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Towards room-temperature superconductivity in low-dimensional C$_{60}$ nanoarrays: An *ab initio* study

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We propose to raise the critical temperature $T_c$ for superconductivity in doped C$_{60}$ molecular crystals by increasing the electronic density of states at the Fermi level $N(E_F)$ and thus the electron-phonon coupling constant in low-dimensional C$_{60}$ nanoarrays. We consider both electron and hole doping and present numerical results for $N(E_F)$, which increases with decreasing bandwidth of the partly filled $h_u$ and $t_{1u}$ derived frontier bands with decreasing coordination number of C$_{60}$. Whereas a significant increase of $N(E_F)$ occurs in 2D arrays of doped C$_{60}$ intercalated in-between graphene layers, we propose that the highest $T_c$ values approaching room temperature may occur in bundles of nanotubes filled by 1D arrays of externally doped C$_{60}$ or La@C$_{60}$, or in diluted 3D crystals, where quasi-1D arrangements of C$_{60}$ form percolation paths.

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The quest for room-temperature superconductivity has lost nothing of its appeal during the 30-year long intense search following the observation of superconductivity in graphitic structures. The valence electrons were correctly reproduces the inter-layer spacing and interaction in graphitic structures. The valence electrons were described by norm-conserving Troullier-Martins pseudopotentials [11] with partial core corrections in the Kleinman-Bylander factorized form [12]. We used a double-zeta polarized basis and limited the range of the localized orbitals in such a way that the energy shift caused by their spatial confinement was no more than 10 meV [13]. The Brillouin zone of a 3D lattice of C$_{60}$ molecules was sampled by $10 \times 10 \times 10$ k-points, that of a 2D lattice by $10 \times 10$ k-points, and that of decoupled 1D chains of C$_{60}$ molecules inside a nanotube by 10 k-points. The DOS was convoluted by 0.02 eV$^{-1}$. In a periodic arrangement, 1D structures were separated by 15 Å thick vacuum regions and 2D structures by 13 Å thick vacuum regions. The charge density and the potentials were determined on a real-space grid with a mesh cutoff energy of 180 Ry, which was sufficient to achieve a total energy convergence of better than 2 meV/atom.

In alkali-doped M$_3$C$_{60}$ (M=K, Rb, Cs) fcc crystals, superconductivity with $T_c \lesssim 40$ K has been observed [14] and explained by electron-phonon coupling that is modul-
related by the lattice constant [6, 7]. The same behavior is expected to occur in the isoelectronic La@C\(_{60}\) that has been isolated from raw soot [15] and found to be stable [16]. When exohedrally doped M\(_3\)C\(_{60}\) crystals are exposed to ambient or harsh conditions, atoms from the environment may penetrate deep inside the lattice, react with the M atoms and destroy superconductivity. This is much less likely to occur in endohedrally doped La@C\(_{60}\) crystals, since the dopant La atoms are enclosed inside the protective C\(_{60}\) cage. As mentioned above, superconductivity in 3D M\(_3\)C\(_{60}\) crystals is caused by strong electron-phonon coupling related to a dynamical Jahn-Teller effect on individual C\(_{60}\) cages, made possible by retardation. The dominant role of the intercalated alkali atoms is to partly fill the \(t_{1u}\) LUMO of C\(_{60}\) that broadens to a narrow band in the M\(_3\)C\(_{60}\) molecular solid. Changes in \(T_c\) caused by pressure or changing the element M can be traced back to changes in the electron-phonon coupling constant \(\lambda = V N(E_F)\) in the McMillan equation [6–8]. Since the on-ball Bardeen-Pines interaction \(V\) does not change, \(\lambda\) is proportional to the C\(_{60}\)-projected DOS at the Fermi level \(N(E_F)\), which – for electron doping – is roughly inversely proportional to the width of the \(t_{1u}\)-derived band. In hole-doped C\(_{60}\), \(E_F\) is expected to be lowered into the \(h_u\)-derived band with an even higher \(N(E_F)\) value, which may be the cause of the high value \(T_c \geq 60\) K that has been reported earlier [5].

