

Enhancing T_c in field-doped fullerenes by applying uniaxial stress

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Capitalizing on the two-dimensional nature of superconductivity in field-effect doped C_{60} , we show that it should be possible to increase the transition temperature T_c by applying uniaxial stress perpendicular to the gate electrode. This method not only holds the promise of substantially enhancing T_c (by about 30 K per GPa), but also provides a sensitive check of the current understanding of superconductivity in the doped fullerenes.

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In a remarkable series of experiments, Schön and collaborators have demonstrated superconductivity in field-effect devices based on fullerene crystals. First they field-doped pure C_{60} with electrons, observing a maximum T_c of 11 K at a doping of about three electrons per molecule in the layer under the gate electrode.¹ Reversing the polarity of the gate voltage, they achieved hole-doping, finding superconductivity with a transition temperature of up to 52 K at a doping level of about 3 to 3.5 holes per molecule.² In the most recent experiments, they observed superconductivity by field-doping C_{60} crystals that were intercalated with chloroform, $CHCl_3$, and $CHBr_3$.³ In these crystals, the volume per C_{60} molecule is increased due to the presence of the intercalated molecules. Superconductivity was observed for electron-doping as well as for hole-doping and it was found that in both cases T_c increases almost linearly with the distance between neighboring C_{60} molecules, reaching 80 K for $C_{60} \cdot 2CHCl_3$ and 117 K for $C_{60} \cdot 2CHBr_3$. After this discovery a “race to beat the cuprates” was announced,⁴ and the search was on for ways to further increase the transition temperature in the fullerenes. Here we show that a feasible method for doing so is the application of uniaxial stress perpendicular to the gate electrode. While this proposal might at first seem counterintuitive, we will demonstrate that it is a natural consequence of the two-dimensional nature of superconductivity in the field-doped fullerenes.

So far superconductivity in field-doped fullerenes has been discussed in close analogy to alkali-doped C_{60} . This was motivated by the remarkable similarities between these two classes of materials:⁵ (i) in both T_c is largest when the t_{1u} band is half filled, and (ii) T_c increases with the distance between the C_{60} molecules in the crystal, which is explained as a consequence of the corresponding increase in the density of states at the Fermi level. Experimentally it is found that for a given nearest-neighbor distance the transition temperature for the alkali- and the electron-field-doped fullerenes is almost identical.³ Nevertheless, there is a fundamental difference between the two classes of materials: the alkali-doped fullerenes are bulk superconductors, while in the field-effect devices superconductivity is restricted to two dimensions. It appears that in the field-doped fullerenes only the first monolayer under the gate electrode is doped. This is confirmed by tight-binding simulations where it is found that the deeper layers carry a negligible charge density.⁶ Experimentally it is supported by the fact that for the increase in T_c upon intercalation of $CHCl_3$ and $CHBr_3$, only the change in the

nearest-neighbor distance seems to matter, while the change in crystal structure appears to have no effect: At the temperatures where superconductivity occurs, pure C_{60} is simple cubic with four molecules (sitting on fcc sites) per unit cell,⁷ while the intercalated crystals are (almost) hexagonal.^{8,9} This suggests that superconductivity in field-doped fullerenes is restricted to a single, triangular layer: a (111) plane in C_{60} and a (001) plane in $C_{60} \cdot 2CHCl_3$ and $C_{60} \cdot 2CHBr_3$.

Given that only a single lattice plane is involved in the superconductivity and given that the transition temperature T_c increases with the distance between neighboring molecules, it should be possible to increase T_c simply by pushing on the gate electrode of the field-effect device. Such uniaxial stress will decrease the spacing of the lattice planes parallel to the gate, but at the same time it will *increase* the distance of the molecules *in* the planes. This is the Poisson effect.¹⁰ We again stress the fundamental difference between the alkali-doped and the field-doped fullerenes. The alkali-doped materials are bulk superconductors. Thus under pressure, even under uniaxial stress, the volume per molecule is reduced, lowering the density of states at the Fermi level and hence T_c . In contrast, in the field-doped fullerenes only the layer under the gate electrode is doped, and therefore hopping to the deeper layers is suppressed by the strong electrostatic potential of the induced space charge.⁶ Thus reducing the distance between the layers will have a negligible effect on the (practically two-dimensional) density of states, which is, however, strongly increased by the increasing distance of the molecules in the plane.

