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# Structure of lithium-doped polyacetylene

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A trigonal structure with three polymer chains per lithium column is proposed for lithium-doped polyacetylene. A calculation of the x-ray diffraction profile, using the unit-cell dimension and the lithium concentration as the only variables, is in good agreement with the observed data. The proposed structure optimizes the electrostatic interactions by maximizing both the $Li^+$-$Li^+$ separations and the coordination of negatively charged carbons and positively charged lithiums. Unlike the tetragonal lattice found in polyacetylene complexed with larger alkali-metal ions ($K^+$, $Rb^+$, and $Cs^+$), the trigonal structure permits the undoped and the doped phases to coexist without any significant lattice mismatch at the boundary between the two phases. While the chain axis expands by ~1% upon doping with lithium, the projected area per chain remains essentially unchanged.

## I. INTRODUCTION

The formation of columns of alkali-metal ions in channels formed by polyacetylene chains is now well established.[1-4] In Fig. 1, the sizes of the various alkali-metal ions are compared with the dimensions of the channel formed by four polyacetylene chains in our previously proposed tetragonal structure. While the channel provides an ideal fit for the $K^+$ ions, the channel has to expand slightly to accommodate the larger $Rb^+$ and $Cs^+$ ions; this expansion of the lattice has been experimentally observed.[1] On the other hand, the small sizes of the $Na^+$ and $Li^+$ ions leaves considerable free volume in such tetragonal phases, so that the $Na^+$ tetragonal phase is metastable and the $Li^+$ tetragonal phase is unobserved. This excess free volume is minimized when columns of these smaller radius ions are formed in channels associated with three polyacetylene chains.[4-6] We now provide evidence for such a structure with three chains per column for the lithium complex, and compare the details of this trigonal structure with the structures observed for other alkali-metal complexes of polyacetylene. We also discuss some important implications of this trigonal phase on the evolution of the doped phases in lithium-doped polyacetylene.

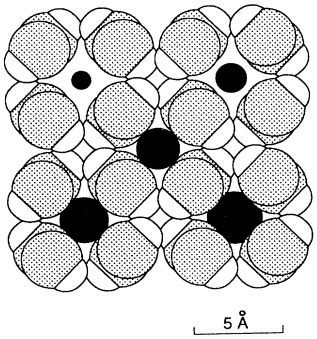

FIG. 1. Comparison of the sizes of the alkali-metal ions and the unrelaxed tetragonal unit cell. $Li^+$ and $Na^+$ are shown in the top row, $K^+$ in the center, and $Rb^+$ and $Cs^+$ in the bottom row.

## II. EXPERIMENTAL METHODS AND RESULTS

All samples used in this Rapid Communication were prepared using polyacetylene obtained by the Shirakawa method. One exception is a sample prepared using the highly oriented polyacetylene obtained from Lugli, Pedretti, and Perego.[7] The polyacetylene films were chemically doped with lithium via different routes: butyllithium in hexane (series *A*), phenyllithium in cyclohexane-diethyl ether (series *B*), and biphenyllithium in 2-methyltetrahydrofuran (THF) (series *C*). The solvent was routinely removed by pumping under dynamic vacuum for 16 h. Some samples were also evacuated at elevated temperatures. Polar solvents such as THF are known to coinsert with lithium;[3] however, the nonpolar solvents used with butyllithium and phenyllithium apparently either do not coinsert or are more easily eliminated. For this reason, the best samples were obtained by chemical insertion from solutions in hexane or cyclohexane-diethyl ether.

The doped samples were sealed under argon atmosphere in quartz capillaries for x-ray diffraction (XRD) measurements. XRD data were obtained on a Huber goniometer using Ni filtered Cu radiation. Several data sets were also recorded on a photographic film on a flat-plate camera with nickel filtered copper radiation. The background scattering due to the capillary was subtracted from the diffractometer data. X-ray diffraction patterns of the proposed structural model were simulated using the "POWDER 10" program of Smith.[8] An isotropic temperature factor of 5 $Å^2$ was assumed for all the atoms. The calculated intensities and the observed intensities were scaled using the most intense reflection at $2\theta \sim 25°$.

