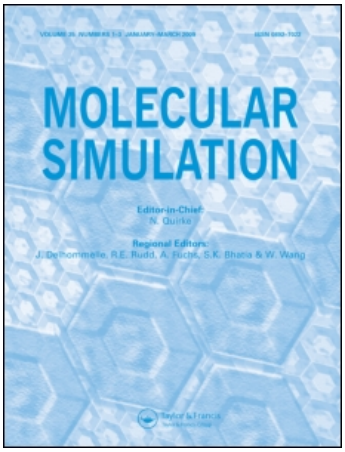

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Interatomic Potentials in Conducting Polymer Systems

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INTERATOMIC POTENTIALS IN CONDUCTING POLYMER SYSTEMS

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Although the crystal structures of some ion-doped lattices of polyacetylene and polyparaphenylene have been investigated by diffraction methods there remain ambiguities both in the overall structures and in the precise locations of the dopant ions. We have used bonding and non-bonding interatomic potentials developed from empirical and quantum chemical data in a CASCADE atomistic lattice simulation method which permits full optimization of the lattic geometry. These calculations lead to stable structures which are consistent with diffraction data, and suggest the tendency of these lattices towards polymorphism.

KEY WORDS: Doped polymers, polyacetylene, polyparaphenylene, crystallographic sites

1 INTRODUCTION

If we wish to model a lattice sufficiently well that the simulation can successfully account for the migration of atomic or molecular species through the lattice, it is generally held that essential requirements are

(1) The precise positions of the atomic constituents of the unit cell.

(2) The electronic charges associated with these atoms.

(3) A set of good quality interatomic potential functions. If the lattice contains a covalent component these functions must describe both the formally bonded atoms and also the non-bonded interactions between molecular units. The functions describing the covalently bonded atoms, moreover, must also be capable of reproducing the directional nature of the covalent bonding.

We have used a version of the atomistic simulation program CASCADE [1] (whose application to ionic lattices is well known) to investigate the structures and dopant migration in ion-doped lattices of polyacetylene (PA) and polyparaphenylene (PPP), which are conducting polymer systems used in electronic devices [2–4]. The directional interactions associated with the covalent sublattice are distinguished from the "non-bonded" interactions by specifying ranges over which the appropriate potentials act, and the directionality is enforced by declaring a set of equilibrium bond angles, each with its appropriate bending force constant. The lattice energy, expressed as a sum of covalent, non-bonding and Madelung contributions, is minimized with respect to the geometry of the unit cell, thus locating a minimum on the energy surface. This variation procedure, which permits changes in bond lengths and bond angles, will be referred to as a "relaxation," and its inclusion is often essential, particularly to locate higher-energy structures.

Unfortunately, in the doped PA and PPP lattices, the requirements (1) to (3) above are not always met. Firstly, the regions of crystallinity in the polymer samples are small; consequently the interpretations of data by various diffraction groups show ambiguity. As a result independent investigations of the same polymer system have furnished not only different lattice vectors and chain setting angles, but occasionally quite different structures. Secondly, although the potential functions describing the bonding interactions probably may be validly "carried over" from model molecules where they are known, such confidence does not extend to the existing set of non-bonded potential functions. Also, the absence of reliable compressibility or dielectric data on these doped polymers precludes the use of bulk properties to determine the desired potentials.

2 APPLICATIONS

2.1 First-stage Li-intercalated graphite C_6Li

Simulation investigations on this lattice system, which has features in common with both ionic lattices and ion-doped conducting polymer lattices, have been described elsewhere [5]. The interlamellar C . . . C interactions were specified by a potential function derived by Crowell [6] to provide good lamellar spacings and satisfatory elasticity parameters for pristine graphite; the Li . . . C interaction was described by a Morse potential whose parameters were derived from a combination of infra-red

