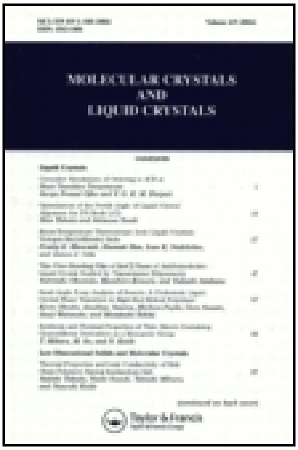

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Charge distribution in C 60 crystal doped by electric field

V. A. Kuprievich [a] , O. L. Kapitanchuk [a] , O. V. Shramko [a] & O. L. Kapitanchuk [b]

[a] Bogolyubov Institute for Theoretical Physics, Kiev, 03143, Ukraine

[b] Department of Physics, National Kiev Shevchenko University, Kiev, 03017, Ukraine

Version of record first published: 18 Oct 2010

To cite this article: V. A. Kuprievich, O. L. Kapitanchuk, O. V. Shramko & O. L. Kapitanchuk (2002): Charge distribution in C 60 crystal doped by electric field, Molecular Crystals and Liquid Crystals, 385:1, 13-19

To link to this article: http://dx.doi.org/10.1080/713738788

*Mol. Cryst. Liq. Cryst.*, Vol. 385, pp. [133]/13–[139]/19
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113015

# CHARGE DISTRIBUTION IN $C_{60}$ CRYSTAL DOPED BY ELECTRIC FIELD

*V. A. Kuprievich, O. L. Kapitanchuk and*
*O. V. Shramko*
*Bogolyubov Institute for Theoretical Physics,*
*03143 Kiev, Ukraine and*

*O. L. Kapitanchuk*
*National Kiev Shevchenko University, Department of Physics,*
*03017 Kiev, Ukraine*

*The calculations of the charge distribution in the $C_{60}$-based FET structure are presented. A simple model is proposed to describe the distribution of injected electrons or holes between two-dimensional layers. The calculations show that the relative layer charges are independent on the total amount of injected charges. The charge density is maximal on the surface layer and drops exponentially with the depth increase. The relative portions of injected charge involved in the top layer are 73 and 64 per cent in the case of electron and hole injection, respectively. Thus, the degree of charge localization on the crystal surface turns to be markedly different from the result obtained earlier within the tight-binding model predicting near-complete localization for the charge concentration providing superconductivity.*

*Keywords*: field effect transistor; charge density; $C_{60}$ ions; superconductivity; organic crystals

## INTRODUCTION

Recently the superconductivity of organic substances due to injection of charges by electric field in the field effect transistor (FET) was reported [1–3]. This new physical phenomenon is considered to be unusual in several aspects. First, the nature of the superconducting objects themselves is unaccustomed: they are organic crystals, anthracene, phenanthrene and fullerene $C_{60}$. Second, the superconductivity of the charges injected by

---

The authors are thankful to V. Loktev and E. Petrov for useful discussions and A. Verbitsky for reading the manuscript. The work of V.K. was partially supported under the NASU program No. 0102U002329.

electric field is unusual: up-to-date the superconductivity of organic crystals was related to the charge transfer, particularly, due to chemical doping. Third, in the case of fullerene $C_{60}$ the superconductivity is observed at extremely high temperature (52 K for pure $C_{60}$ [1] and at even 117 K when doping by bromoform [3]). Fourth, holes injected into the fullerene leads to significantly higher critical temperature than injected electrons, although in the case of the chemical doping, the $C_{60}$ superconductivity is observed with negative charge carriers only.

In the connection with this phenomenon the question on the distribution of charge carriers injected into organic crystal. In the study [1] the amount of induced charges per $C_{60}$ molecule is estimated with the supposition that the additional charges occupy the surface monolayer only. An almost complete surface localization of induced charges is predicted in [4]. This study applies the tight-binding model taking into account electron repulsion by the mean field method. However, in the case of fullerite the Hubbard repulsion $U_0$ on a $C_{60}$ molecule is estimated to be 1 eV or more [5] whereas the magnitude of the interfullerene hopping $t$ is below 50 meV [4]. Thus, the fullerite crystal, which characterized by the $U/t$ ratio more than 20, have to be classified as a system with very strong electron correlation. That is why the results obtained with the use of the one-electron tight-binding model should be taken with care.

