The possible explanation of electric-field-doped C\textsubscript{60} phenomenology in the framework of Eliashberg theory

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In a recent paper (J.H. Schönh, Ch. Kloc, R.C. Haddon and B. Batlogg, Nature 408 (2000) 549) a large increase in the superconducting critical temperature was observed in C\textsubscript{60} doped with holes by application of a high electric field. We demonstrate that the measured $T_c$ versus doping curves can be explained by solving the (four) $s$-wave Eliashberg equations in the case of a finite, non-half-filled energy band. In order to reproduce the experimental data, we assume a Coulomb pseudopotential depending on the filling in a very simple and plausible way. Reasonable values of the physical parameters involved are obtained. The application of the same approach to new experimental data (J.H. Schönh, Ch. Kloc and B. Batlogg, Science 293 (2001) 2432) on electric field-doped, lattice-expanded C\textsubscript{60} single crystals ($T_c$ =117 K in the hole-doped case) gives equally good results and sets a theoretical limit to the linear increase of $T_c$ at the increase of the lattice spacing.

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After obtaining the surface field-effect doping of high-quality organic crystals, J.H. Schönh, Ch. Kloc, R.C. Haddon and B. Batlogg have carried out the same experiment on C\textsubscript{60} crystals achieving superconductivity up to 52 K in hole-doped samples. The fundamental importance of this experiment is due to the fact that the superconductivity is obtained by field-effect doping the original single-crystal material and, thus, without modifying its structural properties. The authors of the experiments believe as plausible that the doping charges are confined only in a single layer of C\textsubscript{60} molecule. The physical parameters of C\textsubscript{60} are rather well known: the symmetry of the order parameter appears to be $s$-wave and the electron-phonon interaction is widely indicated as the main cause for the appearance of superconductivity in this material. In the present paper we show that a theory suitable for reproducing the experimental $T_c$ versus filling data reported in Ref. 1 is the Migdal-Eliashberg theory.

As a first approximation, we neglect these complications and see where the theory in its most simple form and with the smallest number of free parameters can lead. Notice that a study of the phenomenology of field-doped C\textsubscript{60} in the framework of the Eliashberg theory was carried out also in Ref. 14 although in a different way. Figure 1 (a) was obtained by normalizing the original data from Ref. 1 (and from more recent experimental data in lattice-expanded C\textsubscript{60}, as we will discuss later) so that the maximum of $T_c$ corresponds to half filling (here indicated by $n = 1$). In order to fit these experimental data, we solved the Eliashberg equations in the general case of non-half filling, finite bandwidth and flat normal density of states. The physical quantities that appear in the fit are thus: the bandwidth W, the electron-phonon spectral function $\alpha^2 F(\Omega)$ and the Coulomb pseudopotential $\mu$. It is also necessary to set a cut-off energy $\omega_C$ related to the renormalization of the Coulomb pseudopotential. We took the value of W from literature: $W = 250$ meV (independent of doping since the lattice structure does not change) and we assumed the cut-off energy $\omega_C = W$ as in Ref. 10. The spectral function is unknown but, as a first approximation, one can assume that $\alpha^2 F(\Omega)$ is proportional to the phonon density of states $F(\Omega)$ of C\textsubscript{60} (see figure 1 (b)) and nearly equal to the transport spectral function $\alpha^2 F_{tr}(\Omega)$.

