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

K. H. Michel[1] and A. V. Nikolaev[1,2]

[1]*Department of Physics, University of Antwerp, UIA, 2610 Antwerpen, Belgium*
[2]*Institute of Physical Chemistry of RAS, Leninskii Prospect 31, 117915, Moscow, Russia*

The polymer phases of AC_{60} form distinct crystal structures characterized by the mutual orientations of the $(C_{60}^-)_n$ chains. We show that the direct electric quadrupole interaction between chains always favors the orthorhombic structure *Pmnn* 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} ($A_x C_{60}$), 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 *Pmnn*). Polymerization occurs along the orthorhombic $\vec{a}$ axis (the former cubic [110] direction), where the orientation of the polymer chain is characterized by the angle μ of the planes of cycloaddition with the $\vec{c}$ axis. In the *Pmnn* structure (Fig. 1a), these orientations are alternatively μ and $-\mu$, $|\mu| \approx 45° \pm 5°$. 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 *Pmnn* 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 μ (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 re-

sults 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_{1u} 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
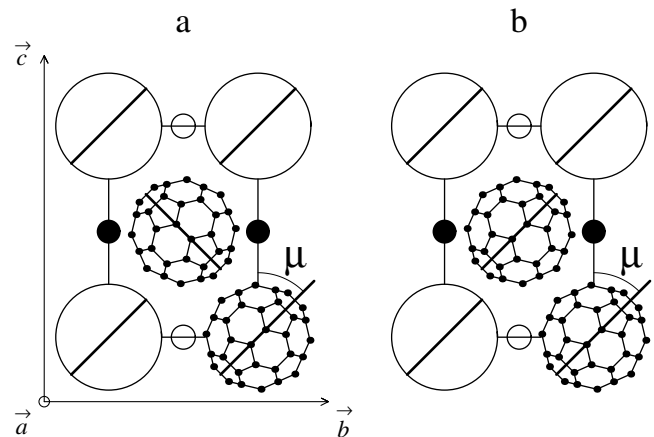

FIG. 1. Crystal structures projected onto the crystallographic $(\vec{b}, \vec{c})$ plane: (a) *Pmnn*; (b) $I2/m$. The thick bars represent the projection of the cycloaddition planes. Polymerization occurs along $\vec{a}$. The alkalis located in $(\vec{b}, \vec{c})$ planes and at $\pm a/2$ are denoted 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], [1$\bar{1}$0], and [001] as new x, y, and z axes (orthorhombic $\vec{a}$, $\vec{b}$, and $\vec{c}$), respectively, we find the deformations

$$\epsilon_{xx} = \frac{K}{dc_{44}}[c_{11}(c_{11} + c_{12} + 2c_{44}) - 2c_{12}^2], \quad (1a)$$

$$\epsilon_{yy} = -\frac{K}{dc_{44}}[c_{11}(c_{11} + c_{12} - 2c_{44}) - 2c_{12}^2], \quad (1b)$$

$$\epsilon_{zz} = -Kc_{12}/d, \quad (1c)$$

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 $\vec{a}$ and elongations along $\vec{b}$ and $\vec{c}$. 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 $Pmnn$, i.e., isostructural with polymerized KC_{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 RbC_{60}, 1314.9 Å^3 and 9.852 Å, than to those of KC_{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 KC_{60} and RbC_{60}, CsC_{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 $|e| = 1$) 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 μ about the chain axis $\vec{a}$. Hence we can treat the three-dimensional crystal in the polymer phase as a two-dimensional problem in the $(\vec{b}\vec{c})$ plane. Here we consider one chain per unit cell with basis vectors $\vec{r}_1 = (\vec{c}/2) + (\vec{b}/2)$ and $\vec{r}_2 = (\vec{c}/2) - (\vec{b}/2)$. The chains are labeled by a two-dimensional array $\vec{n} = (n_1, n_2)$ and lattice vectors are given by $\vec{X}(\vec{n}) = n_1\vec{r}_1 + n_2\vec{r}_2$, 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), $S_l(\vec{n}) = \sin[l\mu(\vec{n})]$. Symmetry of the chain for $\mu \to \mu + \pi$ implies $l = 2, 4, \ldots$. These functions are ungerade in μ, and S_2 is maximum for $\mu = 45°$. Expanding the Coulomb interaction in terms of SAF's we consider in the lowest order of l the quadrupole-quadrupole interaction