The above reasons motivate the present study of charge-profile problem in fullerite. We consider the problem using the approximation that seems to fit better to the electronic characteristics of this material. Specifically, we apply the approach earlier used by us for calculations of charge transfer in the crystals of $A_3C_{60}$ fullerides [6]. The hopping smallness in comparison with electrostatic energies enables us to develop a simple scheme for the calculations of the charge distribution in the $C_{60}$-based FET structure.

## MODEL AND METHOD

As in Ref. [4], we consider the fcc fullerite lattice with a (001) plane parallel to the gate. We are interesting in the distribution of injected charges between the (001) parallel layers of $C_{60}$ molecules that forms square lattices with the side length $b = 10$ A.

Let $\rho_n$ be total number of extra electrons per molecule in the layer $n$, so their charge is $-e\rho_n$ (the case of injected holes is represented by negative $\rho_n$). We consider the system with the $N+1$ layers, the surface layer is labeled by zero.

The basic assumption of our model is neglecting the overlap between $C_{60}$ molecules. Accordingly, the total energy of the crystal is the sum of the energies of the separate layers of molecules that interact electrostatically. The energy $E_n$ per molecule in a layer $n$ with the potential $U_n$ is

$$E_n = \sum_{n=0}^{N} [E_0(\rho_n) - eU_n\rho_n], \tag{1}$$

where $E_0(\rho_n)$ is energy of free molecule with $\rho_n$ extra electrons.

This expression is accurate provided $\rho_n$ is integer, so $E_0(\rho_n)$ can be treated as energies of $C_{60}$ ions with corresponding charges. For noninteger $\rho_n$, it is naturally assumed that $E_0(\rho_n)$ can be interpolated by the quadratic fit,

$$E_0(\rho_n) = E_0(0) + E_1\rho_n + \frac{1}{2}E_2\rho_n^2. \tag{2}$$

Then the minimum condition of total energy with respect to $\rho_n$ leads to equation

$$E_1 + E_2\rho_n - eU_n = \theta, \tag{3}$$

where $\theta$ is a Lagrange multiplier taking into account the additional restriction of fixing total electron number

$$\sum_{n=0}^{N} \rho_n = \rho_{tot}. \tag{4}$$

On the other hand, the layer potentials are, in turn, related to the charges by the Poisson equations. Because of negligible hopping, as it is assumed in our model, the $C_{60}$ molecules interact only electrostatically and can be represented by point charges due to their near spherical form. According to Ref. [4], the potential $U_n$ of layer $n$ is determined by the equation

$$-eU_n = \xi \sum_{m=0}^{N} \min(m,n)\rho_m - \eta\rho_n, \tag{5}$$

where the coefficients $\xi$ and $\eta$ are expressed through $C_{60}$ dielectric constant $\varepsilon$ and the distance $b$ between neighboring molecules

$$\xi = \frac{4\pi e^2}{\varepsilon b\sqrt{2}}, \quad \eta = \frac{3.9e^2}{\varepsilon b}. \tag{6}$$

Excluding $U_n$ from Eqs. (3) and (5) we obtain the system of linear inhomogeneous equations. Together with the condition (4) this system determines the charge densities $\rho_n$,

$$\lambda\rho_n + \sum_{m=0}^{n} m\rho_m + n\sum_{m=n+1}^{N} \rho_m = C, \quad n = 0, 1, \ldots, N, \tag{7}$$

where parameter $\lambda$ is defined by the equality

$$\lambda = (E_2 - \eta)/\xi \tag{8}$$

and $C = (\theta - E_1)/\xi$ is a new constant. As it can be seen from Eq. (7) at $n = 0$, this constant relates to the charge density in surface layer by the equality $C = \lambda\rho_0$.