To determine the proportionality factor between $\alpha^2 F(\Omega)$ and $F(\Omega)$, we took the experimental resistivity data $\rho(T)$ for the electron-doping case from the figure 5 of Ref. 1, in the range between $T = 225$ K and $T = 245$ K. The $\rho(T)$ curves appear to have the same shape and slope at all gate voltages, thus, as a first approximation, the ratio $\lambda_{tr}/\omega_P$ between the transport coupling constant $\lambda_{tr}$ and the plasma frequency $\omega_P$ can be assumed to be doping-independent. The phonon density of states $F(\Omega)$ and the functions $\alpha^2 e,h(\Omega)$ (for both electrons and holes) are doping-independent as well, since the lattice parameters do not change. As a result, also the electron-phonon coupling constants $\lambda_{e,h} = 2 \int d\Omega \alpha_{e,h}^2 F(\Omega)/\Omega$ are independent of doping. From the high-temperature expression of the resistivity: $\rho = 8\pi k_B T \lambda_{tr}/(\omega_P^2 e_0 h^2)$, and by using the value of the plasma frequency reported in literature: $\hbar \omega_P = 1.36$ eV, we can deduce the value of the transport electron-phonon coupling constant $\lambda_{tr}$. In the electron-doping case we find $\lambda_{tr} = 1.1$ and, as a first approximation, we assume $\lambda_{tr} = \lambda_e$. As far as the hole-doped coupling constant $\lambda_h$ is concerned, from resistivity data and from calculations of the electron density of states J.H. Schönh et al. estimate that $\lambda_h/\lambda_e = 1.5$ and so we find $\lambda_h = 1.5 \lambda_e = 1.65$.

In order to obtain the exact maximum value of the crit-
meV}

In conclusion, if \( \Delta = (\omega_D^2 C_0 h^2) \rho_0 / 7.5 \geq h \omega_D \) (where \( \omega_D \) is the Deybe frequency and \( \rho_0 \) is the residual resistivity), the effect of a non-flat NDOS can be neglected. In our case, \( \rho_0 = 250 \div 300 \, \mu \Omega \, \text{cm} \), \( \Delta = 62 \div 74 \, \text{meV} \) and \( h \omega_D \equiv h \omega_{\text{lo}} = 27 \, \text{meV} \), where \( \omega_{\text{lo}} = \exp(\frac{\pi}{\lambda} \int_0^{\infty} d\Omega F(\Omega) \ln \Omega) \).

Since the lattice is not modified by the field-effect doping, we assume the electron-phonon coupling constant \( \lambda \) and the width of the conduction band \( W \) independent of filling \( n \). Now we can try to reproduce the experimental values of \( T_c \) versus \( n \) by solving the Eliashberg equations in the half-filling case. This is a hard task because there are three equations to be solved for the calculation of the gap \( \Delta(i\omega_n) \), the renormalization function \( Z(i\omega_n) \) and the asymmetric part of the self-energy \( \chi(i\omega_n) \) — which is always equal to zero in the half-filling case — plus one equation that represents the conservation of the particles’ number and is necessary for calculating the shift of the chemical potential \( \delta \mu \). Thus the Eliashberg equations in the non-half-filling case, for finite bandwidth and \( s \)-wave symmetry of the order parameter, read:

\[
\Delta(i\omega_n) Z(i\omega_n) = \pi k_B T \sum_{m=-\infty}^{+\infty} \left[ \lambda(i\omega_n - i\omega_m) - \mu^*/W \right] \cdot \\
\vartheta(\omega_C - i\omega_m) P(i\omega_m) \Theta(i\omega_m)
\]

\[
\omega_n Z(i\omega_n) = \pi k_B T \sum_{m=-\infty}^{+\infty} \lambda(i\omega_n - i\omega_m) N(i\omega_m) \Theta(i\omega_m)
\]

\[
\chi(i\omega_n) = -\pi k_B T \sum_{m=-\infty}^{+\infty} \lambda(i\omega_n - i\omega_m) M(i\omega_m)
\]

\[
n = 1 - (\pi k_B T/W) \sum_{m=-\infty}^{+\infty} M(i\omega_m)
\]

where \( \vartheta \) is the Heaviside function, \( i\omega_m = i \pi (2m + 1) k_B T \) with \( m = 0, \pm 1, \pm 2, ... \) and