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

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 $\vec{a}$ axis with respect to each other. For a C_{60}^- molecule at $\vec{n}$ as origin, J_a takes into account the interaction with the two molecules at $\pm a/2$ on the neighboring four chains $X(\vec{n}') = \pm\vec{r}_1$ and $X(\vec{n}') = \pm\vec{r}_2$, and J_b describes the interaction with one molecule on the chains $X(\vec{n}') = \pm(\vec{r}_1 - \vec{r}_2)$. In two-dimensional Fourier space we obtain

$$H_{SS} = \frac{1}{2} \sum_{\vec{q}} J(\vec{q})S_2(\vec{q})S_2(-\vec{q}), \quad (3a)$$

$$J(\vec{q}) = 8J_a \cos\left(\frac{q_y b}{2}\right)\cos\left(\frac{q_z c}{2}\right) + 2J_b \cos(q_y b), \quad (3b)$$

where q_y and q_z are components along the original orthorhombic axes $\vec{b}$ and $\vec{c}$. 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.

TABLE I. Lattice constants a_c refer to cubic, and a_o, b_o, and c_o to simple orthorhombic lattice cells; length in units Å (angström). Interaction energies J_a, J_b, λ_b, λ_c, g_A measured in units K (Kelvin). Quadrupolar radii d_A in units Å. Ratios of g_A's are equal to the corresponding ratios of $1/d_A$'s.

	a_c	a_o	b_o	c_o	J_a	J_b	d_A	λ_b	λ_c	g_A
K	14.06	9.11	9.95	14.32	16.7	−86.2	1.47	14.5	80.0	173
Rb	14.08	9.14	10.11	14.23	17.4	−79.0	1.82	20.7	130.5	140
Cs	14.13	9.10	10.22	14.17	18.2	−74.5	1.87	22.3	141.8	136

From Eq. (3b) we find that $J(\vec{q})$ is negative and maximum in absolute value at the boundary of the Brillouin zone (BZ). For all three compounds we have $|J(\vec{q}_Z)| > |J(\vec{q}_\Gamma)|$, where $\vec{q}_Z = (0, 2\pi/c)$ is a BZ boundary vector and $\vec{q}_\Gamma = (0,0)$ is the BZ center. This result is independent of the strength of the molecular quadrupoles but is a consequence of the orthorhombic lattice. The dominance of $J(\vec{q}_Z)$ leads to a condensation of $S_2(\vec{q})$ for $\vec{q} = \vec{q}_Z$: $\langle S_2(\vec{q}_Z)\rangle = \eta/\sqrt{N}$. Here η is the order parameter amplitude and N is the number of chains (i.e., lattice points in the $(\vec{b}\vec{c})$ plane). Condensation at $\vec{q}_Z$ implies that the chains in the same basal plane $(\vec{a}\vec{b})$ of the orthorhombic lattice all have the same orientation, but the orientation alternates in neighboring planes at distance $c/2$. This is the "antiferrorotational" structure $Pmnn$ (Fig. 1a). We find that the quadrupolar interaction between C_{60} chains leads to $Pmnn$ for KC_{60}, RbC_{60}, and CsC_{60}, irrespective of the different orthorhombic lattice constants. For RbC_{60} and CsC_{60} the experimental result is $I2/m$ [10,12]. We now include the role of the alkali ions with their distinctive polarizability. It is known from work on the ammonium halides [21] that the indirect interaction of two NH_4^+ tetrahedra via the polarizable halide ions plays an essential role in determining the various crystalline phases of the ammonium halides NH_4X, $X = Cl$, Br, and I [22]. However, in the present problem, by symmetry the dipolar polarizability of the alkali metal ions is irrelevant and we have to resort to the quadrupolar polarizability. Since the C_{60}^- units in a polymer chain are rigidly linked in the same orientation, the C_{60}^- chains produce coherent electric field gradients which induce an anisotropic (quadrupolar) deformation of the electron shell of the alkalis. We model the corresponding charge distribution of each alkali by a symmetric linear dumbbell centered on lines along the $\vec{a}$ directions. On the same line, these induced dumbbells are parallel with their axis perpendicular to $\vec{a}$ and a same orientation angle ν with the $\vec{c}$ axis. We consider chains of alkali dumbbells, where the rigid chain aspect is not imposed by intrachain interactions but by the surrounding C_{60}^- chains. The orientational motion of an alkali dumbbell is characterized by the SAF's $s_2(\vec{n}) = \sin[2\nu(\vec{n})]$, where $\vec{n}$ is again a two-dimensional array labeling the chains. The quadrupole-quadrupole interaction between the C_{60}^- chains and the surrounding alkalis is then given by