All experimental strategies used so far to raise \(T_c\) have been based on increasing the C\(_{60}\)-C\(_{60}\) separation \(d_{cc}\) in a 3D fcc crystal, which would lower the width of the LUMO- and HOMO-derived bands and thus increase \(N(E_F)\) in doped crystals. Our approach is quite different [17]: we consider increasing \(N(E_F)\) by reducing the number of C\(_{60}\) nearest neighbors. As seen in Fig. 1(a), this may be achieved simply in a 3D crystal by mixing C\(_{60}\) with clusters of similar size that do not interact with C\(_{60}\), such as BN fullerenes. In this case, the lowered C\(_{60}\) coordination number would decrease the width of the \(t_{1u}\) and \(h_u\) derived bands and thus increase \(N(E_F)\) in doped crystals. Other C\(_{60}\) arrangements with a lower Z include 2D arrays of C\(_{60}\) that could possibly be intercalated in graphite [18, 19], as seen in Fig. 1(b), or 1D arrays of C\(_{60}\) in C\(_{60}\)@CNT peapods [20–22] shown in in Fig. 1(c). As seen in Fig. 1(d), the width of the \(t_{1u}\)-derived band decreases both with increasing the C\(_{60}\)-C\(_{60}\) separation and with the reduction of dimensionality that translates to the reduction of Z, with 1D arrangements appearing optimal. Since superconductivity is suppressed in truly 1D systems according to the Mermin-Wagner theorem [23], we consider bundles of weakly interacting peapods in-

FIG. 1. (Color online) Schematic arrangement of C\(_{60}\) molecules in a pristine (a) 3D fcc crystal, (b) 2D triangular lattice, and (c) 1D array inside a (10,10) carbon nanotube peapod. (d) Width of the \(t_{1u}\)-derived band in a 1D, 2D and 3D arrangement of C\(_{60}\) molecules as a function of the C\(_{60}\)-C\(_{60}\) center-to-center separation \(d_{cc}\). Equilibrium values of \(d_{cc}\) are affected by the C\(_{60}\) orientational disorder, as indicated by the gray strip in (d) for undoped structures. The ‘error bars’ reflect the effect of changing the C\(_{60}\) orientation on the bandwidth. (e) Schematic arrangement of dopant atoms outside the 1D peapod ( ), inside the nanotube but outside the fullerene ( ), and inside the fullerene (+). Dark spheres in (a) represent clusters other than C\(_{60}\) that separate quasi-1D percolating arrays of fullerenes from the surrounding matrix. The planes in (b) are only a visual aid.

FIG. 2. (Color online) Density of states (DOS) and charge redistribution in doped C\(_{60}\) crystals. (a) DOS of the \(t_{1u}\) LUMO-derived bands of C\(_{60}\) in 1D, 2D and 3D periodic C\(_{60}\) arrangements for the C\(_{60}\)-C\(_{60}\) separation \(d_{cc}\) = 9.8 Å. (b) Total and projected DOS of a C\(_{60}\)@(10,10) CNT peapod doped externally by 7 K donor atoms per C\(_{60}\). (c) Charge density difference \(\Delta \rho = \rho_{\text{tot}}(\text{C}_{60}@(10,10)\text{CNT}+7K) - \rho_{\text{tot}}(\text{C}_{60}@\text{CNT})\) by reducing the C\(_{60}\)-C\(_{60}\) separation \(d_{cc}\) = 9.8 Å. (e) Total and projected DOS of a C\(_{60}\)@(10,10) CNT peapod doped externally by 8 F acceptor atoms per C\(_{60}\). (f) Counterpart of (c) for C\(_{60}\)@CNT+7F. In (e) and (f), blue contours for electron deficit are shown for \(\Delta \rho = -3.0 \times 10^{-3} \text{ e/bohr}^3\) and red contours for electron excess are shown for \(\Delta \rho = +3.0 \times 10^{-3} \text{ e/bohr}^3\). All energies are with respect to \(E_F\).
stead of isolated 1D peapods. As we will show in the following, the main role of the nanotube in these systems is to provide a suitable enclosure that aligns \( \text{C}_{60} \) molecules and protects them from the ambient. Due to their weak interaction, bundles of nanotubes have a very similar DOS as isolated nanotubes. Since the same applies to peapods, we will consider an isolated peapod a valid representative of a peapod bundle from the viewpoint of electronic structure.