\[
\mu^* = \mu / [1 + \frac{k_B T \mu}{W} \int_{-W}^{W} d\omega \sum_{m=0}^{+\infty} \frac{\vartheta(\omega_m - \omega_C)}{\omega_m^2 + (\varepsilon - \delta \mu)^2}]
\]

\[
\lambda(i\omega_n - i\omega_m) = \int_0^{+\infty} d\Omega \frac{\alpha^2(\Omega) F(\Omega)}{\Omega^2 + (i\omega_n - i\omega_m)^2}
\]

\[
P(i\omega_m) = \frac{\Delta(i\omega_m) Z(i\omega_m)}{R(i\omega_m)} \cdot N(i\omega_m) = \frac{\omega_m Z(i\omega_m)}{R(i\omega_m)}
\]

\[
R(i\omega_m) = \sqrt{\omega_m^2 Z^2(i\omega_m) + \Delta^2(i\omega_m) Z^2(i\omega_m)}
\]

FIG. 1: (a) Experimental \( T_c \) versus filling \( n \) data for hole doped (full squares) and electron doping (full circles) from [4]; (b) The \( C_{60} \) phonon density of states \( F(\Omega) \) [from 3].
that it is not so sure that the superconductivity in this material is 2D. For completeness we examine both the 2D and 3D cases. From the definition of \( \mu^* \) and from the very simple analytical expression of the Thomas-Fermi dielectric function in the 3D case \( \varepsilon(q, n) = 1 + k_S^2(n)/q^2 \) it follows:

\[
\mu(n) = \frac{1}{4\pi^2\hbar v_F} \int_0^{2k_F} \frac{V(q)}{\varepsilon(q, n)} q dq
\]

where \( V(q) = 4\pi e^2/q^2 \). In the half-filling case, the calculation of the integral gives:

\[
\mu(n = 1) = \left[ \frac{k_S^2(n = 1)}{8k_F^2} \right] \ln[1 + \left( \frac{4k_F^2}{k_S^2(n = 1)} \right)]
\]

where \( k_F \) and \( k_S \) are the Fermi and Thomas-Fermi wave vector, respectively. We can expand the dielectric function in the vicinity of the half filling \((n = 1)\) by remembering that, since the physical parameters \( \lambda, \alpha^2 F(\Omega) \) and \( W \) are fixed, \( T_c \) is maximum when \( \mu(n) \) is minimum, which means that \( \varepsilon(n) \) is maximum (see definition of \( \mu(n) \)) i.e. \( \partial\varepsilon/\partial n = 0 \) for \( n = 1 \). For simplicity, and to minimize the number of free parameters, we arrest the expansion to the second-order terms, even though the range of the series expansion is not so small in the hole-doping case:

\[
\varepsilon(q, n) = \varepsilon(q, n = 1) + \frac{1}{2} \left[ \frac{\partial^2\varepsilon(q, n)}{\partial n^2} \right]_{n = 1} (n - 1)^2 + \ldots
\]

and by substituting in the definition of \( \mu(n) \) we find

\[
\mu(n) = \mu(n = 1) \frac{ln(1 + a^2/[1 + b(n - 1)^2])}{ln(1 + a^2)}
\]

where \( a = 2k_F/k_S(n = 1) \) and \( b = [(1/k_S)((\partial^2 k_S/\partial n^2)]_{n = 1} \). By starting from the values of \( \mu(n = 1) \) that give the exact experimental \( T_c \) in the electron- and hole-doping case and using eq. 12 we can calculate \( 2k_F/k_S(n = 1) \). We obtain 1.05 for hole doping and 0.77 for electron doping. Now we are left with only one free parameter, \( b = [(1/k_S)((\partial^2 k_S/\partial n^2)]_{n = 1} \), that can be adjusted to fit the \( \mu \) versus \( n \) curves with eq. 14. The results are very good (see figure 2 (a) and (b), solid lines): for electron doping \( b = -25 \) and for hole doping \( b = -4 \). Of course, here we used the 3D version of the Thomas-Fermi theory but, as pointed out by the authors of ref. 1-3, the field-effect charge injections is likely to be confined to the first atomic layer of \( C_{60} \) crystal, so it is worthwhile to examine also the 2D case. The analytical expression of the Thomas-Fermi dielectric function is now \( \varepsilon(q, n) = 1 + k_S(n)/q \) and