$$H_{sS} = \sum_{\vec{n}\vec{n}'} [\lambda_b(\vec{n}, \vec{n}') + \lambda_c(\vec{n}, \vec{n}')] S_2(\vec{n}) s_2(\vec{n}'), \quad (4)$$

where $\lambda_b(\vec{n}, \vec{n}')$ accounts for the two alkalis at $\pm a/2$ on the chains $X(\vec{n}') = \pm(\vec{r}_1 - \vec{r}_2)/2$ and where $\lambda_c(\vec{n}, \vec{n}')$ describe the interaction with one alkali on the chains $X(\vec{n}') = \pm(\vec{r}_1 + \vec{r}_2)/2$. In Fourier space we have

$$H_{sS} = \sum_{\vec{q}} \lambda(\vec{q}) S_2(\vec{q}) s_2(-\vec{q}), \quad (5a)$$

$$\lambda(\vec{q}) = 4\lambda_b \cos\left(\frac{q_y b}{2}\right) + 2\lambda_c \cos\left(\frac{q_z c}{2}\right). \quad (5b)$$

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 λ_b and λ_c quoted in Table I. The quantity $|\lambda(\vec{q})|$ is maximum for $\vec{q} = \vec{q}_\Gamma$ in contradistinction with $|J(\vec{q})|$. The intraionic restoring forces which oppose the deformation of the electron shells of the alkalis are described by a sum of single particle energy terms

$$H_{ss} = g_A \sum_{\vec{n}} s_2^2(\vec{n}) = g_A \sum_{\vec{q}} s_2(\vec{q}) s_2(-\vec{q}), \quad (6)$$

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 $\{S_2(\vec{q})\}$ of the latter, we minimize H with respect to $s_2(\vec{q})$ and find

$$s_2(\vec{q}) = -\frac{1}{2} \frac{\lambda(\vec{q})}{g_A} S_2(\vec{q}). \quad (7)$$

Substituting this result for s_2 in H, we get

$$H = \frac{1}{2} \sum_{\vec{q}} \tilde{J}(\vec{q}) S_2(\vec{q}) S_2(-\vec{q}), \quad (8a)$$

where

$$\tilde{J}(\vec{q}) = J(\vec{q}) + C(\vec{q}), \quad (8b)$$

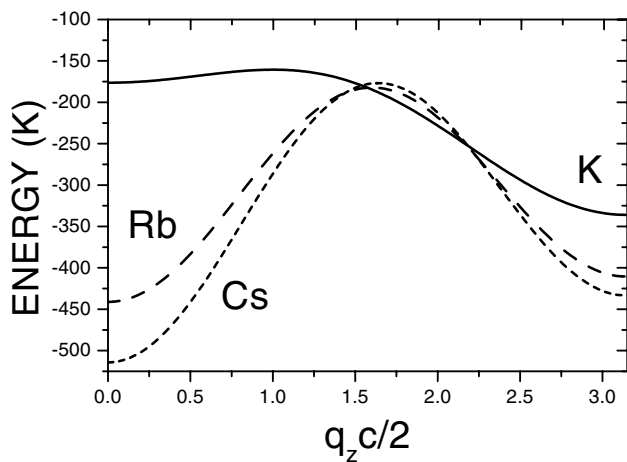$$C(\vec{q}) = -\frac{1}{2} \frac{\lambda^2(\vec{q})}{g_A}. \quad (8c)$$

FIG. 2. Interchain energy $\tilde{J}(\vec{q})$, units K.

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 $\vec{q} = \vec{q}_\Gamma$, it favors a "ferrorotational" structure (space group $I2/m$). On the other hand, the direct quadrupolar interaction between C_{60}^- chains with $|J(\vec{q}_Z)| > |J(\vec{q}_\Gamma)|$ 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 $|\tilde{J}(\vec{q}_Z)| > |\tilde{J}(\vec{q}_\Gamma)|$, 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 KC_{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 RbC_{60} [10] and even more for CsC_{60} [12], the alkali mediated interaction $C(\vec{q}_\Gamma)$ 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 ϵ_{yz} shear modes and hence to a deviation of the $(\vec{b}, \vec{c})$ angle α from 90° in the $I2/m$ structure. However, this RT coupling is not the driving process of the monoclinic structure. Indeed, the deviations of α 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 RbC_{60} and 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 KC_{60}, $J_a > \lambda_b \lambda_c / g_A$, the antiferrorotational structure is realized. Within the present theory, the alkalis 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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