Coupling to haloform molecules in intercalated $C_{60}$?

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For field-effect-doped fullerenes it was reported that the superconducting transition temperature $T_c$ is markedly larger for $C_{60}$–2CHX$_3$ (X=Cl, Br) crystals, than for pure $C_{60}$. Initially this was explained by the expansion of the volume per $C_{60}$-molecule and the corresponding increase in the density of states at the Fermi level in the intercalated crystals. On closer examination it has, however, turned out to be unlikely that this is the mechanism behind the increase in $T_c$. An alternative explanation of the enhanced transition temperatures assumes that the conduction electrons not only couple to the vibrational modes of the $C_{60}$-molecule, but also to the modes of the intercalated molecules. We investigate the possibility of such a coupling. We find that, assuming the ideal bulk structure of the intercalated crystal, both a coupling due to hybridization of the molecular levels, and a coupling via dipole moments should be very small. This suggests that the presence of the gate-oxide in the field-effect-devices strongly affects the structure of the fullerene crystal at the interface.

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In a series of papers Schön and collaborators announced a number of amazing results: Doping pure $C_{60}$ using a field-effect device, they found superconductivity up to temperatures of 11 K for electron-doping and 52 K for hole-doping. Replacing pure $C_{60}$ by crystals intercalated with chloroform (CHCl$_3$) and bromoform (CHBr$_3$), they reported transition temperatures of about 18 and 25 K for electron-doping, and 80 and 117 K for hole-doping, respectively. Initially it was speculated that this increase in $T_c$ was due to the expansion of the lattice upon intercalation of the CHX$_3$-molecules and the correspondingly larger density of states (DOS) at the Fermi level — a mechanism similar to that seen in the alkali doped fullerenes.

While the alkali doped fullerenes are bulk superconductors, the induced charge in the field-effect-doped materials is believed to be essentially confined to a single $C_{60}$-monolayer. This monolayer is believed to be a [111]-layer for pure $C_{60}$ and a [010]-layer for $C_{60}$–2CHX$_3$. Analyzing the low-temperature phase of the haloform intercalated fullerenes shows, that the expansion of the unit cell volume induced by the intercalated molecules mainly results from an increase in the distance between these layers, while the density of states in these layers does not correlate with the observed $T_c$.

It was proposed that the transition temperature increases not because of an enhanced density of states at the Fermi level, but because of an additional coupling to the intercalated CHX$_3$ (X=Cl, Br) molecules. Here we ask if indeed there is such a coupling. Possible mechanisms are (i) hybridization of the molecular levels with the HOMO/LUMO of $C_{60}$ and (ii) coupling via the dipole moment or the polarizability of the intercalated molecules. We find that the overlap between the states of the intercalated molecules with the relevant orbitals of $C_{60}$ ($h_u$ for hole- and $t_{1u}$ for electron-doping) is very small. Moreover, group theory puts rather strong constraints on this type of coupling. The second coupling mechanism also does not seem to be viable, as electrostatic interactions should be strongly reduced by the efficient screening found in the fullerenes. Since our results were obtained for the ideal bulk structure, the experimental results may imply that the presence of the gate oxide in the field-effect-device strongly affects the structure of the fullerene crystal at the interface.

Hybridization: To understand the electron-phonon coupling to the intercalated haloform molecules, we calculate the coupling constant

$$\lambda = \frac{2}{N(0)} \sum_i \sum_{\nu_i,q} \frac{1}{2M_{\nu_i}^2 \Omega_{\nu_i,q}^2} \sum_{n,m,k} |\langle n,k|V_{\nu_i,q}|m,k+q \rangle|^2 \delta(\epsilon_{n,k}) \delta(\epsilon_{m,k+q} - \Omega_{\nu_i,q}).$$