At this point the obvious questions are: Will uniaxial stress really affect the molecules under the gate electrode? And if so, how large will the effect be? The first problem that comes to mind is that the molecules under the gate might be held in place through interactions with the Al_2O_3 gate oxide. In this case the response of the molecules to stress would be determined by the hard oxide rather than by the elastic constants of the soft organic crystal. Strong bonding of the C_{60} molecules to the gate dielectric seems, however, quite unlikely, and there is even direct evidence for the mobility of the molecules that carry the source-drain current: Upon cooling, solid C_{60} undergoes an orientational phase transition at about 260 K, which is accompanied by a substantial reduction in volume (the distance between the molecules decreases by more than 0.3%, see Fig. 1),⁷ while the thermal expansion of aluminum oxide does not show any significant structure in that temperature range.¹¹ Nevertheless, the order-

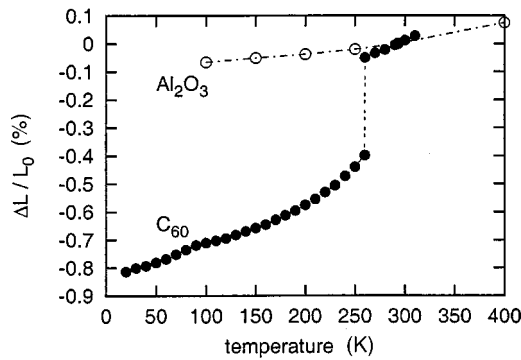


FIG. 1. Linear thermal expansion of a C_{60} single crystal⁷ and of Al_2O_3 .¹¹

ing transition shows up in the resistivity of field-doped C_{60} (Fig. 5 of Ref. 2), indicating that the molecules in the relevant layer indeed remain mobile.

The next question is whether it is experimentally feasible to apply pressure of any significant magnitude to field-effect devices based on delicate organic crystals. As it turns out, the necessary techniques are well established for the investigation of quasi-two-dimensional organic conductors: The whole device is embedded in a suitable epoxy or frozen in oil, and the application of pressures of up to 1 GPa at temperatures down to 0.5 K to samples of millimeter dimensions is straightforward.^{12,13} Ironically, one of the major problems in such experiments seems to be the suppression of the Poisson effect,¹³ the very effect which is desired in the present case. Thinking about C_{60} under pressure one might worry about polymerization. Pressures of the order of 1 GPa can, however, be considered low.¹⁴ Moreover, under uniaxial stress there is a greater chance that the crystal will loose cohesion and be squeezed, than that the resilient C_{60} molecules will form chemical bonds.

How large an effect on T_c can we expect? For an estimate we calculate the Young modulus E and the Poisson ratio σ for C_{60} under uniaxial stress. In terms of the elastic constants, the elastic response to stress in the [100] direction is given by

$$E_{[100]} = \frac{(c_{11} - c_{12})(c_{11} + 2c_{12})}{c_{11} + c_{12}}, \quad \sigma_{[100]} = \frac{c_{12}}{c_{11} + c_{12}}.$$

For stress in the [111] direction we find

$$E_{[111]} = \frac{3(c_{11} + 2c_{12})c_{44}}{c_{11} + 2c_{12} + c_{44}}, \quad \sigma_{[111]} = \frac{c_{11} + 2(c_{12} - c_{44})}{2(c_{11} + 2c_{12} + c_{44})}.$$

Table I gives a list of representative theoretical values for the elastic constants of C_{60} from the literature and from calculations using the Girifalco¹⁷ and the Pacheco-Ramalho¹⁸ potentials. There is a remarkably large spread in the predicted elastic constants, which vary by up to a factor of 2. The Young moduli fall in the ranges $E_{[100]} \approx 10$ –16 GPa and $E_{[111]} \approx 18$ –30 GPa. The Poisson ratios differ, however, by only about ten percent: $\sigma_{[100]} \approx 0.32$ and $\sigma_{[111]} \approx 0.2$. Using the slope $c \approx 230$ K/Å of T_c as a function of $a = \sqrt{2}d$, where d is the distance to the nearest molecule in the doped

TABLE I. Elastic constants for a C_{60} crystal at $T=0$. Elastic constants, bulk modulus [$B=(c_{11}+2c_{12})/3$], and Young moduli E are in GPa; Poisson ratios σ are dimensionless.

