Ferroelectricity in \((\text{K@C}_{60})_n\)

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A theoretical analysis of the ground state of long-chain \((\text{K@C}_{60})_n\) is presented. Within mean field theory, a ferroelectric ground state is found to be stable because of the pseudo-Jahn-Teller mixing of the \(b_{1u}\) and the \(b_{2g}\) band with a zone-center optical phonon involving the displacement of the endohedral \(\text{K}^+\) ions. A phase diagram for this model is derived in the narrow bandwidth regime.

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Introduction

Fullerenes have proven to be useful building blocks in the synthesis of novel molecular solids. Metals, insulators, ferromagnets, and superconductors have all been fashioned out of fullerenes. A variety of fullerene-based polymeric structures have also been synthesized and characterized[1, 2, 3, 4, 5]. Linear chains of C\(_{60}\) ferromagnets, and superconductors have all been fashioned out of fullerenes. A variety of fullerene-based polymeric atom, the \((t)\) formation can be understood[11] as a consequence of the pseudo-Jahn-Teller effect (PJT) where the can result from the endohedral doping of isolated fullerenes with metal atoms, so-called metallofullerenes. The dipole the properties of fulleride solids. Theoretical studies show that sizeable electric dipole moments[6, 7, 8, 9, 10, 11] of the dipole formation can be understood[11] as a consequence of the pseudo-Jahn-Teller effect (PJT) where the \(t_{1u}\) and \(t_{1g}\) electronic states of the metallofullerene are mixed by a \(t_{1u}\) distortion involving the displacement of the central metal atom, the \((t_{1u} \oplus t_{1g}) \otimes t_{1u}\) model.

The properties of a linear chain of metallofullerenes are investigated in what follows. A lattice generalization of the \((b_{1u} \oplus b_{2g}) \otimes b_{1u}\) PJT model is explored. A phase diagram for this model is derived in the narrow bandwidth regime. It is shown that within mean field theory, a ferroelectric ground state is stable when the coupling constant \(g\) exceeds a critical value \(g_0\) which depends on the cation force constant \(\kappa\) and the \(b_{1u} - b_{2g}\) energy spacing \(\Delta\).

Model Hamiltonian

ESR measurements on endohedral polymeric \((\text{KC}_{60})_n\) are consistent with one electron transfer from K atoms to the \(\text{C}_{60}\) chains. Adjacent \(\text{C}_{60}\) molecules bond with a preferred orientation as indicated in Fig. 1. The axis of the chain bisects a pair of hexagon-hexagon bonds on every \(\text{C}_{60}\) molecule. It is assumed that endohedral polymeric \((\text{K@C}_{60})_n\) will have the same structure.

Such an arrangement of metallofullerenes with the \(\text{K}^+\) ions centered with respect to the \(\text{C}_{60}\) cages will have a point group symmetry of \(D_{2h}\), as the chain axis is coincident with one of the molecule’s two-fold rotation axes. Facing hexagon-hexagon bonds on adjacent \(\text{C}_{60}\) molecules align, and the two intermolecular bonds together with the two facing hexagon-hexagon bonds complete a four-membered ring. A coordinate system is chosen so that the chain axis is labeled by \(z\) and the four-membered rings lie in the \(yz\)-plane as indicated in Fig. 1.

In an isolated alkali-doped metallofullerene, the highest occupied molecular orbital (HOMO) has a three-fold spatial degeneracy and transforms as \(t_{1u}\) under the icosahedral group. With the site symmetry lowered to \(D_{2h}\), this three-fold degeneracy is lifted and the \(t_{1u}\) multiplet is split into its components under \(D_{2h}\): \(b_{1u}\), \(b_{2u}\), and \(b_{3u}\). Ligand-field analysis indicates that the \(b_{2u}\) and \(b_{1u}\) levels which transform as \(y\) and \(x\) will be closely spaced in energy, while the \(b_{1u}\) will be lowered by more than the splitting \(\delta\) between \(b_{2u}\) and \(b_{3u}\).