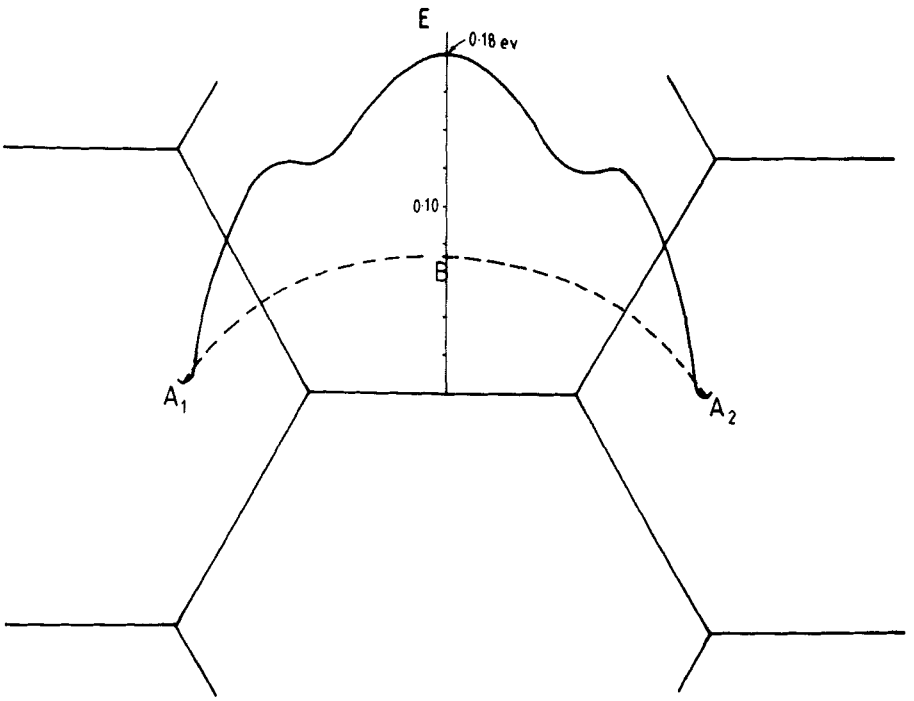


Figure 1 Broken line: The adiabatic pathway calculated for a Li^+ ion migrating between two adjacent vacancies. Continuous line: Energy profile, showing the barrier for the migration.

measurements on lithium π-complexes of aromatic rings and quantum chemical calculations [5]. The Li^+ intercalate ions occupied six-fold axial sites between carbon hexagons in adjacent lamellae, in such a way that each C atom was equidistant from a Li^+ ion, and was therefore assigned a nett charge of $(-1/6)e$.

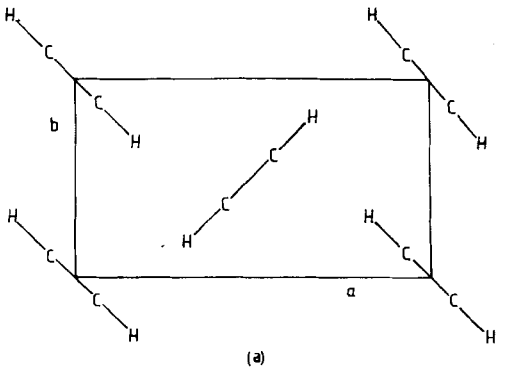
The result of this investigation (Figure 1) provided a route for the migration of a lithium atom between two Li^+ vacancies, and an estimate of the energy barrier as 0.18 eV, a figure which compares well with the experimental activation energy of 0.19 eV from lithium-7 NMR line-widths [7], although short of the 0.6 eV obtained from lithiume-8 beta-NMR studies [8].

2.2 Polyacetylene lattice systems

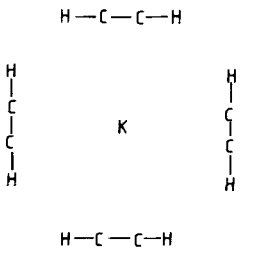
We present here a summary of results, full details of which will shortly appear in a series of papers [9–11].

2.2.1 Pristine trans-polyacetylene

Although most of the diffraction investigations on *trans*-polyacetylene [12–14] agree



(a)



(b)

Figure 2a The unit cell of *trans*-polyacetylene, projected on the ab plane, i.e. normal to the chain direction. The same figure represents polyparaphenylene and also the latter lattice doped with lithium, with the Li^+ ions occupying sites half-way along the a and b axes.

Figure 2b A molecular channel in potassium-doped polyacetylene, projected normal to the chain direction.

on the monoclinic lattice with an ab angle of approximately 90°C (Figure 2a), Table 1 shows that the consensus does not extend to the lattice vectors or to the setting angle – the angle between the polymer planes and the a axis. It has been suggested [15] that at least part of the ambiguity may be a consequence of different preparative conditions.

Using bond energies, bond lengths, stretching and bending force constants from model hydrocarbons to construct Morse potentials [12] for C–C and C–H bonds, and 'Williams IV' potentials [16] to describe the non-bonding interactions, we found two stable structures differing by 0.17 eV, with cell dimensions and setting angles shown in Table 1. The setting angles were not unlike the experimental values found by the various diffraction groups.

It is notable that when simulation calculations are performed on a rigid PA lattice, i.e. when the lattice energy is *not* optimized with respect to bond angles and bond lengths, we find only one stable structure [9], with a setting angle of 62°.

2.2.2 Potassium-doped polyacetylene

Diffraction studies [17–20] of the structure obtained when potassium enters the PA lattice lead to approximately square channels formed by the polymer chains, with K^+ ions occupying axial sites along the centres of the channels (Figure 2b). However neither the positions of the K^+ sites nor their separations have been unambiguously determined. The use of the measured stoichiometry ($CHK_{0.18}$) is unreliable to ascertain the latter, since the doping is known to be inhomogeneous, but would suggest two $K^+ \ldots K^+$ separations: one corresponding to a K^+ ion at every $-CH = CH-$ segment along the polymer axis, and another to a K^+ site at alternate segments.