X-ray diffraction data in the form of diffraction spacings (*d* spacings) from lithium-doped polyacetylene samples are given in Table I. The samples prepared by different routes gave very similar patterns. The coherence

TABLE I. Summary of data for lithium-polyacetylene complexes.

| | | | Diffraction spacings (Å)[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Dopant level (%)[b] | $\sigma$ ($S$/cm)[c] | 110 | 300 | 220 | 122 | 410+113 | 330 | 600 | $a$ (Å)[d] |
| ($A$) | | | | | | | | | | |
| 1 | · · · | · · · | 6.30 | 3.67 | 3.18 | · · · | 2.36 | 2.10 | · · · | 12.62(9) |
| ($B$) | | | | | | | | | | |
| 1 | · · · | · · · | 6.15 | 3.55 | 3.10 | · · · | 2.33 | 2.05 | 1.78 | 12.33(4) |
| 2 | · · · | 200 | 6.30 | 3.62 | 3.15 | 2.69 | · · · | 2.09 | · · · | 12.50(3) |
| 3 | 16.4 | 164 | 6.35 | 3.65 | · · · | · · · | 2.39 | 2.09 | · · · | 12.63(7) |
| 4 | · · · | 170 | 6.25 | 3.60 | · · · | · · · | 2.33 | 2.07 | · · · | 12.43(7) |
| 5 | 15.0 | 139 | 6.30 | 3.64 | 3.15 | · · · | 2.38 | 2.09 | · · · | 12.59(3) |
| 6 | · · · | · · · | 6.28 | 3.65 | · · · | · · · | 2.37 | 2.10 | · · · | 12.60(4) |
| 7 | · · · | · · · | 6.20 | 3.60 | 3.18 | 2.65 | 2.30 | 2.08 | · · · | 12.44(19) |
| 8 | 10.0 | 130 | 6.30 | 3.64 | 3.12 | 2.70 | · · · | 2.10 | · · · | 12.57(6) |
| ($C$) | | | | | | | | | | |
| 1 | 17.0 | 60 | 6.20 | 3.70 | · · · | · · · | · · · | 2.06 | · · · | 12.52(25) |
| 2 | · · · | · · · | 6.20 | 3.60 | · · · | · · · | · · · | · · · | · · · | 12.44 |

[a] Indices based on space group $R3$; $hkl$ and $kh\bar{l}$, reflections which have the same $d$ spacings, are not shown separately.

[b] Elemental analysis.

[c] Four-probe measurement.

[d] Numbers in parentheses are standard deviations in hundredths of Å.

length estimated from the equatorial reflections was typically ~60 Å, and is similar to that found for other alkali-metal polyacetylene complexes.[1] The $d$ spacings in Table I could be indexed with a trigonal lattice, using a unit-cell parameter in chain-axis projection of $a' = 7.1-7.3$ Å. As we shall see later, a larger cell with $a = 2a' \cos 30°$ $= 12.3-12.6$ Å and $c = 7.5$ Å describes the structure in three dimensions. The lowest value for the $a$-axis length (12.33 Å) was obtained for the highly oriented polymer (sample 1, series $B$), while this length for unoriented films varied from 12.4 to 12.6 Å. For highly ordered lithium-doped polyacetylene, the most probable value of $a$-axis length is 12.4 Å. This value will be used in the remainder of the paper.

## III. DISCUSSION

Our proposed model to interpret the XRD data from lithium-doped polyacetylene is shown in Fig. 2. The major energetic advantages of the proposed structure are as follows: (i) The $Li^+$ ions are fully coordinated by carbon atoms. There are no nearest-neighbor lithium ion-hydrogen interactions. (ii) Hydrogens on one chain are nearest neighbors to carbons on the neighboring chain. (iii) All $Li^+$ ion columns are equidistant from each other. The intensities calculated using the above model are superimposed on the observed diffraction data in Fig. 3. The agreement between the calculated and the observed profiles suggests that the model we have proposed is basically correct. There are two choices of unit cells. The smaller unit cell with $a' = 7.15$ Å (hexagonal space group $P3$) can account for all the equatorial reflections. However, a larger unit cell with $a = \sqrt{3}a' = 12.4$ Å is required to describe the three-dimensional structure. There are three $C_2H_2$ chemical units along the chain axis in the proposed unit cell, and thus the chain-axis dimension is $c = 7.5$ Å. In this structure, which assumes that the $Li^+$ ion columns are commensurate with the neighboring polyacetylene chains, the alkali-metal atoms are located successively at heights of 0, $\frac{1}{3}$, and $\frac{2}{3}$ in the three columns within the unit cell. Note that it is not necessary for the lithium columns to be commensurate with the polyacetylene chains. In fact, we have shown in iodine-doped polyacetylene that the positions of the iodine atoms in neighboring columns are uncorrelated.[9,10] However, staggering of the alkali-metal ions would reduce the electrostatic energy from intercolumn $Li^+$-$Li^+$ interactions. The nearest-neighbor intercolumn $Li^+$-$Li^+$ separation in the commensurate structure is 7.5 Å if the stoichiometry is $CHLi_{0.111}$, which may also be written as $(C_3H_3)_3Li$. The trigonal space group $R3$ describes this structure using the fewest parameters. Whether or not this phase is trigonal