It can be argued using symmetry considerations that the \(b_{2u}\) state will be lower in energy than the \(b_{3u}\) state. The HOMO is composed primarily of radially directed atomic \(p\) orbitals. Since the \(b_{3u}\) state must transform as \(x\), the \(yz\)-plane must be a nodal plane for this state, as any combination of \(p_z\) orbitals centered on the sites of the

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In the $b_{2u}$ state, however, these C atoms can contribute $p_z$ character and satisfy the symmetry requirement of oddness under $y \to -y$. Consequently, the $b_{2u}$ state has a lower energy through $\sigma$-bonding to nearest neighbors along the chain axis.

The lowest unoccupied molecular orbital (LUMO) in an alkali-doped metallofullerene transforms as $t_{1g}$. In analogy with the HOMO, in the polymer, this multiplet is split into $b_{1g}$, $b_{2g}$, and $b_{3g}$ with the ordering given in Fig. 2.

It has been previously shown[11] that there is strong vibronic mixing of the $t_{1u}$ and $t_{1g}$ orbitals in metallofullerenes through central atom displacements. A lattice generalization of that pseudo-Jahn-Teller (PJT) model is now described.

The Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{PJT}} + \mathcal{H}_{\text{elast}} \tag{1}$$

where

$$\mathcal{H}_0 = -t \sum_n (c_{1n}^\dagger c_{1n+1} + c_{2n}^\dagger c_{2n+1} + \text{h.c.}) + \sum_n \Delta c_{2n}^\dagger c_{2n} \tag{2}$$

where $n$ runs over endofullerene site, $c_{1n}^\dagger$ ($c_{1n}$) creates (annihilates) an electron in orbital $b_{1u}$ at site $n$, $c_{2n}^\dagger$ ($c_{2n}$) creates (annihilates) an electron in orbital $b_{2g}$ at site $n$, and $\Delta$ is the energy spacing between the $b_{1u}$ and $b_{2g}$ orbitals. The hopping matrix is taken to be diagonal in orbital type and spin, and the spin indices are suppressed for clarity.

The pseudo-Jahn-Teller Hamiltonian on the $n$th endofullerene is taken to be

$$\mathcal{H}_{\text{PJT}} = -\frac{g\Delta}{a} \sum_n (c_{1n}^\dagger c_{2n} Q_n + \text{h.c.}) \tag{3}$$

where $a$ is the equilibrium spacing between successive endofullerenes, and $g$ is a dimensionless coupling constant.

The point group symmetry only allows for vibronic mixing of $b_{1u}$ and $b_{2g}$ orbitals with a displacement transforming as $b_{3u}$. Hence, $Q_n$ is a displacement on the $n$th endofullerene in the $x$ direction, perpendicular to the plane of the four-membered rings.

$\mathcal{H}_{\text{elast}}$ is the elastic energy for the displacements of the K$^+$ ions.

$$\mathcal{H}_{\text{elast}} = \frac{\kappa}{2} \sum_n Q_n^2 \tag{4}$$

FIG. 1: Bonding structure of $(\text{KC}_{60})_n$. 
FIG. 2: Correlation diagram of $t_{1u}$ and $t_{1g}$ manifolds under an axial ligand field.

With the following transformations,

$$c_{\alpha k} = \frac{1}{\sqrt{N}} \sum_n e^{i kn} c_{\alpha n}$$  \hspace{1cm} (5)$$

$$Q_k = \frac{1}{\sqrt{N}} \sum_n e^{i kn} Q_n$$  \hspace{1cm} (6)$$

the Hamiltonian can be written in the $k$-space representation

$$\mathcal{H} = \sum_{\alpha,k} \epsilon_{\alpha}(k)c_{\alpha k}^\dagger c_{\alpha k} - \frac{g\Delta}{\sqrt{N}a^2} \sum_{k,q}(c_{1k+q}^\dagger c_{2k}Q_q + \text{h.c.}) + \frac{1}{2}\kappa \sum_q |Q_q|^2$$ \hspace{1cm} (7)$$

where $\epsilon_g(k) = \Delta - 2t \cos k$ and $\epsilon_u(k) = -2t \cos k$.

