Theory of Distinct Crystal Structures of Polymerized Fullerides $AC_{60}$, $A = K$, Rb, Cs: The Specific Role of Alkalis

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The polymer phases of $AC_{60}$ form distinct crystal structures characterized by the mutual orientations of the $(C_{60})_x$ chains. We show that the direct electric quadruple interaction between chains always favors the orthorhombic structure $Pmn$ with alternating chain orientations. However, the specific quadrupolar polarizability of the alkali metal ions leads to an indirect interchain coupling which favors the monoclinic structure $I2/m$ with equal chain orientations. The competition between direct and indirect interactions explains the structural difference between $KC_{60}$ and RbC$_{60}$. CsC$_{60}$.

Alkali metal doped C$_{60}$ ($A_1C_{60}$), $A = K$, Rb, Cs, forms stable crystalline phases (fullerides) with a broad range of physical and chemical properties comprising superconductors and polymer phases. For a review, see Refs. [1,2]. In particular the $x = 1$ compounds [3] exhibit plastic crystalline phases with cubic rock-salt structure at high temperature ($T \geq 350$ K) and polymeric phases [4–6] of reduced symmetry at lower $T$. In the latter the $C_{60}$ molecules are linked through a $[2+2]$ cycloaddition [6], a mechanism originally proposed for photoinduced polymerization [7] in pristine C$_{60}$. From x-ray powder diffraction [6] it was concluded that the crystal structure of both $KC_{60}$ and RbC$_{60}$ was orthorhombic (space group $Pmn$). Polymerization occurs along the orthorhombic $\bar{a}$ axis (the former cubic [110] direction), where the orientation of the polymer chain is characterized by the angle $\mu$ of the planes of cycloaddition with the $\bar{c}$ axis. In the $Pmn$ structure (Fig. 1a), these orientations are alternatively $\mu$ and $-\mu$, $|\mu| = 45^\circ \pm 5^\circ$. Notwithstanding this apparent structural similarity, the electronic and magnetic properties of $KC_{60}$ on one hand and RbC$_{60}$ and CsC$_{60}$ on the other hand were found to be very different [2]. ESR and optical conductivity data [5,8] show that RbC$_{60}$ and CsC$_{60}$ exhibit a transition from a quasi-one-dimensional metal to an insulating magnetic state near 50 K, while $KC_{60}$ stays metallic and nonmagnetic at low $T$. NMR spectra also showed marked differences between $KC_{60}$ and Rb, Cs polymers [9]. The contradiction between similar crystalline structures and different electromagnetic properties was resolved by single crystal x-ray diffraction and diffuse scattering studies [10]. Indeed the polymer phases of $KC_{60}$ and RbC$_{60}$ are different. While the space group $Pmn$ is confirmed for $KC_{60}$, it is found that RbC$_{60}$ is body-centered monoclinic, with space group $I2/m$. In the latter structure, the polymer chains have the same orientation $\mu$ (Fig. 1b). Electronic band structure calculations for the $I2/m$ structure have shown the importance of transverse interchain coupling for RbC$_{60}$ [11]. Recently [12], high-resolution synchrotron powder diffraction results demonstrated that CsC$_{60}$ has the same structure as RbC$_{60}$.

In this paper we study the mechanism which leads to the distinct polymer phases and we demonstrate the active role of the distinctive quadrupolar electronic polarizability of the alkali ions (cations). We start from the high temperature orientationally disordered cubic phase (space group $Fm\bar{3}m$) and describe the formation of the polymer phases as a scenario with several steps: (i) The charge transfer of one electron from the alkali atom to the C$_{60}$ molecule leads to an occupation of the lowest unoccupied molecular orbital levels which are of $t_{1g}$ symmetry. Thereby the crystal field of the C$_{60}$ ion acquires an electronic component [13] which favors the same orientation of neighboring molecules along [110] such that the stereospecific cycloaddition occurs. (ii) The cycloaddition between neighboring molecules then acts as a negative internal stress (chemical pressure) along [110]. (iii) The mutual orientation of neighboring C$_{60}$ chains, which distinguishes between the

FIG. 1. Crystal structures projected onto the crystallographic ($\bar{b}, \bar{c}$) plane: (a) $Pmn$; (b) $I2/m$. The thick bars represent the projection of the cycloaddition planes. Polymerization occurs along $\bar{a}$. The alkalis located in ($\bar{b}, \bar{c}$) planes and at $\pm a/2$ are denoted by full (+) and empty (−) circles.
orthorhombic and the monoclinic structures, should depend on the intercalated alkali ions.

