Room Temperature Organic Superconductor?

N. Breda\textsuperscript{1,2}, R.A. Broglia\textsuperscript{1,3,4}, G. Colò\textsuperscript{1,3}, G. Onida\textsuperscript{5,6}, D. Provasi\textsuperscript{1} and E. Vigezzi\textsuperscript{3}

\textsuperscript{1}Dipartimento di Fisica, Università di Milano, Via Celoria 16, I-20133 Milano, Italy
\textsuperscript{2}INFM, Unità di Milano, Italy
\textsuperscript{3}INFN, Sezione di Milano, Italy
\textsuperscript{4}The Niels Bohr Institute, University of Copenhagen, D-2100 Copenhagen, Denmark
\textsuperscript{5}Dipartimento di Fisica dell’ Università di Roma Tor Vergata, Via della Ricerca Scientifica, I-00133 Roma, Italy
\textsuperscript{6}INFM, Unità di Roma Tor Vergata, Italy (October 27, 2018)

Abstract

The electron–phonon coupling in fullerene C\textsubscript{28} has been calculated from first principles. The value of the associated coupling constant $\lambda/N(0)$ is found to be a factor three larger than that associated with C\textsubscript{60}. Assuming similar values of the density of levels at the Fermi surface $N(0)$ and of the Coulomb pseudopotential $\mu^*$ for C\textsubscript{28}–based solids as those associated with alkali doped fullerides $A_3C_{60}$, one obtains $T_c(C_{28}) \approx 8T_c(C_{60})$

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The valence properties of small fullerenes \([1]\), in particular of the smallest fullerene yet observed \(C_{28}\), is a fascinating question at the fundamental level as well as in terms of its potential applications for the synthesis of new materials \([4–7]\). In supersonic cluster beams obtained from laser vaporization, \(C_{28}\) is the smallest even-numbered cluster, and thus the fullerene displaying the largest curvature, which is formed with special abundance. In fact, under suitable conditions, \(C_{28}\) is almost as abundant as \(C_{60}\) \([3]\). At variance with its most famous family member \(C_{60}\), \(C_{28}\) is expected to form a covalent crystal (like \(C_{36}\) \([8–10]\)), and not a Van der Waals solid \([11]\). However, similarly to \(C_{60}\), fullerene \(C_{28}\) maintains most of its intrinsic characteristics when placed inside an infinite crystalline lattice \([2]\). The transport properties of the associated metal doped fullerides, in particular superconductivity, can thus be calculated in terms of the electron–phonon coupling strength \(\lambda\) of the isolated molecule, and of the density of states of the solid \([12,13]\). In keeping with the fact that curvature–induced hybridization of the graphite sheet \(\pi\) orbitals, seems to be the mechanism explaining (cf. \([12–15]\) and refs. therein) the large increase in \(T_c\) in going from graphite intercalated compounds \((T_c \approx 5 K)\) \([16]\) to alkali–doped \(C_{60}\) fullerides, \((T_c \approx 30 – 40 K)\) \([17–19]\), fullerene \(C_{28}\) is a promising candidate with which to form a high–\(T_c\) material. These observations call for an accurate, first–principle investigation of the electronic and vibrational properties, as well as of the electron–phonon coupling strength of this system. In the present work we present the results of such a study, carried out within \(ab–initio\) density functional theory (DFT) in the local spin density approximation (LSDA). Our findings are that the associated value of \(\lambda/N(0)\) is a factor 2.5 and 1.2 larger than that associated with \(C_{60}\) \([13]\) and \(C_{36}\) \([3]\) respectively. Under similar assumptions for the density of levels at the Fermi energy \(N(0)\) and for the Coulomb pseudopotential \(\mu^*\) as those associated with alkali-doped fullerides \(A_3C_{60}\), one will thus expect \(T_c(C_{28}) \approx 8T_c(C_{60})\), opening the possibility for \(C_{28}\)–based fullerides which are superconducting at, or close to, room temperature.