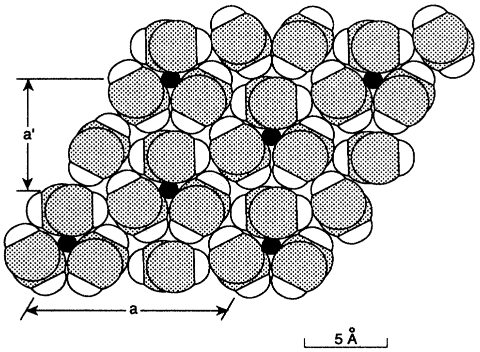

FIG. 2. Structural model proposed for the lithium-polyacetylene complex. The unit-cell is based on space group $R3$, and the dimensions are $a = 12.4$ Å ($a' = 7.16$ Å) and $c = 7.5$ Å. The distance in chain-axis projection between the lithium ion and the center of the chain in projection is 2.15 Å.

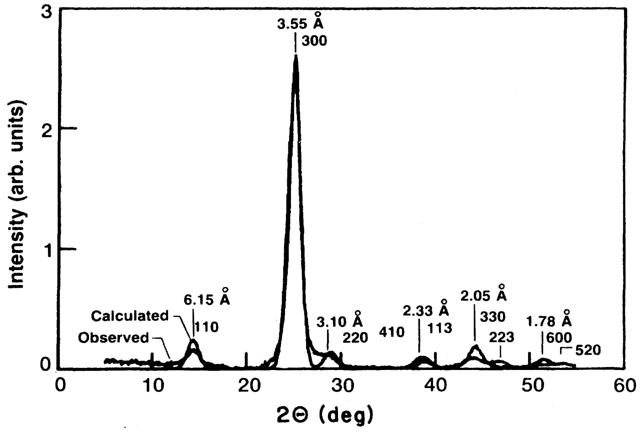

FIG. 3. Comparison of the observed and calculated intensity profiles (space group $R3$; $a = 12.35$ Å; CHLi$_{0.06}$). The observed data is the equatorial scan from a highly oriented film (sample 1, series *B*, Table I). Indices which have the same *d* spacings ($hkl$ and $kh\bar{l}$) are not shown separately. Off-equatorial reflections ($l \neq 0$) shown in the calculated profile are not expected to be present in the observed equatorial data.

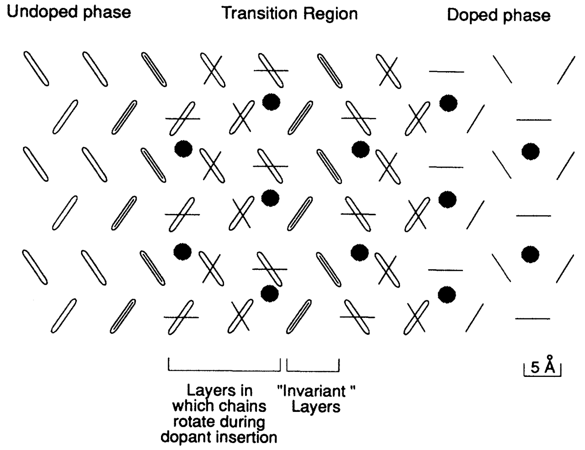

FIG. 4. Superposition of the lattices of undoped and lithium-doped polyacetylene in chain-axis projection. The open cigar-shaped boxes represent polyacetylene in the undoped phase. The lines represent the polyacetylene chains in the doped trigonal phase. The shaded circles are the Li$^+$ ions.

or falls within the broader category of hexagonal is not firmly established.

