the explicit influence of dynamic and nondynamic correlation energy on HOMO-LUMO gap. The results obtained from Choi *et al.*¹⁴ evidently support the dominant role of electronic correlation on quenching of HOMO-LUMO gap. HOMO-LUMO gap is an approximate measure of band gap in solid. Among the two different exchange-correlation functionals (VWN and BLYP) used in this paper, the superiority of BLYP (dynamical) over LDA is that it includes fluctuation in electron density in space because of its GGA nature. Based on comparison of DFT methods that include correlation to different degrees, we conclude that correlation lowers the band gap in Na and K doped *trans*-polyacetylene and in Li doped sample the gap completely disappears.

IV. CONCLUSION

In summary, we have presented the detailed results from a series of simulations implemented in ADF software by which we have investigated the effect of correlation on electronic band structure of highly doped *trans*-polyacetylene. The major findings of the present investigation are (i) small lattice dimerization, (i.e., remnant of Peierls distortion exists even in the heavily doped *trans*-polyacetylene sample and has been observed in all the cases, (ii) charge induced clo-

sure of the Peierls gap is not a necessary condition to arrive at a metallic state in such systems, (iii) electronic correlation, as described at the DFT level, with a charge induced small Peierls distortion is sufficient to achieve metallic state of highly doped *n*-type *trans*-polyacetylene even in one dimension. Finally, the detailed role of dynamic and static correlation effect on the band structure of doped *trans*-polyacetylene will be considered in a future work.

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- ¹S. Welter, K. Brunner, J. W. Hofstra, and L. De. Cola, *Nature (London)* **421**, 54 (2003).
- ²S. Chakrabarti, D. Banerjee, and R. Bhattacharya, *J. Phys. Chem. B* **106**, 3061 (2002).
- ³S. Chakrabarti, S. N. Bhattacharya, D. Banerjee, and R. Bhattacharyya, *J. Chem. Phys.* **113**, 7593 (2000).
- ⁴E. M. Conwell, H. A. Mizes, and S. Jeyadev, *Phys. Rev. B* **41**, 5067 (1990).
- ⁵J. Paloheimo and J. Von Boehm, *Phys. Rev. B* **48**, 16948 (1993).
- ⁶D. B. Tanner, G. L. Doll, A. M. Rao, P. C. Eklund, G. A. Arbuckle, and A. G. MacDiarmid, *Synth. Met.* **141**, 75 (2004).
- ⁷S. Chakrabarti, *J. Chem. Phys.* **110**, 9305 (1999).
- ⁸S. Chakrabarti, B. Das, P. Banerji, D. Banerji, and R. Bhattacharya, *Phys. Rev. B* **60**, 7691 (1999).
- ⁹A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, *Rev. Mod. Phys.* **60**, 781 (1988).
- ¹⁰J. L. Brédas, in *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Dekker, New York, 1986), Vol. II, pp. 860–907.
- ¹¹V. Bezugly and U. Birkenheuer, *Chem. Phys. Lett.* **399**, 57 (2004).
- ¹²J. L. Brédas, R. R. Chance, and R. Silbey, *J. Phys. Chem.* **85**, 756 (1981).
- ¹³G. Sun, J. Kürti, M. Kertesz, and R. H. Baughman, *J. Chem. Phys.* **117**, 7691 (2002).
- ¹⁴C. H. Choi, M. Kertesz, and A. Karpfen, *J. Chem. Phys.* **107**, 6712 (1997).
- ¹⁵W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ¹⁶R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).
- ¹⁷<http://www.scm.com>.
- ¹⁸S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- ¹⁹(a) A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988); (b) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ²⁰C. S. Yannoni and T. C. Clarke, *Phys. Rev. Lett.* **51**, 1191 (1983).
- ²¹C. R. Fincher, Jr., C.-E. Chen, A. J. Heeger, and A. G. MacDiarmid, *Phys. Rev. Lett.* **48**, 100 (1982).
- ²²H. Kahlert, O. Leitner, and G. Leising, *Synth. Met.* **17**, 467 (1987).
- ²³D. K. W. Mok, R. Neumann, and N. C. Handy, *J. Phys. Chem.* **100**, 6225 (1996).
- ²⁴J. Malék, S.-L. Drechsler, S. Flach, E. Jeckelmann, and K. Kládsko, *J. Phys. Soc. Jpn.* **72**, 2277 (2003).
- ²⁵C. Wu, X. Sun, and K. Nasu, *Phys. Rev. Lett.* **59**, 831 (1987).
- ²⁶G. Sun, M. Kertesz, J. Kürti, and R. H. Baughman, *Phys. Rev. B* **68**, 125411 (2003).
- ²⁷M. J. Rice, *Phys. Lett.* **A71**, 152 (1979).