The equilibrium geometry of \(C_{28}\) obtained in the present calculation is similar to that proposed by Kroto and co–workers \([20]\), and has the full \(T_d\) point group symmetry. All atoms are three fold coordinated, arranged in 12 pentagons and 4 hexagons. The large ratio of pentagons to hexagons makes the orbital hybridization in \(C_{28}\) more of \(sp^3\) type rather than \(sp^2\), the typical bonding of graphite and \(C_{60}\). The \(sp^3\)–like hybridization is responsible for a series of remarkable properties displayed by small fullerenes in general and by \(C_{28}\) in particular. Some of these properties are : a) the presence of dangling bonds, which renders \(C_{28}\) a strongly reactive molecule, b) the fact that \(C_{28}\) can be effectively stabilized (becoming a closed shell system displaying a large HOMO–LUMO energy gap) by passivating the four tetrahedral vertices either from the outside \((C_{28}H_4)\) or from the inside \((U@C_{28})\) \([3]\). It also displays a number of hidden valences: in fact, \(C_{28}H_{10}, C_{28}H_{16}, C_{28}H_{22}\) and \(C_{28}H_{28}\) are essentially as stable as \(C_{28}H_4\) (all displaying HOMO–LUMO energy gap of the order of 1.5 eV) \([1]\), in keeping with the validity of the free–electron picture of \(\pi\)–electrons which includes, as a particular case, the tetravalent chemist picture, c) while typical values of the matrix elements of the deformation potential involving the LUMO state range between 10–100 meV, the large number of phonons which couple to the LUMO state produces a total electron–phonon matrix element of the order of 1 eV (cf. Table 1), as large as the Coulomb repulsion between two electrons in \(C_{28}\). This result (remember that the corresponding electron–phonon matrix element is \(\sim 0.1 \text{ eV}\) and the typical Coulomb repulsion is \(\sim 0.5 – 1 \text{ eV}\) for \(C_{60}\) \([13]\)) testifies to the fact that one should expect unusual properties for both the
normal and the superconducting state of $C_{28}$-based fullerides, where the criticisms leveled off against standard theories of high $T_c$ of fullerenes (cf. e.g. refs. [13,21–24] and refs. therein) will be much in place.

In Fig 1(a), we report the electronic structure of $C_{28}$ computed within the Local Spin Density approximation, as obtained from a Car–Parrinello [25] molecular dynamics scheme [26,27]. Near the Fermi level we find three electrons in a $t_2$ orbital, and one in a $a_1$ orbital, all with the same spin, in agreement with the results of [3]. The situation is not altered, aside from a slight removal of the degeneracy, when the negative anion, $C_{28}^-$, is considered (see Fig. 1(b)). In this case, the additional electron goes into the $t_2$ state, and has a spin opposite to that of the four valence electrons of neutral $C_{28}$.

The wavenumbers, symmetries, and zero-point amplitudes of the phonons of $C_{28}$ are displayed in Table 1, together with the matrix elements of the deformation potential defining the electron–phonon coupling with the LUMO state. The total matrix element summed over all phonons is equal to 710 meV. The partial electron–phonon coupling constants $\lambda_\alpha/N(0)$, also shown in Table 1, sum up to 214 meV. This value is a factor 2.5 larger than that observed in $C_{60}$ [13], and a factor 1.2 larger than the value recently predicted for $C_{36}$ [9]. In Fig. 2 we display the values of $\lambda/N(0)$ for $C_{70}$, $C_{60}$, $C_{36}$ and $C_{28}$ [9,30,32], which testify to the central role the $sp^3$ curvature induced hybridization has in boosting the strength with which electrons couple to phonons in fullerenes [12,13].

In keeping with the simple estimates of $T_c$ carried out in refs. [13,9] for $C_{60}$ and $C_{36}$ based solids, we transform the value of $N(0)$ of Table 1 into a critical temperature by making use of McMillan’s solution of Eliashberg equations [33,34]

$$T_c = \frac{\omega_{ln}}{1.2} \exp \left[ -\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right],$$

where $\omega_{ln}$ is a typical phonon frequency (logarithmic average), $\lambda$ is the electron–phonon coupling and $\mu^*$ is the Coulomb pseudopotential, describing the effects of the repulsive Coulomb interaction. Typical values of $\omega_{ln}$ for the fullerenes under discussion is $\omega_{ln} \approx 10^3 K$ (cf. e.g. [35,36]). Values of $N(0)$ obtained from nuclear magnetic resonance lead to values of 7.2 and 8.1 states/eV–spin for $K_2C_{60}$ and $Rb_3C_{60}$, respectively (cf. ref. [13] and refs. therein). Similar values for $N(0)$ are expected for $C_{36}$ [9]. Making use of these values of $N(0)$ for all $C_n$–based solids ($n=70,60,36$ and 28), one obtains $0.2 \leq \lambda \leq 3$ for the range of values of the associated parameter $\lambda$. The other parameter entering Eq. (1), namely $\mu^*$ and which is as important as $\lambda$ in determining $T_c$ is not accurately known. For $C_{60}$, $\mu^*$ is estimated to be $\approx 0.25$ [13]. Using this value of $\mu^*$, and choosing $N(0)$ so that $T_c \approx 19.5K$ for $C_{60}$, as experimentally observed for $K_3C_{60}$ [13], one obtains $T_c(C_{28}) \approx 8T_c(C_{60})$ and $T_c(C_{28}) \approx 1.3T_c(C_{36})$ [37].