c_{11}	c_{12}	c_{44}	B	$E_{[100]}$	$\sigma_{[100]}$	$E_{[111]}$	$\sigma_{[111]}$	
14.1	6.0	7.7	8.7	10.5	0.30	17.8	0.16	Ref. 15 pot. II
14.9	6.9	8.1	9.6	10.5	0.32	19.0	0.17	Ref. 15 pot. I
16.1	8.2	8.2	10.8	10.5	0.34	19.6	0.20	PR potential
24.4	12.4	12.4	16.4	16.1	0.34	29.7	0.20	GF potential
24.5	12.3	11.8	16.4	16.3	0.33	28.5	0.21	Ref. 16

layer that was found experimentally,³ we can estimate the increase in transition temperature under uniaxial stress: $\Delta T_c/p = ca_0\sigma/E$. For a hole-doped C_{60} crystal under uniaxial stress in the [111] direction we thus find $\Delta T_c^{[111]}/p \approx 22$ –36 K/GPa. Should the [100] plane be the relevant for superconductivity, the effect would be even larger: $\Delta T_c^{[100]}/p \approx 65$ –105 K/GPa.

The effect of uniaxial stress on the transition temperature in field-doped fullerenes should be large, indeed. Already a modest force of 20 N on a crystal with an area of a square millimeter should increase T_c by about half a Kelvin or more. Such an effect should be observable when monitoring the source-drain resistivity of the field-effect device just above the ambient-pressure transition temperature. The increase in T_c is of course limited by the yield stress of the C_{60} crystal. To get a feeling for the behavior of C_{60} under finite stress, Fig. 2 shows the increase in the intermolecular distance d in the plane and the decrease in distance between the lattice planes as a function of the applied stress in [111] direction. For finite stresses the increase in d is even larger than expected from the elastic constants. Eventually the slope of $\Delta d/d_0$ becomes infinite, which means that the crystal is squeezed. This happens above 1.5 GPa. In the calculations an ideal geometry is enforced, so they should greatly overestimate the yield strength of a real, free-standing crystal. Nevertheless, stabilizing the crystal by embedding it in epoxy or frozen oil, it should be possible to nondestructively apply substantial pressures. With this method, uniaxial

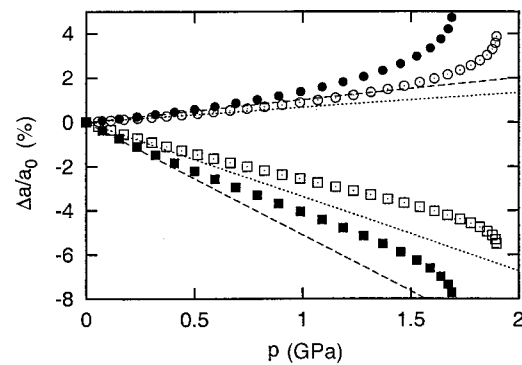


FIG. 2. Response to uniaxial stress in [111] direction calculated using the Girifalco (open symbols and dotted lines) and the Pacheco-Ramalho (filled symbols and dashed lines) potential. The lines show the deformation expected from the Young modulus, and the symbols show the calculated deformations under finite stress.

stresses of more than 0.5 GPa have been applied to weakly bound molecular crystals like the BEDT-TTF salts.^{12,13}

In our estimate of the change in transition temperature under uniaxial stress, we have assumed that the interpretation given in Ref. 3 is correct, namely that the distance of the molecules in the doped lattice plane is the only relevant parameter for determining T_c . A recent structural analysis of the low temperature phases of $C_{60} \cdot 2CHCl_3$ and $C_{60} \cdot 2CHBr_3$ has, however, cast doubts on this interpretation.⁹ It might therefore be possible that other effects, like the different molecular orientations or the presence of the intercalants, substantially influence superconductivity. In that respect, investigating the change in T_c under uniaxial stress could help to clarify the situation.

In summary, the application of uniaxial stress is a straightforward and feasible way for enhancing the transition temperatures of field-doped fullerenes even further. We have shown that the enhancement is significant, about 30 K per GPa, so that already the effect of very small pressures should be measurable. Besides the potential for achieving record

T_c 's, such experiments would deepen our understanding of the physics behind the increase in transition temperature, since they would allow us to study the effect of an increased spacing between the molecules without having to introduce additional molecules. Due to the softness of the fullerene crystals it is tempting to speculate that it might even be possible to push the field-doped fullerenes across the Mott transition.¹⁹ Then, by continuously varying the distance between the molecules (by the applied stress) and the doping (by the gate voltage), it should be possible to study the physics of a doped Mott insulator. From the alkali-doped fullerenes we know that T_c decreases when the lattice constant is increased too much.^{20,21} It will thus be interesting to see whether T_c in the field-doped fullerenes will be limited by the Mott transition, or if the maximum T_c is realized in the Mott-insulating regime—at some optimal doping.

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