Even in pristine systems with no intercalants, we found the \( \text{C}_{60}-\text{C}_{60} \) separation \( d_{cc} \) to depend on the \( \text{C}_{60} \) orientation and the dimensionality of the system. Different fullerene orientations, each with a specific optimum \( d_{cc} \) value, were found to be energetically degenerate within \( \lesssim 2 \) meV/atom and separated by minute activation barriers. At nonzero temperatures during synthesis and observation, the fullerenes will explore these orientational degrees of freedom causing orientational disorder and changing \( d_{cc} \), as observed in the 3D lattice [24]. The equilibrium value of \( d_{cc} \) decreases by \( \approx 0.1 \text{ Å} \) and its orientational dependence increases when reducing the dimensionality to 2D and 1D. Also in view of the soft \( \text{C}_{60}-\text{C}_{60} \) interaction, we always expect a nonzero range of \( d_{cc} \) values in any experimental sample. In pristine \( \text{C}_{60} \), we expect \( d_{cc} \) values roughly covering the \( 9.8 - 10.1 \text{ Å} \) range shown by the dark band in Fig. 1(d).

As seen in Fig. 1(e), the geometry is more complex in alkali intercalated peapods, where intercalant atoms may occupy sites outside the nanotube, inside the nanotube but outside \( \text{C}_{60} \), or inside the \( \text{C}_{60} \) molecule such as the La@\( \text{C}_{60} \) metallofullerene [16]. Since also these sites are energetically near-degenerate, the precise geometry may be barely controllable during synthesis. In the 3D \( \text{M}_{3}\text{C}_{60} \) system, moreover, \( d_{cc} \) has been found to increase from \( 9.8 \text{ Å} \) to \( 10.3 \text{ Å} \) with increasing atomic number of the alkali element \( \text{M} \) [6]. We find a similar \( \text{M} \)-dependent increase in \( d_{cc} \) also in 2D and 1D systems, where \( \text{M} \) atoms separate fullerenes. 1D peapods with the narrowest bandwidth and potentially highest \( N(E_F) \) could be doped by donor or acceptor atoms. For most of this study, we will focus on donor doping, causing partial filling of the \( t_{1u} \)-derived band, and will show later that acceptor doping may be hard to achieve.

The DOS shape of the \( t_{1u} \) LUMO-derived band in quasi-1D, 2D triangular and 3D fcc lattices of \( \text{C}_{60} \) is depicted in Fig. 2(a) and that of the \( h_u \) HOMO-derived band in the same lattices is shown in Fig. 2(d). Clearly, the DOS at \( E_F \) reaches its maximum near half-filling of these bands in quasi-1D structures. Since the \( t_{1u} \) LUMO-derived band holds up to 6 electrons and the \( h_u \) HOMO-derived band up to 10 electrons, half-filling of these bands requires either 3 extra electrons or depletion of 5 electrons from each \( \text{C}_{60} \). Comparing our results in Figs. 2(a) and 2(d), we note that acceptor doping – if achievable – would result in a significantly higher \( N(E_F) \) than donor doping. The calculated DOS of a \( \text{C}_{60}@(10,10) \) peapod doped externally by 7 K atoms per \( \text{C}_{60} \) is shown in Fig. 2(b) and the DOS of the corresponding peapod doped externally by 8 F atoms per \( \text{C}_{60} \) is shown in Fig. 2(e). Comparing the partial densities of states in these two cases, we conclude that \( \text{C}_{60} \)-derived states are barely affected by those of the surrounding nanotube due to a very small hybridization. In the case of donor doping by K depicted in Fig. 2(b), we clearly observe partial filling of the \( t_{1u} \)-derived band of \( \text{C}_{60} \) as well as the nearly-free electron bands of the (10, 10) nanotube [25]. To get a better feel for the charge flow in the system, we plotted the charge density difference defined by \( \Delta \rho = \rho_{tot}(\text{C}_{60}@\text{CNT}+7\text{K})-\rho_{tot}(\text{C}_{60}@\text{CNT})-\sum_{\text{at}} \rho_{at}(\text{K atom}) \) in Fig. 2(c). Obviously, there is a net electron flow from K atoms to the \( \text{C}_{60}@(10,10) \) peapod, with the excess charge accommodated both by the \( \text{C}_{60} \) and the nanotube. Integration of the \( \text{C}_{60} \)-projected DOS in Fig. 2(b) up to \( E_F \) indicates a partial population of the \( t_{1u} \)-derived band by 0.4 electrons.