In analogy with $(\text{KC}_60)_n$, the $t_{1u}$ and $t_{1u}$ bands in $(\text{K@C}_60)_n$ are expected to have a width of the order of $\frac{1}{2}$ eV. Hence, $(\text{K@C}_60)_n$ is expected to be in the narrow bandwidth regime where the $b_{1u} - b_{2g}$ orbital splitting is much larger than the bandwidth, $\Delta >> 4t$. 
FIG. 3: Ground state energy per unit length \( E \) vs. \( Q = 2g\Delta|Q_q|/a\sqrt{N} \) for \( q = 0 \) and \( q = \pi \) (dashed). The values \( g = 20 \), \( t = 0.5 \) eV, \( \Delta = 1 \) eV and \( \kappa = 1.6 \) eV/Å\(^2\) were chosen. Top right graph shows detail in vicinity of a minimum.

Mean Field Theory

With a single mode of distortion given by a non-vanishing \( Q_q \), \( \mathcal{H} \) can be diagonalized with a canonical transformation so that

\[
\mathcal{H} = \sum_k \left( E_{k+} n_{k+} + E_{k-} n_{k-} \right) + \frac{\kappa}{2} |Q_q|^2
\]

where

\[
E_{k\pm} = \frac{1}{2} (\epsilon_u(k) + \epsilon_g(k + q)) \pm \frac{1}{2} \sqrt{(\epsilon_g(k + q) - \epsilon_u(k))^2 + \frac{4g^2\Delta^2}{Na^2}|Q_q|^2}
\]

and \( n_{k\pm} \) are the usual occupation number operators of the vibronic quasiparticles.

The ground state energy of chain with one electron per endofullerene on average is obtained by half-filling the lowest energy vibronic band. In the continuum limit,

\[
E(Q_q) = \frac{Na}{\pi} \int_{-\pi/2a}^{\pi/2a} dk \ E_{k-} + \frac{\kappa}{2} |Q_q|^2
\]

The ground state energy can be calculated to \( \mathcal{O}(\frac{4t^2}{\Delta^2}) \)

\[
E(Q_q) \approx \frac{Na\Delta}{2} \left[ 1 - \left( \frac{4t}{\Delta} \right)^2 \cos^2 qa/2 - \sqrt{1 + \frac{Q_q^2}{\pi^2}} - \left( \frac{4t}{\Delta} \right)^2 \sin^2 qa/2 \right. \\
- \left. \frac{4t^2}{\Delta^2} \frac{Q_q^2}{\pi^2} \left( 1 + \frac{1}{\pi} \sin qa \right) \right] + \kappa|Q_q|^2/2
\]

where \( Q_q^2 = 4g^2|Q_q|^2/Na^2 \).

At \( q = 0 \), the energy is a minimum for non-vanishing \( Q_q \) when \( g > g_0 \) where \( g_0 = \sqrt{\kappa a^2/2\Delta} \). The results for the ferroelectric and antiferroelectric cases are displayed in Fig.
When $g > g_0$ the energy minimum is found at $q = 0$, corresponding to a ferrodistortive transition. This displacement creates local electric dipoles on the endofullerenes that are aligned perpendicular to the $yz$-plane, yielding a uniaxial ferroelectric phase (FE). A paraelectric (PE) phase exists along the line segment $g > g_0$ and $t = 0$ where independent, local dipole moments form on the endofullerenes. The symmetric phase (S), where no local dipole moments form, is stable for $g < g_0$. These results are summarized in zero-temperature phase diagram pictured in Fig. 4.

Acknowledgments

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