\[
\mu(n) = \frac{k_F}{\pi\hbar v_F} \int_0^{2k_F} \frac{V(q)}{\varepsilon(q, n) \sqrt{4k_F^2 - q^2}} dq
\]

where \( V(q) = 2\pi e^2/q^2 \). By following the same approach as before we find:

\[
\mu(n = 1) = 2 \left[ \frac{\arctan\left( \frac{q}{\sqrt{a^2 - 1}} \right)}{\sqrt{a^2 - 1}} - 1 \right]
\]
and finally

$$
\mu(n) = \mu(n = 1) \frac{\sqrt{a^2 - 1}}{\sqrt{a^2 - 1}} \cdot \frac{[\arctan(\frac{n}{\sqrt{a^2 - 1}}) - 1]}{[\arctan(\frac{n}{\sqrt{a^2 - 1}}) - 1]} \quad (17)
$$

with $a^* = a[1 + 0.5b(n - 1)^2]$.

In this case, from eq. 16, we can calculate $a \equiv 2k_F/k_S(n = 1)$. We find two solutions: 1.9 and 13.8 for hole doping and 2.1 and 10.3 for electron doping. Again we have only one free parameter, $b = (1/k_S)[\partial^2 k_S/\partial n^2]_{n=1}$, that can be adjusted to fit the $\mu$ versus $n$ curves with eq. 17. We find $b = -43$ and $b = -73$ for electron doping while for hole doping we have $b = -4$ and $b = -8$, since now two possible values for $a$ are present. In the range of interest, the results are exactly equal to the 3D case and the 2D curves perfectly overlap those obtained in that case. If we compare the 2D and 3D densities of charge carriers obtained from the $a$ values of the fits to the values predicted at optimal doping and corresponding to 3 carriers per $C_{60}$ ($\sim 3 \cdot 10^{18}$ carriers/m² and $\sim 4.2 \cdot 10^{27}$ carriers/m³, respectively) we obtain interesting results. The 3D density and the 2D one obtained from the small $a$ values are of the same order of magnitude of the predicted densities, even if they don’t coincide. On the contrary the 2D density obtained from the large $a$ values is more than 2 orders of magnitude greater than the predicted one and, thus, the corresponding solution for $a$ must be rejected on the basis of physical arguments. It follows that the results of the fit by using our model do not allow us to understand whether the system is better described by 2D or 3D approach, even if the experimental results clearly point to a 2D nature of the charge injected region.

Note that, surprisingly, the curves $T_c(n)/T_c(n = 1)$ and $\mu(n = 1)/\mu(n)$ are perfectly superimposed.

Now, since we have the approximate analytical dependence of $\mu$ from $n$, we can solve the Eliashberg equations for any value of the filling and calculate different physical quantities. By using the standard technique of Padé approximants we can carry out the analytical continuation of $Z(\omega_n)$, $\Delta(\omega_n)$, $\chi(\omega_n)$ and of the normalized superconductive density of states (DOS) $N_S(\omega_n)/N_N(\omega_n) = [N(\omega_n)\Theta(\omega_n) − M(\omega_n)]/[N_N(\omega_n)\Theta_N(\omega_n) − M_N(\omega_n)$. Here the quantities with suffix $N$ are calculated for $\Delta(\omega_n) = 0$. In figure 3, we can see how the shape of $Z(\omega)$, $\Delta(\omega)$ and $\chi(\omega)$ changes for three different values of the doping in the hole-doped case: $n = 1$ ($T_c = 51$ K), $n = 1.189$ ($T_c = 46$ K) and $n = 1.287$ ($T_c = 39$ K). Figure 4 shows the normalized superconductive DOS as a function of the energy, calculated by the analytical continuation of the imaginary-axis DOS for the same doping values as in Fig. 3. In the non-half-filling cases ($n = 1.189$ and $n = 1.287$) the calculated DOS is asymmetric. In principle low-temperature SIN tunneling experiments on this field-doped material would make it possible to observe this asymmetry. The calculated values of the ratio $2\Delta/k_BT_c$ are slightly greater than the experimental results of Ref. 3.