Here $N(0)$ is the total density of states per spin at the Fermi level, $i$ runs over the different molecules in the unit cell, $\nu_i$ labels the vibrational modes of molecule $i$, and $q$ is the phonon wave vector. Expanding the Bloch function $|n,k\rangle$ in molecular orbitals $\alpha_j$ on molecule $j$ at position $r_j$ in unit cell $R$

$$|n,k\rangle = \frac{1}{\sqrt{N}} \sum_{R,j} e^{ik(R+r_j)} \sum_{\alpha_j} e_n^{\alpha_j}(k) |\Phi_{R,j,\alpha_j}\rangle,$$

the electron-phonon matrix element is given by a sum over the matrix elements $\langle \Phi_{R,j,\alpha_j}|V_{\nu_i,q}|\Phi_{R',j',\alpha'_{j'}}\rangle$. For a
molecular solid we can neglect the intermolecular electron-phonon coupling and thus obtain

\[ \langle n, k | V_{\mathbf{q}} | m, k + q \rangle = \frac{1}{\sqrt{N}} \sum_{\alpha_i, \alpha_i'} c_{\alpha_i}(k) c_{\alpha_i'}^{m}(k + q) V_{\alpha_i, \alpha_i'}(\nu_i), \]

where \( V_{\alpha_i, \alpha_i'}(\nu_i) \) is the electron-vibration matrix element on molecule \( i \). Writing the partial density of states as

\[ n_{\alpha, \alpha'}(\varepsilon) = \frac{1}{N} \sum_{n, k} c_{\alpha}^{n}(k) c_{\alpha'}^{n}(k) \delta(\varepsilon - \varepsilon_{n, k}), \]

we finally obtain

\[ \lambda = \frac{2}{N(0)/N} \sum_{i} \sum_{\nu_i} \frac{1}{2M_{\nu_i}} \sum_{\alpha_i, \alpha_i', \alpha_i'', \alpha_i'''} \sqrt{\Omega_{\alpha_i, \alpha_i'}(\nu_i)} V_{\alpha_i', \alpha_i'''}(\nu_i) n_{\alpha_i, \alpha_i'''}(0) n_{\alpha_i', \alpha_i'''}(\Omega_{\nu_i}). \]

Thus a vibrational mode of a molecule only contributes to the electron-phonon coupling, if (i) there is a molecular orbital that contributes significantly to the density of states at the Fermi level and (ii) the electron-vibration matrix element does not vanish. In the case of \( \text{C}_{60} \), the relevant orbitals are the \( t_{1u} \) (\( h_u \)) for electron (hole) doping and the non-vanishing electron-vibration matrix elements are found by reduction of the symmetric tensor product \( t_{1u} \otimes s t_{1u} = A_g \oplus H_g \) \( (h_u \otimes s h_u = A_g \oplus G_g \oplus 2H_g) \).

To estimate the contribution of the molecular levels of the CHX$_3$-molecules to the density of states at the Fermi level we have performed all-electron density functional calculations using the Gaussian-orbital code NRLMOL employing the PBE functional. The basis set is 4s3p1d for H, 5s4p3d for C, 6s5p3d for Cl, and 7s6p4d for Br. The position of the energy levels of CHX$_3$ (\( X=\text{Cl}, \text{Br}, 1 \)) compared to those of \( \text{C}_{60} \) are shown in figure. While the levels of the chloroform molecule are fairly distant from the HOMO/LUMO levels of \( \text{C}_{60} \), the levels of bromoform and, in particular, iodoform move much closer. This implies that the contribution of the haloform orbitals to the density of states at the Fermi level should increase when replacing chlorine by bromine, suggesting an explanation of the increase in transition temperature.

To estimate the actual contribution of the CHX$_3$ levels to the density of states at the Fermi level, we perform calculations both for an isolated \( \text{C}_{60} \)-molecule and for a system consisting of a \( \text{C}_{60} \)-molecule and the twelve closest neighboring CHX$_3$-molecules at the experimentally determined positions. We then calculate \( \sum_{m, n} \langle \Psi_m | \Phi_n \rangle | \Phi_n \rangle | \Psi_m \rangle \), where the \( \Psi_m \) are the \( t_{1u} \) (\( h_u \)) derived orbitals for the \( \text{C}_{60} \)-molecule with the neighboring CHX$_3$-molecules and the \( \Phi_n \) are the \( t_{1u} \) (\( h_u \)) orbitals of the isolated \( \text{C}_{60} \)-molecule. If there were no hybridization between \( \text{C}_{60} \) and CHX$_3$, the overlap would be equal to the number of \( \text{C}_{60} \)-derived orbitals considered (3 for \( t_{1u} \) and 5 for \( h_u \)). The deviation from this number is a measure of the hybridization between \( \text{C}_{60} \) and CHX$_3$.