We first show that the orthorhombic lattice is the result of the cycloaddition. By using concepts of the theory of elasticity [14], we find that the cubic crystal is deformed into an orthorhombic one (point group $D_{2h}$). Taking the cubic [110], [110], and [001] as new $x$, $y$, and $z$ axes (orthorhombic $\hat{a}$, $\hat{b}$, and $\hat{c}$), respectively, we find the deformations

\[ \epsilon_{xx} = \frac{K}{d} [c_{11}(c_{11} + c_{12} + 2c_{44}) - 2c_{12}^2], \]

\[ \epsilon_{yy} = -\frac{K}{d} [c_{11}(c_{11} + c_{12} - 2c_{44}) - 2c_{12}^2], \]

\[ \epsilon_{zz} = -Kc_{12}/d, \]

where $c_{ij}$ are the cubic elastic constants, $d = c_{11}(c_{11} + c_{12}) - 2c_{12}^2$, and $K < 0$ is the uniaxial stress. Obviously $\epsilon_{xx} < 0$, $\epsilon_{yy} > 0$, and $\epsilon_{zz} > 0$, which corresponds to the contraction along $\hat{a}$ and elongations along $\hat{b}$ and $\hat{c}$. We next investigate the orientation of the polymer chains. Following the experimental breakthrough [10], preliminary calculations of interchain energies have been performed [15]. The interaction energy is highly sensitive to the lattice constants and a plausible scenario is that $C_{60}$-$C_{60}$ interchain distances impose different relative chain orientations. However, the last argument is at variance with single crystal x-ray diffraction results of pressure polymerized $C_{60}$ [16]. There the space group is $Pmn2_1$, i.e., isostructural with polymerized $C_{60}$. However, the orthorhombic cell volume of polymerized $C_{60}$ and the distance between a corner and the center of the cell, 1326 Å$^3$ and 9.956 Å, respectively, are closer to the corresponding values in Rb$C_{60}$, 1314.9 Å$^3$ and 9.852 Å, than to those of $C_{60}$, 1298 Å$^3$ and 9.836 Å. We conclude that the alkalis must play a more specific role in triggering the structural difference between $K_{60}$ and Rb$C_{60}$, Cs$C_{60}$. From the theory of bilinear rotation-translation (RT) coupling between molecular rotations and lattice displacements of the counterions, which plays an essential role in determining the elastic properties of ionic molecular crystals [17], one finds an effective rotation-rotation (RR) interaction that competes with the direct intermolecular RR interaction. However, the lattice mediated RR interaction is found to be independent of the alkali mass and hence no distinction on the basis of the different masses is possible. A further distinctive property of the alkali metal ions is the dipolar electronic polarizability, with values 0.9, 1.7, and 2.5 Å$^3$ for $K^+$, Rb$^+$, and Cs$^+$, respectively [18]. We also expect that the quadrupolar polarizability is larger for the heavy alkali metal ions than for $K^+$. In the following we will show that the electric quadrupole interaction between $C_{60}$ chains and the alkali ions leads to an effective orientational interaction between the $C_{60}$ chains.

We will first study the electric multipole interaction between polymer chains. Polymerization reduces the symmetry; the $C_{60}$ chain is composed of units with $D_{2h}$ symmetry. We have used a tight-binding model to study the electronic charge distribution on the $C_{60}$ units in the chain [19]. The charge is mainly concentrated in the equatorial region of $C_{60}$, in agreement with recent NMR results [20]. We find that only even l multipoles are allowed; in particular, each $C_{60}$ unit has an electric quadrupole. In the following we adopt a simple model of charge distribution. By using the labeling of C atoms of [20], we locate a charge of 0.15 (units $e$) on each bond C15-C16. These charges are fixed at a distance $d = 3.52$ Å from the center of the $C_{60}$ ball. Such a charge distribution is sufficient to obtain a quadrupole [see also Eq. (2)]; the accompanying monopole is irrelevant. The chains are taken as rigid units where the sole degree of freedom is the rotation angle $\mu$ about the chain axis $\hat{a}$. Hence we can treat the three-dimensional crystal in the polymer phase as a two-dimensional problem in the ($\hat{b}\hat{c}$) plane. Here we consider one chain per unit cell with basis vectors $\hat{r}_1 = (\hat{c}/2) + (\hat{b}/2)$ and $\hat{r}_2 = (\hat{c}/2) - (\hat{b}/2)$. The chains are labeled by a two-dimensional array $n = (n_1, n_2)$ and lattice vectors are given by $X(n) = n_1 \hat{r}_1 + n_2 \hat{r}_2$, where $n_1$, $n_2$ are integers. The Coulomb interaction between chains depends on their mutual orientation. We introduce symmetry adapted rotator functions (SAF’s), $S_l(n) = \sin(l \mu(n))$. Symmetry of the chain for $\mu \rightarrow -\mu + \pi$ implies $l = 2, 4, \ldots$. These functions are ungerade in $\mu$, and $S_2$ is maximum for $\mu = 45^\circ$. Expanding the Coulomb interaction in terms of SAF’s we consider in the lowest order of $l$ the quadrupole-quadrupole interaction