Assuming commensurability we simulated both these lattices, and called them respectively PAK1 and PAK2. In PAK1 a K^+ ion is surrounded by four $-CH = CH-$ segments. If we assume that the electrons from the potassiums are transferred just to the carbon-atom sublattice, the charge distribution is unambiguously -0.25 e associated with each C atom. In PAK2 in which the doping is half this level, we could propose two charge distributions: if the distribution is assumed to be even, each C atom will have a charge of -0.125 e; it might be argued, however, that in this case only *alternate* $-CH = CH-$ segments are adjacent to a dopant K^+ ion, and would be expected to bear a higher charge than their neighbours. Accordingly we simulated two PAK2 lattices: one with evenly charged C atoms, and another in which the C atoms bore the sequence of charges -0.25 e, -0.25 e, 0, 0, -0.25 e, . . .

Table 1 Crystal structural data on pristine polyacetylene

		Experimental data			*Calculated*	
	ref.	*12*	*13*	*14*	*I*	*II*
lattice vectors	a	7.41	7.32	7.32	6.95	7.10
	b	4.08	4.24	4.24	4.10	4.57
	c	4.96	4.96	4.96	4.97	4.97
chain setting angle	ϕ	51°	55°	24°	62°	22°

For all the lattices described in the previous paragraph we found that stable structures could be generated only when the K^+ sites were located over the centres of the C = C bonds, a fact which is consistent with the results of semi-empirical calculations on these doped polymer chains [21]. In fact, when the K^+ sublattice is displaced from such a position, the K^+ ions return to the sites described on relaxtion.

On creating a vacancy in the K^+ sublattices of either PAK1 or of PAK2 we find [11] that the lines of dopant ions on each side of the vacancy move towards each other, effectively "closing ranks" to eliminate the vacancy. For PAK2 this occurs for both of the two charge distributions considered. This behaviour distinguishes such a dopant vacancy from that described in Li-intercalated graphite, where the energy barrier is sufficient to keep a Li^+ vacancy localized at the original site.

The instability of K^+ vacancies in PA thus precludes a migration of a dopant ion by the 2-vacancy-1-interstitial mechanism investigated in C_6Li, since we would expect ion transport in the former to proceed by a concerted mechanism involving several K^+ ions.

2.3 Polyparaphenylene lattice systems

2.3.1 Pristine polyparaphenylene

The PPP lattice, which has a unit cell which can be represented by a diagram similar to Figure 2a for PA, stabilized to a global minimum structure with a setting angle of 62°, and to a second structure, 0.2 eV higher, with a setting angle of 40°. These angles may be compared with 57° and 45° obtained respectively from the neutron-[22] and electron-[23] diffraction work of Stamm et al., who suggest that the origin of this variation may be polymorphism arising from different conditions obtaining in the preparation of samples for these two methods. We again noted the necessity of permitting a complete lattice relaxation to occur in order to locate the higher-energy structure.

2.3.2 Alkali-metal-doped polyparaphenylene

Diffraction studies [13, 14] show that when lithium enters the PPP latice it leaves the position of the host sublattice almost undisturbed. The unit cell, containing a phenyl ring from each of two PPP chains, is associated with a dopant site mid-way along the a and b axes.

Our simulation method failed to generate a stable latticec when Li^+ occupied *both* the specified sites. Relaxation to the experimental structure occurred only when the dopant ion occupied the site on either the a or the b axis (these positions are symmetrically equivalent). This result is consistent with the empirically determined maximum doping level of 50%; however the distribution of the dopants in the sites is not known experimentally. Other semi-doped structures, defined by doubling the length of the unit cell along the chain axis, and (i) declaring the a and b sites to be occupied in one half of the cell and vacant in the other half, or (ii) allowing Li^+ to occupy a and b sites alternately, failed to produce a stable lattice.

When potassium enters the PPP lattice it produces a more significant change [19] in the structure of the polymer sublattice than is the case with lithium (this is also true when the polymer is PA). Our calculations produced a simulated lattice with cell vectors and chain setting angles close to experimental values, but predict a stability for the 'fully doped' structure, i.e. that in which all the specified sites are occupied by K^+ ions.

3 CONCLUSIONS

We obtained the results described here using potentials based on

(1) standard non-bonded interatomic potentials obtained principally by averaging those derived from crystal structural data or from quantum chemical calculations on a collection of interacting systems, and

(2) bonded interatomic potentials of Morse form, whose parameters are derived from experimental data on model compounds.

The results show that despite the "unsophisticated" nature of the potentials used, calculations produce structures which are consistent with available diffraction structural data, and, provided the lattice is allowed to relax fully, can predict polymorphisms which may also be consistent with empirical investigations.

Lattice defect calculations on lithium-intercalated graphite and to potassium-doped polyacetylene produce results which are physically reasonable, and lead, in the former case, to an energy barrier agreeing well with experiment. This fact is encouraging, considering that the theory upon which CASCADE is based was originally developed for lattices that are of essentially ionic character [1].

We are currently extending the calculations described so as to investigate the migration of various ionic species through polyacetylene and polyparaphenylene.

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