There are three polyacetylene chains per alkali-metal columm in the proposed model shown in Fig. 2. The stoichiometry, assuming three carbon atoms per Li$^+$ ion along the column in each channel, is $(C_3H_3)_3Li$ or CHLi$_{0.111}$. This concentration provides a 3.75 Å distance between the Li$^+$ ions within a column, which can be compared with 4.42 and 4.26 Å observed, respectively, for the inter- and intralayer Li$^+$-Li$^+$ distances in the LiC$_6$ graphite complex. The observed maximum dopant concentration of CHLi$_{0.19}$ (Ref. 3) cannot be explained by this or any other model requiring three chains per column, since such a complex would require a Li$^+$-Li$^+$ distance of only 2.2 Å, which is much shorter than even the van der Waals diameter of 3.14 Å for metallic lithium. At lithium concentrations higher than 11%, it is likely that solvent molecules are incorporated along with Li$^+$ ions, and that the resulting new complex of solvated ions and polyacetylene permits higher concentrations of lithium per CH unit of the polyacetylene backbone. Solvation of Li$^+$ ions might also occur at low lithium dopant concentrations as well, but such solvation is not evident in our samples used for XRD measurements. This conclusion is also supported by the similarity between our diffraction data and the data of Leitner *et al.* for $(CH)_x$ doped with lithium in vacuum.[2] Increased Li$^+$ concentrations without solvation might result in the insertion of a second set of alkali-metal columns in the columnar interchain voids which are equidistant from the Li$^+$ columns shown in Fig. 2. Complete insertion might result in a composition as heavily doped as CHLi$_{0.22}$ corresponding to $(C_3H_3)_3Li_2$.

Our structural model for the lithium-polyacetylene complex is similar to that proposed by Winokur *et al.* for sodium-polyacetylene complexes.[6] However, Winokur *et al.* do not assign any symmetry elements, nor do they provide the unit-cell dimensions of the structure which they used to explain their observed XRD data. Based on the present work, it appears likely that a trigonal structure may also be valid for sodium-doped polyacetylene, at least at doping levels less than 11%. If this is the case, then the *a*-axis length would be larger for the sodium complex. The values calculated from our data for sodium- and lithium-doped polyacetylene are 13.0 and 12.4 Å, respectively. The difference of 0.6 Å is comparable with the 0.7-Å difference in the van der Waals diameters of Na$^+$ and Li$^+$ ions (1.9 and 1.2 Å, respectively).

The rearrangement of the chains that occurs during the transformation of the pseudohexagonal lattice of the undoped polymer to the trigonal (hexagonal) lattice of the doped phase can be brought about by a simple rotation of the polymer chains about their chain axis (Fig. 4). Insertion of Li$^+$ ions requires essentially no lateral translation of the polymer chains. In fact, the area per chain in projection is almost the same as that of the undoped polyacetylene.[11] For comparison, the chain axis of polyacetylene expands by ~1% upon lithium doping.[12]

During a transition from undoped polyacetylene to our proposed structure for lithium-doped polyacetylene (Fig. 4), we note that some of the chain layers would remain essentially unchanged during doping ("invariant layers"), and only the chains between these invariant layers would have to rotate by ~60° to accomodate the Li$^+$ ions. The invariant layers provide a largely strain-free phase boundary between undoped and doped phases. The lack of interfacial strain would result in enhanced nucleation kinetics for the lithium-doped trigonal phase. A two-phase (first-order) doping process is supported by the data of Leitner *et al.*[2] These data show that during doping a gradual increase in the intensities of the reflections, which we assign to the trigonal phase, is accompanied by corresponding decreases in the intensities of the reflections assigned to undoped polyacetylene.

As an alternative to the presently proposed structure, the $Li^+$ ions are small enough (van der Waals radius of 0.6 Å) that they can be directly inserted into the undoped polyacetylene lattice without chain rearrangement. We have previously shown that holes of radius 0.6 Å exist in the polyacetylene crystal lattice, and that these holes can accommodate the lithium ions.[13] A similar structure has also been proposed by Leitner *et al.*[2] However, the resulting structure is not apparently energetically favorable at appreciable doping levels where mixing entropy cannot compensate for the lower enthalpy of the trigonal phase.

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