PHYSICAL REVIEW B VOLUME 62, NUMBER 1 1 JULY 2000-I

C_{28}: A possible room temperature organic superconductor

N. Breda
Dipartimento di Fisica, Università di Milano, Via Celoria 16, I-20133 Milano, Italy
and INFM, Unita di Milano, Milano, Italy

R. A. Broglia
Dipartimento di Fisica, Università di Milano, Via Celoria 16, I-20133 Milano, Italy;
INFN, Sezione di Milano, Milano, Italy;
and The Niels Bohr Institute, University of Copenhagen, D-2100 Copenhagen, Denmark

G. Colò
Dipartimento di Fisica, Università di Milano, Via Celoria 16, I-20133 Milano, Italy
and INFN, Sezione di Milano, Milano, Italy

G. Onida
Dipartimento di Fisica, Università di Roma Tor Vergata, Via della Ricerca Scientifica, I-00133 Roma, Italy
and INFM, Unità di Roma Tor Vergata, Roma, Italy

D. Provasi
Dipartimento di Fisica, Università di Milano, Via Celoria 16, I-20133 Milano, Italy

E. Vigezzi
INFN, Sezione di Milano, Milano, Italy

(Received 11 January 2000)

The electron-phonon coupling in fullerene C_{28} has been calculated from first principles. The value of the associated coupling constant $\lambda/N(0)$ is found to be a factor 3.4 larger than that associated with C_{60}. Assuming similar values of the density of levels at the Fermi surface $N(0)$ and of the Coulomb pseudopotential μ^* for C_{28}-based solids as those associated with alkali doped fullerides A_3C_{60}, one obtains $T_c(C_{28}) \approx 8T_c(C_{60})$.

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.[2–7] 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}, Refs. 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 λ 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 π orbitals, seems to be the mechanism explaining (cf. Refs. 12–15 and references therein) the large increase in T_c in going from graphite intercalated compounds ($T_c \approx 5$ K) (Ref. 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 3.4 and 1.2 larger than that associated with C_{60} (Ref. 13) and C_{36} (Ref. 9), respectively. Under similar assumptions for the density of levels at the Fermi energy $N(0)$ and for the Coulomb pseudopotential μ^* 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 threefold 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: (i) the presence of dangling bonds, which renders C_{28} a strongly reactive molecule, (ii) the fact that C_{28} can be effectively stabilized [becoming a closed-shell system displaying a large

TABLE I. Phonon wave numbers, 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_α 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.	Γ_α (10^{-3} Å)	Matrix element g_α [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
771	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

highest occupied molecular orbital–lowest unoccupied molecular orbital (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 π electrons which includes, as a particular case, the tetravalent chemist picture, (iii) while typical values of the matrix elements of the deformation potential involving the LUMO state range between 10 and 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 I), 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 eV and the typical Coulomb repulsion is $\sim$0.5–1 eV for C_{60} (Ref. 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 and 21–24 and references therein) will be much in place.

In Fig. 1(a), we report the electronic structure of C_{28} ccomputed 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 Ref. 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}.

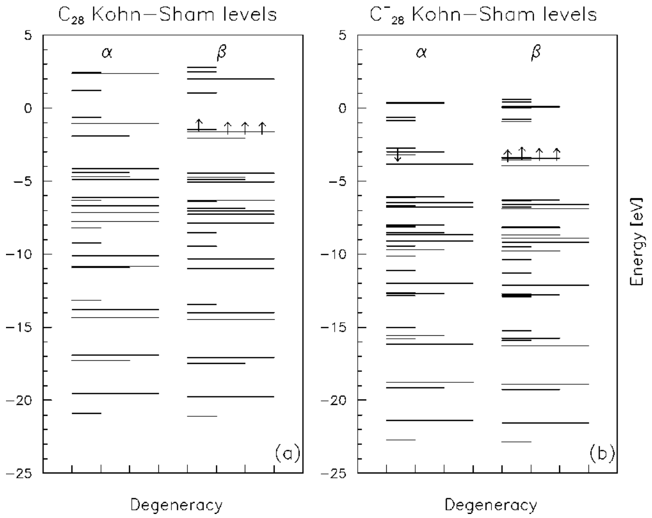

FIG. 1. Kohn-Sham levels of the neutral (a) and negatively charged (b) C_{28} cluster calculated within the LSD approximation. α and β label the z projection of the electron spin and arrows represent the valence electrons.