To treat the system (7), let us write it in the matrix form

$$(\mathbf{A} + \lambda\mathbf{I})\boldsymbol{\rho} = C\mathbf{V}, \tag{9}$$

where $\mathbf{I}$ is unit matrix, $\mathbf{V}$ is the column vector, all the components of which are units, and $\mathbf{A}$ is $(N+1) \times (N+1)$ matrix of form

$$\mathbf{A} = \begin{pmatrix} 0 & 0 & 0 & 0 & \cdot \\ 0 & 1 & 1 & 1 & \cdot \\ 0 & 1 & 2 & 2 & \cdot \\ 0 & 1 & 2 & 3 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}. \tag{10}$$

To find $\rho_n$, let us solve the eigenvalue problem of the matrix $\mathbf{A}$,

$$\mathbf{X}^+\mathbf{A}\mathbf{X} = \boldsymbol{\varepsilon}, \quad \mathbf{X}^+\mathbf{X} = \mathbf{I}, \tag{11}$$

where $\mathbf{X}$ is square matrix the column of which are eigenvectors of $\mathbf{A}$ and $\varepsilon$ is diagonal matrix of corresponding eigenvalues. Then one can obtain from (9) and (11)

$$\boldsymbol{\rho} = C\mathbf{X}(\boldsymbol{\varepsilon} + \lambda\mathbf{I})^{-1}\mathbf{X}^+\mathbf{V}. \tag{12}$$

Eq. (12) shows that the shape of charge profile defined by the relative charge distribution is independent on $\rho_{\text{tot}}$. The $\rho_n$ values obtained at any nonzero $C$ are further normalized to $\rho_{\text{tot}}$, thus satisfying also the additional condition (4).

## NUMERICAL RESULTS AND DISCUSSION

The quantity $1-\rho_n/\rho_{\text{tot}}$ determines the relative part of injected charge below the surface layer of the crystal. Its dependence on the parameter $E_2$ is depicted in Figure 1, as the result of calculations with $N = 50$. We consider only the solutions at $E_2 > \eta$ that have physical meaning and all the $\rho_n$ has the same sign as the constant $C$ in (12). The Figure 1 shows that the charge density at $(E_2 - \eta) \to +0$ is completely localized on the surface molecules. As $E_2$ rises, the charges markedly expands into deeper layers. To obtain numerical estimations in real $C_{60}$ crystal, only $E_2$ in the approximation (2) should be evaluated. Considering Eq. (2) as a fit to the

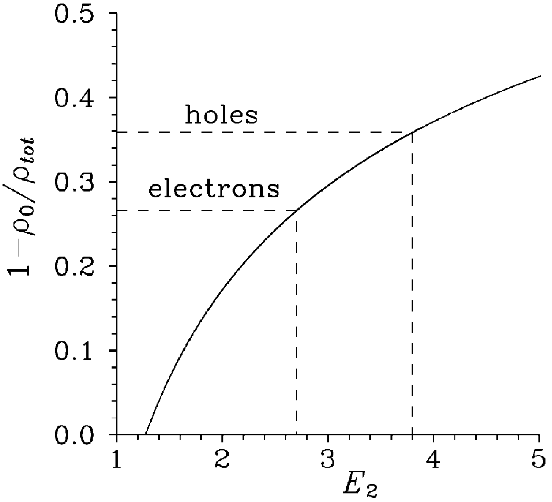

**FIGURE 1** Relative occupation of undersurface layers, $1-\rho_0/\rho_{\text{tot}}$, vs curvature $E_2$ of energy-charge fit (2). Dashed lines indicate the results of calculations for injected electrons and holes in $C_{60}$-based FET structure.

ground-state energies of $C_{60}$ molecule and its ions one obtains the following estimations of $E_2$ for injected charges of both signs

$$E_2 = E(0) + E(2) - 2E(1) = A(C_{60}) - A(C_{60}^-) = 2.7\,\text{eV (for electrons)},$$
$$E_2 = E(0) + E(-2) - 2E(-1) = -I(C_{60}) + I(C_{60}^+) = 3.8\,\text{eV (for holes)},$$

where $A$ are electron affinities and $I$ are ionization potentials with known experimental values (in eV) [7–9]:

$$A(C_{60}) = 2.7, A(C_{60}^-) \approx 0, I(C_{60}) = 7.6, I(C_{60}^+) = 19.0 - 7.6 = 11.4.$$

Using the estimation of parameter $\xi$ in (6) $\xi = 2.9\,\text{eV}$ [4], we obtain $\eta = 3.9\,\xi\sqrt{2}/4\pi = 1.27\,\text{eV}$. With above estimations of $E_2$ the degree of charge delocalization $1-\rho_n/\rho_{\text{tot}}$ is evaluated as 0.266 for electrons and 0.359 for holes, as it is illustrated in Figure 1. In other words, about one quarter of injected electron charge and one third of hole charges turns out to be beneath the surface layer of $C_{60}$ crystal.