Very recently J.H. Schön et al. have intercalated single crystals of $C_{60}$ with CHCl₃ and CHBr₃ in order to expand the lattice (see figure 1). The maximum of the critical temperature (onset of resistive transition) in the hole-doped $C_{60}/CHBr₃$ is 117 K. We can try to explain
these new experimental data by following the approach previously illustrated. We note that the maximum of $T_c$ occurs at the same value of doping in the three hole-doped and electron-doped cases (see figure 1 (a)).

As a first approximation we can assume that the Coulomb pseudopotential is, for $n = 1$, the same as in the bare $C_{60}$. For simplicity, we also use the electron-phonon spectral function of $C_{60}$ simply multiplied by a constant in order to obtain the correct $T_c$. These two approximations can be justified by: (i) the presence of an almost constant density of charge carriers in the bare and intercalated $C_{60}$; (ii) the weak dependence of $T_c$ from the details of the actual form of the spectral function (i.e., the chemical potential at $T_c$ strongly depends on $\omega_{\text{log}}$ and on the total energy range of the spectral function that are likely not to be changed very much by the intercalation). The values of the coupling constant $\lambda$ necessary to get the new experimental critical temperatures are 2.11 and 2.76 in the hole-doped case ($T_c = 80$ K and $T_c = 114$ K, respectively) and 1.24 and 1.37 in the electron-doped case ($T_c = 18$ K and $T_c = 26$ K, respectively).

In figure 5 the $\mu$ and $\mu^*$ values calculated by the solution of Eliashberg equations (1)-(4) applied to the $T_c(n)$ data of lattice-expanded $C_{60}$ are shown, as well as the best fit obtained by using eq. 14 and eq. 17. Also now the fitting curves obtained by using the 2D and 3D formula are perfectly superimposed. It is clear that the fits are equally good as those shown in Fig. 2.

Unexpectedly, we find that in all cases the shift of the chemical potential at $T = T_c$, calculated by solving the Eliashberg equations, is a linear function of the filling as we can see in the six panels of figure 6. The reason of this behaviour will be the subject of further investigation.

Figure 7 (a) shows that the calculated coupling constant $\lambda$ is a linear function of the lattice constant $d$. We can now extrapolate this behaviour to calculate the coupling constant of a hypothetical material with lattice constant $d \approx 14.6\,\text{Å}$ (the increase is of 1% with respect to the case where $T_c = 117$ K$^{[21]}$, $\lambda_h = 3.51$ and $\lambda_e = 1.52$. With these $\lambda$ values and, by using the Eliashberg equations, we determine the corresponding critical temperatures that are 135 K and 35 K, respectively. Finally, figure 7 (b) reports the critical temperature as a function of the coupling constant, for constant $\mu$ and $n = 1$, in the hole- and electron-doped case. The critical temperature, in the hole-doped case, does not increase linearly for $\lambda \gtrsim 3$ ($d \gtrsim 14.5\,\text{Å}$), in disagreement with the theoretical predictions of Ref. 12. On the contrary, $T_c$ drops to zero for $\lambda \lesssim 0.8$ ($d \lesssim 13.9\,\text{Å}$) as reported in Ref. 20.}

In the inset of figure 7 (b) we can observe that also the parameter $b$ is a linear function of the lattice constant $d$. All the results are finally summarized in table I. In principle, the predictions of Fig. 7(b) will be the subject of further investigation. As far as the lattice constant dependence of $T_c$ shown in Table I is concerned, we admit to that the $T_c$ enhancement might be not due...
to the increase of the lattice constant but due to the enhanced polarization and the resulting enhanced screening of the Coulomb interaction. Unfortunately, the formalism proposed here is not powerful enough to discriminate between both scenarios.