We conclude that $C_{28}$-fullerene displays such large electron–phonon coupling matrix elements as compared to the repulsion between two electrons in the same molecule, that it qualifies as a particular promising high $T_c$ superconductor. From this vantage point of view one can only speculate concerning the transport properties which a conductor constructed making use of $C_{20}$ [10] as a building block can display. In fact, this molecule is made entirely out of 12 pentagons with no hexagons, being the smallest fullerene which can exist according to Euler theorem for polyhedra, and thus displaying the largest curvature a carbon cage can have.
Calculations have been performed on the T3E Cray computer at CINECA, Bologna.
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TABLE I. Phonon wavenumbers, symmetries and zero-point amplitudes ($\Gamma_\alpha \equiv (\hbar/2M\omega_\alpha)^{1/2}$) (columns 1, 2 and 3) of the phonons of C$_{28}$ which couple to the LUMO state. In columns 4 and 5 the corresponding electron–phonon matrix elements $g_\alpha$ and partial coupling constants $\lambda_\alpha/N(0)$ are displayed. In the last row we show the corresponding summed values.

| $1/\lambda$ [cm$^{-1}$] | symm. | $\Gamma_\alpha$ ($10^{-3}$\AA) | Matrix element $g_\alpha$ [meV] | $\lambda_\alpha/N(0)$ [meV] |
|--------------------------|-------|-----------------|-------------------|-------------------|
| 351                      | $E$   | 63.3            | 7.9               | 1.0               |
| 391                      | $T_2$ | 59.9            | 10.7              | 2.4               |
| 524                      | $T_2$ | 51.8            | 49.7              | 38.0              |
| 565                      | $A_1$ | 49.9            | 12.9              | 0.8               |
| 570                      | $E$   | 49.6            | 37.0              | 12.9              |
| 607                      | $E$   | 48.1            | 55.7              | 27.5              |
| 707                      | $T_2$ | 44.6            | 42.5              | 20.6              |
| 724                      | $T_2$ | 44.1            | 42.8              | 20.4              |
| 763                      | $A_1$ | 42.9            | 46.2              | 7.5               |
| 781                      | $T_2$ | 42.7            | 12.4              | 1.6               |
| 791                      | $T_2$ | 42.1            | 0.9               | 0.0               |
| 976                      | $E$   | 37.9            | 43.6              | 10.5              |
| 983                      | $T_2$ | 37.8            | 15.2              | 1.9               |
| 1093                     | $T_2$ | 35.9            | 3.4               | 1.0               |
| 1101                     | $A_1$ | 35.7            | 45.2              | 50.0              |
| 1116                     | $E$   | 35.5            | 68.9              | 22.8              |
| 1171                     | $A_1$ | 34.6            | 6.4               | 0.1               |
| 1191                     | $T_2$ | 34.3            | 43.6              | 12.9              |
| 1220                     | $A_1$ | 33.9            | 30.5              | 2.0               |
| 1260                     | $T_2$ | 33.4            | 21.2              | 2.9               |
| 1306                     | $E$   | 32.8            | 57.5              | 13.6              |
| 1381                     | $T_2$ | 31.9            | 6.7               | 0.3               |
| 1414                     | $E$   | 31.5            | 49.2              | 9.2               |
| **Total:**               |       | **710**         | **214**           |
FIGURES

Fig. 1. Kohn–Sham levels of the neutral (a) and negatively charged (b) C_{28} cluster calculated within the LSD approximation. $\alpha$ and $\beta$ label the $z$–projection of the electron spin and arrows represent the valence electrons.

Fig. 2. Calculated electron-phonon coupling constant $\lambda/N(0)$ for C_{70}, C_{60}, C_{36}, C_{28} (cf. Table I).
$\lambda/N(0)$ vs. number of atoms

$\lambda/N(0)$ (meV) vs. number of C atoms