The wave numbers, symmetries, and zero-point amplitudes of the phonons of C_{28} are displayed in Table I, 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 I, sum up to 214 meV. This value is a factor 2.5 larger than that observed in C_{60},[13] and a

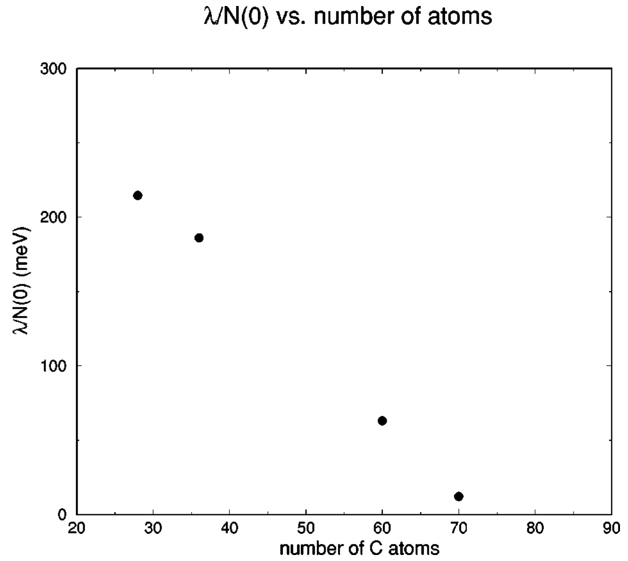

FIG. 2. Calculated electron-phonon coupling constant $\lambda/N(0)$ for C_{70} (Ref. 30), C_{60} (Ref. 13), C_{36} (Ref. 9), C_{28} (cf. Table I).

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.[12–15]

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

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

where ω_{ln} is a typical phonon frequency (logarithmic average), λ is the electron-phonon coupling and μ^* is the Coulomb pseudopotential, describing the effects of the repulsive Coulomb interaction. Typical values of ω_{ln} for the fullerenes under discussion is $\omega_{ln}\approx 10^3$ K (cf., e.g., Refs. 35 and 36). Values of $N(0)$ obtained from nuclear magnetic resonance lead to values of 8.1 and 12 states/eV spin for K_3C_{60} and Rb_3C_{60}, respectively (cf. Ref. 13 and references 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 $0.1\leqslant\lambda\leqslant 3$ for the range of values of the associated parameter λ. The other parameter entering Eq. (1), namely μ^* and which is as important as λ in determining T_c is not accurately known. For C_{60}, μ^* is estimated to be ≈ 0.25.[13] Using this value of μ^*, and choosing $N(0)$ so that $T_c\approx 19.5$ K 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 the other fullerene C_{20} as a building block, can display.[40] 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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[1] C. Milani, C. Giambelli, H.E. Roman, F. Alasia, G. Benedek, R.A. Broglia, S. Sanguinetti, and Y. Yabana, Chem. Phys. Lett. **258**, 554 (1996).

[2] E. Kaxiras, L.M. Zeger, A. Antonelli, and Yu-min Juan, Phys. Rev. B **49**, 8446 (1994).

[3] T. Guo, M.D. Diener, Yan Chai, M.J. Alford, R.E. Haufler, S.M. McClure, T. Ohno, J.H. Weaver, G.E. Scuseria, and R.E. Smalley, Science **257**, 1661 (1992).