In conclusion, the experimental results concerning the complete doping dependence of \( T_c \) in field-effect hole-doped and electron-doped \( \text{C}_60 \) can be naturally explained by the Eliashberg theory generalized to the case where the conduction band is finite, non half-filled and the Coulomb pseudopotential is filling-dependent in a very simple and physically reasonable way. All the values of the physical parameters of the present model appear plausible.

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1. J.H. Schön, Ch. Kloc, R.C. Haddon and B. Batlogg, Nature 408 (2000) 549.
2. J.H. Schön, Ch. Kloc, R.C. Haddon and B. Batlogg, Science 288 (2000) 656.
3. J.H. Schön, Ch. Kloc, H.Y. Hwang and B. Batlogg, Science 292 (2001) 252.
4. G.M. Eliashberg, Sov. Phys. JETP 3 (1963) 696.
5. J.P. Carbotte, Rev. Mod. Phys. 62 (1990) 1028.
6. P.B. Allen and B. Mitrovich, Theory of superconducting \( T_c \), in Solid State Physics, Vol. 37, edited by H. Ehrenreich F. Seitz, D. Turnbull, (Academic Press, New York, 1982); D.J. Scalapino, in Superconductivity, Vol. 1, edited by R.D. Parks (M. Dekker, New York, 1969).
7. F. Marsiglio and J.P. Carbotte, cond-mat/0106143; G. Varelogiannis, Z. Phys. B 104 (1997) 411; S.V. Shulga, cond-mat/0101243; H. J. Kaufmann, E. G. Maksimov, E. K. H. Salje, cond-mat/9805105.
8. F. Marsiglio, Jour. of Low Temp. Phys. 87 (1992) 659.
9. Han-Yong Choi, Phys. Rev. B 53 (1996) 8591.
10. G.A. Umbrano, R.S. Gonnelli, Physica C, 341-348 (2000) 205.
11. E. Cappelluti, C. Grimaldi, L. Pietronero and S. Strässerl, Phys. Rev. Lett. 85 (2000) 4771.
12. O. Gunnarson, Rep. Prog. Phys. 69 (1997) 575.
13. L. Forró and L. Mihály, Rev. Mod. Phys. 64 (2001) 649.
14. A. Bill and V.Z. Kresin, cond-mat/0109553.
15. P.B. Allen, Phys. Rev. B 17 (1978) 3725; G. Grimvall, The electron-phonon interaction in metals, Vol. 16, edited by E.P. Wohlfarth, (North Holland, Amsterdam, 1980).
16. Han-Yong Choi and M.J. Rice, Phys. Rev. B 49 (1994) 7048.
17. S. Wehrli, D. Poilblanc and T.M. Rice, Eur. Phys. J. B 23 (2001) 345.
18. P. Morel, P.W. Anderson, Phys. Rev. 125 (1962) 1263.
19. R.E. Dinnebier, o. Gunnarson, H. Brumm, E. Koch, P.W. Stephens, a. Huq, M. Jansen, Science 296 (2002) 109.
20. F. Stern, Phys. Rev. Lett. 18 (1967) 546; E. Canel, M.P. Matthews and R.K.P. Zia, Phys. Kondens. Materie 15, (1972) 191; J. Lee and H.N. Spector, J. Appl. Phys. 54 (1983) 6098.
21. J.H. Schön, Ch. Kloc and B. Batlogg, Science 293 (2001) 2432.
22 G. Varelogiannis, Physica C 51 (1995) 51.