The calculated DOS of an acceptor-doped peapod, shown in Fig. 2(e), presents a very different picture. We selected F as a suitable electron acceptor due to its high electronegativity. Unlike in previous studies of acceptor-doped \( \text{C}_{60} \), where covalently bonded halogen atoms disrupted the \( \pi \)-electron network on the molecules [26], F atoms were bonded on the outside of the nanotube surrounding \( \text{C}_{60} \) molecules. Thus, we found the \( h_u \)-derived band of \( \text{C}_{60} \) to be essentially unaffected by the presence of the surrounding nanotube and the 8 F atoms per \( \text{C}_{60} \) outside the nanotube, but the \( \text{C}_{60} \) molecules remained charge neutral. The \( h_u \)-derived narrow band band remained completely filled, located about 1 eV below \( E_F \). We found F atoms to bind covalently to the outside of the nanotube, causing pyramidalization, disrupting its \( \pi \)-electron network and opening up a gap at the Fermi level, which turned the system into a semiconductor. This can be clearly seen when inspecting the charge flow in this system in Fig. 2(f). We found F atoms to strongly hybridize with the C atoms of the tube, redistributing the charge only within the F/CNT subsystem, with no effect on the net charge of \( \text{C}_{60} \). Since hole doping of \( \text{C}_{60} \) appears very difficult, we will focus on electron doping of the \( t_{1u} \)-derived band of \( \text{C}_{60} \) chains in the following.

As mentioned earlier, the electronic band structure of \( \text{C}_{60} \) arrays should depend to a nontrivial degree on the orientation of the \( \text{C}_{60} \) molecules that will affect their interaction [27]. We studied 5 different orientations, identified in Fig. 3(a), which result in a different degree of inter-ball hybridization. Due to their energetic near-degeneracy, we expect many \( \text{C}_{60} \) orientations to coexist within a quasi-1D \( \text{C}_{60} \) array inside a peapod. The DOS for a chain of \( \text{C}_{60} \) molecules at different orientations and the \( \text{C}_{60}-\text{C}_{60} \) separation \( d_{cc} = 9.8 \text{ Å} \) is shown in Fig. 3(b). We note that the maximum DOS value changes significantly with orientation. Therefore, in Fig. 3(c), we plot-
FIG. 3. (Color online) Properties of 1D arrays of C\textsubscript{60} molecules found in CNT peapods. (a) Ball-and-stick models of different atomic arrangements at the C\textsubscript{60}-C\textsubscript{60} interface. Considered are double-bonds facing double-bonds (d), hexagons facing hexagons (h), pentagons facing pentagons (p). α and β arrangements are obtained by a 90° rotation of C\textsubscript{60} molecules in p arrangement about two different axes that are orthogonal to the chain axis and to each other. (b) DOS of the t\textsubscript{1u} LUMO-derived bands of C\textsubscript{60} for the C\textsubscript{60} orientations, defined in (a), at the C\textsubscript{60}-C\textsubscript{60} separation d\textsubscript{cc} = 9.8 Å. All energies are with respect to \(E_F\). (c) Maximum DOS value of t\textsubscript{1u}-derived bands in 1D, 2D and 3D crystals of C\textsubscript{60}. The 'error bars' reflect the effect of changing the C\textsubscript{60} orientational disorder, as indicated by the gray strips in (c) and (d) for doped structures. The lines in (c) and (d) are guides to the eye.