As shown in table, we find that the deviation is very small for both CHCl$_3$ and CHBr$_3$, i.e., there is essentially no hybridization of the haloform-levels with the HOMO/LUMO of the \( \text{C}_{60} \)-molecule: Less than 3% for \( \text{C}_{60} \)-2CHBr$_3$ and less than 1.5 % for \( \text{C}_{60} \)-2CHCl$_3$. Only the \( g_g \) and \( h_g \) levels that are well below the Fermi level show appreciable hybridization, as could be expected from the energetic proximity of these levels and the occupied levels of CHCl$_3$ and CHBr$_3$. Therefore, the contribution of the CHX$_3$-levels to the electron-phonon coupling should be very small.

The situation changes, of course, in the field-doped layer. There will be an additional electrostatic potential, which can lead to a shift in the relative positions of the electronic levels of the \( \text{C}_{60} \) and the intercalated haloform molecules. One might then speculate that for a certain external field one can line up the HOMO or LUMO of the different molecules, thereby maximizing the mixing and consequently a possible coupling to the haloform modes. For that field one would then expect to find the maximum transition temperature. Since the energetic positions of the molecular levels of CHCl$_3$ and CHBr$_3$ are quite different (cf. figure), the fields required for bringing say the HOMO of CHCl$_3$ in line with that of \( \text{C}_{60} \) is substantially larger than that required for CHBr$_3$. Hence one would expect that the transition temperature for \( \text{C}_{60} \)-2CHCl$_3$ peaks at a gate-voltage significantly different from that for \( \text{C}_{60} \)-2CHBr$_3$. Since the gate-voltage also corresponds to the induced charge carrier density, from the above scenario one would expect that the transition temperatures for the different crystals would show a maximum at different doping levels – contrary to the experimental finding reported in reference.
couple to the molecular vibrations of symmetry $A_1$, not to the two-fold degenerate $E$ modes (cf. tables I and II). Only the two-fold degenerate molecular levels of symmetry $e$, which are even further away from the Fermi level than the HOMO/LUMO, can couple to all the modes. Hence even if there is some contribution of the HOMO/LUMO levels of the CHX$_3$ molecules to the density of states at the Fermi level, coupling to the majority of molecular modes would be forbidden by symmetry.

**Electrostatic coupling:** Due to the dipole moment of the haloform molecules ($3.4\times10^{-30}$ Cm for CHCl$_3$ and $3.3\times10^{-30}$ Cm for CHBr$_3$) one might speculate that there is coupling to the intercalated molecules due to electrostatic interactions. An analogous scenario was put forward for the case of the alkali-doped fullerene $A_3C_{60}$, where it was suggested early on that the superconductivity is mediated by coupling to the vibrations of the alkali ions. Experimentally, however, no isotope effect was found for the alkalis. This could be explained as a consequence of the efficient screening in the alkali-doped fullerenes, which leads to a strong reduction in the coupling to the alkali-modes. A similar mechanism should be at work in the field-doped fullerenes, reducing the coupling to the dipole moments of the haloform molecules. In addition, one would expect, that even the unscreened coupling to dipoles (haloform molecules) should be weaker than the coupling to monopoles (alkali ions). Moreover, the dipole moments of CHCl$_3$ and CHBr$_3$ are very similar, while, because of the lattice expansion, the bromoform molecules are more distant from the C$_{60}$ than the chloroform molecules. Based on a coupling to the dipole moment, one would therefore expect that $T_c$ in C$_{60}$·2CHBr$_3$ should be lower than in C$_{60}$·2CHCl$_3$ – contrary to the experimental finding. A coupling via the dipole moments thus seems very unlikely.