\[ H_{SS} = \frac{1}{2} \sum_{n\bar{n}} [J_a(n, \bar{n}) + J_b(n, \bar{n})] S_2(n) S_2(\bar{n}). \]

More involved molecular charge distributions would lead to higher ($l \geq 4$) multipoles [13], but their interactions are negligible. We observe that nearest neighbor chains are shifted by a translation $a/2$ along the $\bar{a}$ axis with respect to each other. For a $C_{60}$ molecule at $\bar{n}$ as origin, $J_a$ takes into account the interaction with the two molecules at $±a/2$ on the neighboring four chains $X(\bar{n}) = ±\bar{r}_1$ and $X(\bar{n}) = ±\bar{r}_2$, and $J_b$ describes the interaction with one molecule on the chains $X(\bar{n}) = ±(\bar{r}_1 - \bar{r}_2)$. In two-dimensional Fourier space we obtain

\[ H_{SS} = \frac{1}{2} \sum_{\bar{q}} J(\bar{q}) S_2(\bar{q}) S_2(-\bar{q}), \]

\[ J(\bar{q}) = 8J_a \cos\left(\frac{q_y b}{2}\right) \cos\left(\frac{q_z c}{2}\right) + 2J_b \cos(q_y b), \]

where $q_y$ and $q_z$ are components along the original orthorhombic axes $\hat{b}$ and $\hat{c}$. With the simple model of charge distribution for the $C_{60}$ units and the orthorhombic lattice constants of Table I, we have calculated the quadrupolar interaction energies $J_a$ and $J_b$ quoted in Table I.
that the quadrupolar interaction between C
ternates in neighboring planes at distance
lattice all have the same orientation, but the orientation al-

\[
J = \sum_{\tilde{n}\tilde{n}'} [\lambda_b(\tilde{n}, \tilde{n}') + \lambda_c(\tilde{n}, \tilde{n}')] S_2(\tilde{n}) S_2(\tilde{n}'),
\]

(4)

where \(\lambda_b(\tilde{n}, \tilde{n}')\) accounts for the two alkalis at \(\pm a/2\) on
the chains \(X(\tilde{n}') = \pm (t_1 - t_2)/2\) and where \(\lambda_c(\tilde{n}, \tilde{n}')\) de-
scribe the interaction with one alkali on the chains \(X(\tilde{n}') = \pm (t_1 + t_2)/2\). In Fourier space we have

\[
H_{ss} = \sum_{\tilde{q}} \lambda(\tilde{q}) S_2(\tilde{q}) S_2(-\tilde{q}),
\]

(5a)

\[
\lambda(\tilde{q}) = 4 \lambda_b \cos \left(\frac{q a}{2}\right) + 2 \lambda_c \cos \left(\frac{q c}{2}\right).
\]

(5b)

We take dumbbells with charges \(q_A\) at distances \(\pm d_A\) from the
center. Here \(A\) refers to K, Rb, or Cs. The numerical
values of \(d_A\) (Table I) are the average radii of valence
electron \(d\) shells calculated with atomic wave functions
\(3d_{3/2}, 4d_{3/2}\), and \(5d_{3/2}\) for \(K^+, Rb^+,\) and \(Cs^+\), respectively.
We consider \(d\) shells because they can support an
electric quadrupole moment. We observe that the values
for \(Cs^+\) and \(Rb^+\) are close to each other but differ from
\(K^+\). The alkali ions are isoelectronic with the rare gas
atoms Ar, Kr, and Xe. There the role of excited \(d\) states
has been found to be important in the explanation of the
face-centered cubic structure [23]. With the same value
\(q_A = 0.15|e|\) for the three cases, we have calculated the
interaction energies \(\lambda_b\) and \(\lambda_c\), quoted in Table I. The
quantity \(\lambda(\tilde{q})\) is maximum for \(\tilde{q} = \tilde{q}_1\) in contrast with
\(J(\tilde{q})\). The intraionic restoring forces which op-
pose the deformation of the electron shells of the alkalis
are described by a sum of single particle energy terms

\[
H_{ss} = g_A \sum_{\tilde{n}} s_2^2(\tilde{n}) = g_A \sum_{\tilde{q}} s_2(\tilde{q}) s_2(-\tilde{q}),
\]

