RAPID COMMUNICATIONS

PHYSICAL REVIEW B **67**, 161402(R) (2003)

Possibility of Coupling to haloform molecules in intercalated C_{60}

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(Received 24 July 2002; published 14 April 2003)

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}. As a possible mechanism it was proposed that there is not only coupling to the vibrational modes of the C_{60} molecule, but also to the modes of the intercalated molecules. We investigate the possiblity 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.

DOI: 10.1103/PhysRevB.67.161402

PACS number(s): 74.70.Wz

It was proposed that the transition temperatures in field-doped fullerene crystals intercalated with $CHX_3(X=\mathrm{Cl,Br})$ should be enhanced, compared to pure field-doped C_{60}, due to the additional coupling to the vibrations of the intercalated $CHX_3(X=\mathrm{Cl,Br})$ molecules.[1] Here we ask if indeed there is such a coupling. Possible mechanisms are (i) hybridization of the molecular levels with the highest occupied (HOMO) or lowest unoccupied molecular orbital (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 doping 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.[2,3]

Hybridization. To understand the electron-phonon coupling to the intercalated haloform molecules, we calculate the coupling constant[4] for a molecular solid with more than one molecule per unit cell,

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

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, ν_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 α_j on molecule j at position r_j in unit cell R

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

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[5] and thus obtain

$$\langle n,k|V_{\nu_i,q}|m,k+q\rangle=\frac{1}{\sqrt{N}}\sum_{\alpha_i,\alpha'_i}\overline{c^n_{\alpha_i}(k)}c^m_{\alpha'_i}(k+q)V_{\alpha_i,\alpha'_i}(\nu_i),$$

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

$$n_{\alpha,\alpha'}(\varepsilon)=\frac{1}{N}\sum_{n,k}\overline{c^n_{\alpha}(k)}c^n_{\alpha'}(k)\delta(\varepsilon-\varepsilon_{n,k}),$$

we finally obtain

$$\lambda=\frac{2}{N(0)/N}\sum_i\sum_{\nu_i}\frac{1}{2M_{\nu_i}\Omega^2_{\nu_i}}\times\sum_{\alpha_i,\alpha'_i,\alpha''_i,\alpha'''_i}\overline{V_{\alpha_i,\alpha'_i}(\nu_i)}V_{\alpha''_i,\alpha'''_i}(\nu_i)\times n_{\alpha_i,\alpha''_i}(0)n_{\alpha'_i,\alpha'''_i}(\Omega_{\nu_i}).$$

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 C_{60}, the relevant orbitals are the t_{1u} (h_u) for electron (hole) doping and the nonvanishing 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,[6] employing the Perdew-Burke-Ernzerhof functional.[7] 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 ($X=$Cl,Br,I) compared to those of C_{60} are shown in Fig. 1. While the levels of the chloroform molecule are fairly distant form the HOMO/LUMO levels of 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.

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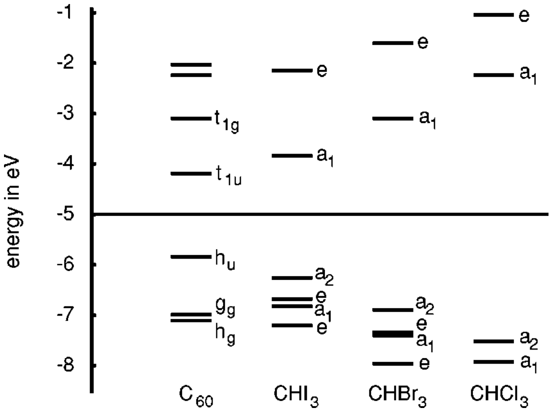

FIG. 1. Molecular levels of C_{60} and CHX_3 (X=Cl,Br,I). Note that the HOMO and LUMO of the haloform molecules are singly degenerate (irreducible representations a_1 or a_2 of the symmetry group C_{3v}).