ted the range of achievable maxima of \(N(E_F)\) as 'error bars' for different C\textsubscript{60}-C\textsubscript{60} orientations. Depending on the exact position of the intercalant atoms and fullerene orientation, we found the optimum C\textsubscript{60}-C\textsubscript{60} separations to cover the range \(d_{cc} \approx 9.8 - 10.3\) Å, indicated by the gray strip in Fig. 3(c). Higher \(d_{cc}\) values than in pristine peapods, achieved in case that the fullerenes are separated by heavy alkalis such as Cs, result in very high values of \(N(E_F)\) for favorable C\textsubscript{60} orientations.

To estimate the critical temperature for superconductivity \(T_c\), we used McMillan’s equation [6–8] for 1D systems in Fig. 3(d). We used the parameters of Ref. [7], namely \(\hbar \omega_{t\text{1u}}/k_B = 2800\) K, \(\mu^* = 0.2\) for the effective mass and \(V = 52\) meV for the Bardeen-Pines interaction, which are not affected by the averaged local arrangement of C\textsubscript{60} molecules. Using \(\lambda = V N(E_F)\) for the electron-phonon coupling constant, we were able to convert \(N(E_F)\) values for 3D, 2D and quasi-1D systems with different C\textsubscript{60}-C\textsubscript{60} distances and C\textsubscript{60} orientations to potentially achievable \(T_c\) values and present our results in Fig. 3(d). Since dynamical orientational disorder and resulting fluctuations in the C\textsubscript{60}-C\textsubscript{60} distance are a natural phenomenon that is particularly prominent in realistic 1D systems, we can estimate ranges of \(d_{cc}\) and \(T_c\) values at best. Our estimates indicate that, in the best imaginable scenario, \(T_c\) near room temperature may be achievable using bundles of donor-doped peapods.

Clearly, there are limits to the range of C\textsubscript{60}-C\textsubscript{60} separations \(d_{cc}\) compatible with superconductivity. Increasing \(d_{cc}\) decreases the inter-ball hopping integral \(t\), while not affecting the on-ball Coulomb integral \(U\). At large C\textsubscript{60}-C\textsubscript{60} separations, the \(U/t\) ratio should increase beyond a critical value that would change doped C\textsubscript{60} from a metal to a Mott-Hubbard insulator [28, 29].

In summary, we have proposed a viable way to further increase \(T_c\) for superconductivity by increasing the C\textsubscript{60}-projected density of states (DOS) at the Fermi level \(N(E_F)\) and thus the electron-phonon coupling constant in doped low-dimensional C\textsubscript{60} nanoarrays. We considered intercalation by both electron donors and acceptors, as well as electron doping in a solid formed of La@C\textsubscript{60} endohedral complexes. We found that \(N(E_F)\) increases with decreasing bandwidth of the partly filled \(h_u\) HOMO- and t\textsubscript{1u} LUMO-derived frontier bands, which may be achieved by reducing the coordination number of C\textsubscript{60}. \(N(E_F)\) increases significantly by changing from 3D C\textsubscript{60} crystals to 2D arrays of doped fullerenes intercalated in-between graphene layers and reaches its maximum in doped quasi-1D arrays of C\textsubscript{60} molecules inside C\textsubscript{60}@CNT peapods formed of (10,10) CNTs. Whereas partial filling of the t\textsubscript{1u}-derived band may be achieved by adsorbing alkali atoms outside the 1D peapod, the desired depopulation of the \(h_u\)-derived band could not be achieved by F atoms adsorbed on the nanotube surrounding the C\textsubscript{60} molecules. Our results indicate that the highest \(T_c\) values may occur in electron-doped C\textsubscript{60} peapods containing Cs or in dilute 3D crystals, where quasi-1D arrangements of C\textsubscript{60} form percolation paths. Only experimental evidence will show if low-dimensional arrays of doped C\textsubscript{60} will become superconducting with \(T_c\) approaching room temperature, or rather turn to a Mott-Hubbard insulator.
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