(6)

with \(g_A > 0\). The self-energy \(g_A\) is inversely proportional
to the quadrupolar electronic polarizability and hence
\(g_{Cs} < g_{Rb} < g_K\) (see Table I). These concepts are
inspired from the shell model of lattice dynamics [24].
The direct interchain coupling of alkali quadrupoles is
numerically found to be small and will be neglected. We
consider the total interaction \(H = H_{ss} + H_{Ss} + H_{ss}\).
The induced alkali quadrupoles follow adiabatically the
motion of the \(C_{60}\) chains. For a given configuration
\(\{S_2(\tilde{q})\}\) of the latter, we minimize \(H\) with respect to \(s_2(\tilde{q})\) and find

\[
s_2(\tilde{q}) = -\frac{1}{2} \frac{\lambda(\tilde{q})}{g_A} S_2(\tilde{q}).
\]

(7)

Substituting this result for \(s_2\) in \(H\), we get

\[
H = \frac{1}{2} \sum_{\tilde{q}} \tilde{J}(\tilde{q}) S_2(\tilde{q}) S_2(-\tilde{q}),
\]

(8a)

where

\[
\tilde{J}(\tilde{q}) = J(\tilde{q}) + C(\tilde{q}),
\]

(8b)

\[
C(\tilde{q}) = -\frac{1}{2} \frac{\lambda^2(\tilde{q})}{g_A}.
\]

(8c)
The coupling to the alkalis leads to an effective orientational interaction $C(\vec{q})$ between $C_{60}$ chains. This interaction is attractive and, since $|C(\vec{q})|$ with $\lambda(\vec{q})$ is maximum at $\vec{q} = \vec{q}_F$, it favors a “ferrorotational” structure (space group $I2/m$). On the other hand, the direct quadrupolar interaction between $C_{60}$ chains with $|J(\vec{q}_Z)| > |J(\vec{q}_F)|$ favors the antiferrorotational structure. The system of interacting polymer chains described by Eq. (8a) chooses the lowest energy structure which is $Pmnn$ or $I2/m$ depending on whether $|J(\vec{q}_F)| > |J(\vec{q}_F)|$, i.e., $J_a > \lambda_b \lambda_c / g_A$, or the opposite holds, respectively. By using the numerical values from Table I, we have plotted $\tilde{J}(\vec{q})$ for $\vec{q} = (q_y = 0, q_z)$ in Fig. 2. For $K\text{C}_{60}$ [6] with the small polarizability of the $K^+$ ion, the direct interchain interaction $J(\vec{q}_Z)$ dominates and leads to $Pmnn$ while, for $\text{RbC}_{60}$ [10] and even more for $\text{CsC}_{60}$ [12], the alkali mediated interaction $C(\vec{q}_F)$ dominates and leads to $I2/m$.

A condensation of $S_2(\vec{q})$ at the BZ center leads, via coupling to the center-of-mass displacements of the alkali ions (bilinear RT coupling), to $\varepsilon_{2c}$ shear modes and hence to a deviation of the $(\hat{b}, \hat{c})$ angle $\alpha$ from 90° in the $I2/m$ structure. However, this RT coupling is not the driving process of the monoclinic structure. Indeed, the deviations of $\alpha$ are very small [10,12].

In conclusion we have shown that the cycloaddition between $C_{60}$ units leads to an orthorhombic lattice structure. The concomitant symmetry reduction produces a quadrupolar electric charge distribution on the $C_{60}$ units. The interaction between $C_{60}$ chains has two competing components: a direct quadrupole-quadrupole interaction $J(\vec{q})$ and an indirect one $C(\vec{q})$. The latter is mediated by the induced quadrupoles on the polarized alkali metal ions. The direct quadrupolar interaction drives the antiferrorotational structure $Pmnn$ while the indirect one yields the ferrorotational structure $I2/m$. In $\text{RbC}_{60}$ and $\text{CsC}_{60}$ with larger electronic polarizability and quadrupolar radius $d_A$ of the alkalis, $\lambda_b \lambda_c / g_A > J_a$, the ferrorotational structure is realized while, in $K\text{C}_{60}$, $J_a > \lambda_b \lambda_c / g_A$, the antiferrorotational structure is realized. Within the present theory, the alkali play a specific role beyond the function of lattice spacers. The study of alkali specific effects is a problem of broad interest and likely to be relevant for the understanding of superconducting fullerides [25].

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