**Conclusions:** In most of the arguments we have given above, we have assumed that the structure and symmetry of the bulk crystal is also relevant in the region under the gate oxide. Our results show that with this assumption it seems hard to understand the observed increase in transition temperature of the haloform intercalated fullerenes. This then suggests that the crystal structure under the gate oxide must be markedly different from the bulk structure. Possible effects are a different orientation of the molecules at the interface, a reduction of the symmetry, some bonding to the oxide, some additional screening due to the presence of the oxide, or a reorientation of the haloform molecules in the strong electric field used for in field-doping. It therefore seems that a correct picture that allows to understand the experimental results reported in reference 3 must involve more than just assuming that a monolayer of the ideal crystal is doped with charge carriers.

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TABLE I: Overlap \( \sum_{m,n} \langle \Psi_m | \Phi_n \rangle \langle \Phi_n | \Psi_m \rangle \) between the molecular orbitals \( \Psi_m \) of \( C_{60} \) with the twelve closest neighboring CHX\(_3\) (X=Cl, Br) molecules and the molecular orbitals \( \Phi_n \) of the isolated \( C_{60} \) molecule. The first column gives \( \sum_{m,n} \langle \Phi_m | \Phi_n \rangle \langle \Phi_n | \Phi_m \rangle \), the degeneracy of the levels.

| MO | \( C_{60} \) | CHBr\(_3\) | CHCl\(_3\) |
|----|-------------|-------------|-------------|
| \( t_{1g} \) | 3 | 0.97 | 2.93 |
| \( t_{1u} \) | 3 | 2.91 | 2.96 | LUMO |
| \( h_u \) | 5 | 4.88 | 4.95 | HOMO |
| \( g_u \) | 4 | 2.30 | 3.20 |
| \( h_g \) | 5 | 1.61 | 4.04 |

TABLE II: Vibrational modes of CHX\(_3\) molecules and their symmetry

| meV | CHCl\(_3\) | CHBr\(_3\) |
|-----|-------------|-------------|
| 32.5 | 45.4 | 82.8 | 94.4 | 150.8 | 374.4 |
| 19.1 | 27.5 | 66.8 | 81.3 | 141.6 | 374.9 |

TABLE III: Electron-phonon coupling for the HOMO and LUMO of the CHX\(_3\) molecule: reduction of the symmetric tensor product into irreducible representations. Coupling between different molecular orbitals: reduction of the tensor product. The electrons can only couple to the two-fold degenerate vibrational modes (\( E \)) when a two-fold degenerate molecular level (\( e \)) is involved.

| \( C_{3v} \) | \( E \) | 2\( C_3 \) | 3\( C_3 \) |
|-----------|--------|-----------|-----------|
| LUMO | \( a_1 \otimes a_1 \) | 1 | 1 | 1 | \( A_1 \) |
| HOMO | \( a_2 \otimes a_2 \) | 1 | 1 | 1 | \( A_1 \) |
|       | \( e \otimes e \) | 3 | 0 | 1 | \( A_1 \otimes E \) |
|       | \( a_1 \otimes a_1 \) | 1 | 1 | 1 | \( A_1 \) |
|       | \( a_1 \otimes a_2 \) | 1 | 1 | -1 | \( A_2 \) |
|       | \( a_1 \otimes e \) | 2 | -1 | 0 | \( E \) |
|       | \( a_2 \otimes a_2 \) | 1 | 1 | 1 | \( A_1 \) |
|       | \( a_2 \otimes e \) | 2 | -1 | 0 | \( E \) |
|       | \( e \otimes e \) | 4 | 1 | 0 | \( A_1 \otimes A_2 \otimes E \) |

FIG. 1: Molecular levels of \( C_{60} \) and CHX\(_3\) (X=Cl, Br, I). Note that the HOMO and LUMO of the haloform molecules are singly degenerate (irreducible representations \( a_1 \) or \( a_2 \) of the symmetry group \( C_{3v} \)).