The calculated charge distributions between the layers for electrons and holes in the $N = 50$ crystal is shown in Figure 2. It is clear that the injected charge densities fall with the distance from the surface strictly exponentially in both cases, with the electron density dropping more rapidly than hole one.

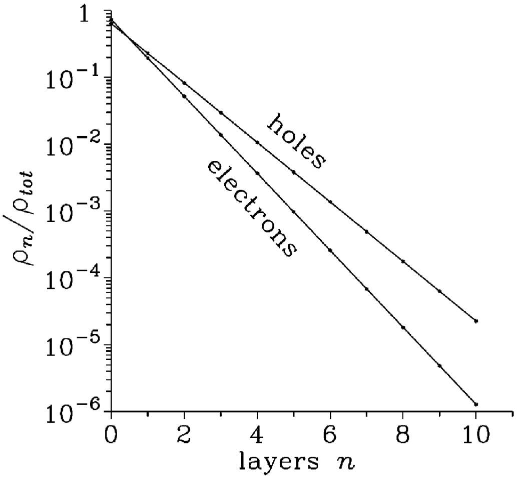

**FIGURE 2** Charge density distributions (in logarithmic scale) calculated for injected electrons and holes in $C_{60}$-based FET structure.

## CONCLUSION

We summarize our results and their main differences from that obtained in Ref. [4]. (i) The charge profile in [4] substantially depends on the charge concentration whereas our relative distribution is independent of it. (ii) According to [4] 98% of the total charge is confined to the surface layer for doping $\rho_{\text{tot}}$ higher than 0.3, in opposite to our calculations showing this degree less than 75% at any doping. The both results are in qualitative agreement with respect to domination of injected charges in the top layer. At the same time, our calculations show the possible nonnegligible occupation of undersurface layers. The question on their role in the conductivity properties of fullerite in the FET structures needs to be considered separately. However, just now our results suggest that the existing estimations of charge concentration providing the highest $T_c$ in the superconductive FET structures seem to be subject to refinement.

## REFERENCES

[1] Schön, J. H., Kloc, Ch., & Batlogg, B. (2000). Superconductivity in molecular crystals induced by charge injection. *Nature*, *406*, 704–706.
[2] Schön, J. H., Kloc, Ch., & Batlogg, B. (2000). Superconductivity at 52 K in hole-doped $C_{60}$. *Nature*, *408*, 549–552.

[3] Schön, J. H., Kloc, Ch., & Batlogg, B. (2001). High-temperature superconductivity in lattice-expanded $C_{60}$. ***Science***, ***293***, 2432–2434.

[4] Wehrli, S., Poilblanc, D., & Rice, T. M. (2001). Charge profile of surface doped $C_{60}$. ***Eur Phys J B.***, ***23***, 345–348.

[5] Gunnarsson, O. (1997). Superconductivity in fullerides. ***Rev Mod Phys.***, ***69***, 575–606.

[6] Kuprievich, V. A., Shramko, O. V., & Kapitanchuk, O. L. (2001). Electronic states of $C_{60}$ ions vs electron interaction and energetics of $A_3C_{60}$ fullerides. ***Mol Cryst Liq Cryst.***, ***361***, 31–35.

[7] Steger, H., de Vries, J., Kamke, B., Kamke, W., & Drewell, T. (1992). Direct double ionization of $C_{60}$ and $C_{70}$ fullerenes using synchrotron radiation. ***Chem Phys Lett.***, ***194***, 452–456.

[8] Hrusak, J., & Schwarz, H. (1993). ***Ab initio*** MO calculations on the electronic and geometric structure of fullerene dications ${C_{60}}^{(2+)}$ and the double-ionization energy of $C_{60}$. ***Chem, Phys, Lett.***, ***205***, 187–190.

[9] Hettich, R. L., Compton, R. N., & Ritchie, R. H. (1991). Doubly charged negative ions of carbon-60. ***Phys Rev Lett.***, ***67***, 1242–1245.