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 C_{60} molecule and for a system consisting of a C_{60} molecule and the twelve closest neighboring CHX_3 molecules at the experimentally determined positions.[8] We then calculate $\Sigma_{m,n}\langle\Psi_m|\Phi_n\rangle\langle\Phi_n|\Psi_m\rangle$, where the Ψ_m are the t_{1u} (h_u) derived orbitals for the C_{60} molecule with the neighboring CHX_3 molecules and the Φ_n are the t_{1u} (h_u) orbitals of the isolated C_{60} molecule. If there were no hybridization between C_{60} and CHX_3, the overlap would be equal to the number of 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 C_{60} and CHX_3. As shown in Table I, 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 C_{60} molecule: less than 3% for $C_{60}2CHBr_3$ and less than 1.5% for $C_{60}2CHCl_3$. 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 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. Fig. 1), the fields required for bringing say the HOMO of $CHCl_3$ in line with that of C_{60} is substantially larger than that required for $CHBr_3$. Hence one would expect that the transition temperature for $C_{60}2CHCl_3$ peaks at a gate voltage significantly different from that for $C_{60}2CHBr_3$. Since the gate voltage also corresponds to the induced charge carrier density, form the above scenario one would expect that the transition temperatures for the different crystals would show a maximum at different doping levels.

TABLE I. Overlap $\Sigma_{m,n}\langle\Psi_m|\Phi_n\rangle\langle\Phi_n|\Psi_m\rangle$ between the molecular orbitals Ψ_m of C_{60} with the twelve closest neighboring CHX_3 (X=Cl,Br) molecules and the molecular orbitals Φ_n of the isolated C_{60} molecule. The first column gives $\Sigma_{m,n}\langle\Phi_m|\Phi_n\rangle\langle\Phi_n|\Phi_m\rangle$, 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_g	4	2.30	3.20	
h_g	5	1.61	4.04	

TABLE II. Vibrational modes of CHX_3 molecules and their symmetry (Ref. 9).

meV	E	A_1	A_1	E	E	A_1
$CHCl_3$	32.5	45.4	82.8	94.4	150.8	374.4
$CHBr_3$	19.1	27.5	66.8	81.3	141.6	374.9

In addition, group theory puts further constraints on this coupling via selection rules for the electron-vibration matrix elements. As seen from Fig. 1, the HOMO/LUMO levels of the haloform molecules are singly degenerate of symmetry a_2 and a_1, respectively. Decomposing the (symmetric) tensor product of these irreducible representations, we find that they can only couple to the molecular vibrations of symmetry A_1, not to the twofold degenerate E modes (cf. Tables II and III). Only the twofold 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

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 twofold degenerate vibrational modes (E) when a twofold degenerate molecular level (e) is involved.

	C_{3v}	E	$2C_3$	$3c_v$	
LUMO	$a_1\otimes_s a_1$	1	1	1	A_1
HOMO	$a_2\otimes_s a_2$	1	1	1	A_1
	$e\otimes_s e$	3	0	1	$A_1\oplus E$
	$a_1\otimes a_1$	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	$A_1\oplus A_2\oplus E$

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 (3.4×10^{-30} C m for $CHCl_3$ and 3.3×10^{-30} C m 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.[10] Experimentally, however, no isotope effect was found for the alkalis.[11] 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.[2,3] 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 $C_{60}2CHCl_3$. A coupling via the dipole moments thus seems very unlikely.

Conclusions. We have shown that the contribution of the haloform modes to the electron-phonon coupling in $CH_3(X=Cl,Br)$ intercalated C_{60} should be very small: for the A modes it is small because of the small overlap, while for the E modes the coupling to the levels closest to the Fermi level even vanishes because of symmetry. Likewise, electrostatic coupling due to the permanent dipole moment of the haloform molecules should be small. Thus coupling to haloform molecules should have a negligible effect on the superconducting properties of haloform intercalated fullerenes.

We would like to thank A. Burkhardt for valuable discussions and M.R. Pederson and J. Kortus for their support in using the NRLMOL code.

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