[4] D.M. Bylander and L. Kleinman, Phys. Rev. B **47**, 10 967 (1993).

[5] B.I. Dunlop, O. Häberben, and N. Rösch, J. Phys. Chem. **96**, 9095 (1992).

[6] M.R. Pederson and N. Laouini, Phys. Rev. B **48**, 2733 (1993).

[7] A. Canning, G. Galli, and J. Kim, Phys. Rev. Lett. **78**, 4442 (1997).

[8] J.C. Grossman, M. Coté, S.G. Louie, and M.L. Cohen, Chem. Phys. Lett. **284**, 344 (1998).

[9] M. Coté, J.C. Grossman, M.L. Cohen, and S.G. Louie, Phys. Rev. Lett. **81**, 697 (1998).

[10] C. Piskoti, J. Yager, and A. Zettl, Nature (London) **373**, 771 (1998).

[11] M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, New York, 1996).

[12] M. Schlüter, M. Lannoo, M. Needels, G.A. Baraff, and D. Tomanek, Phys. Rev. Lett. **68**, 526 (1992).

[13] O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997).

[14] A. Devos and M. Lannoo, Phys. Rev. B **58**, 8236 (1998).

[15] V.H. Crespi, Phys. Rev. B **60**, 100 (1999).

[16] I.T. Belash, A.D. Bronnikov, O.V. Zharikov, and A.V. Pal'nichenko, Synth. Met. **36**, 283 (1990).

[17] K. Tanigaki, T.W. Ebbesen, S. Saito, J. Mizuki, J.S. Tsai, Y. Kubo, and S. Kuroshima, Nature (London) **352**, 222 (1991).

[18] T.T.M. Palstra, O. Zhou, Y. Iwasa, P.E. Sulewski, R.M. Fleming, and B.R. Zegarski, Solid State Commun. **93**, 327 (1995).

[19] T.T.M. Palstra, A.F. Hebard, R.C. Haddon, and P.B. Littlewood, Phys. Rev. B **50**, 3462 (1994).

[20] H. Kroto, Nature (London) **329**, 529 (1987).

[21] P. Anderson (unpublished).

[22] L. Pietronero and S. Strässler, Europhys. Lett. **18**, 627 (1992).

[23] L. Pietronero, S. Strässler, and C. Grimaldi, Phys. Rev. B **52**, 10 516 (1995).

[24] C. Grimaldi, L. Pietronero, and S. Strässler, Phys. Rev. B **52**, 10 530 (1995).

[25] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[26] J. Hutter *et al.*, MPI Für Festkörperforschung, Stuttgart, and IBM research, 1990–1997. The code has been partially modified to calculate the matrix elements of the deformation potential.

[27] The whole calculation (i.e., geometry optimization of the cluster, Kohn-Sham levels, phonons and deformation potential) has been carried out by setting C_{28} in a fcc supercell with lattice constant $a=26$ a.u. A norm-conserving Trouiller-Martins (Refs. 28 and 29) pseudopotential has been employed in the calculation, with a cutoff of 40 Ry.

[28] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[29] M. Fuchs, and M. Scheffler, Comput. Phys. Commun. **119**, 67 (1999).

[30] D. Provasi, N. Breda, R.A. Broglia, G. Colò, H.E. Roman, and G. Onida, Phys. Rev. B **61**, 7775 (2000).

[31] O. Gunnarsson, Phys. Rev. B **51**, 3493 (1995).

[32] N. Breda, R.A. Broglia, G. Colò, H.E. Roman, F. Alasia, G. Onida, V. Ponomarev, and E. Vigezzi, Chem. Phys. Lett. **286**, 350 (1998).

[33] W.C. McMillan, Phys. Rev. **167**, 331 (1968).

[34] G.M. Eliashberg, Zh. Éksp. Teor. Fiz. **38**, 966 (1960) [Sov. Phys. JETP **11**, 696 (1960)].

[35] D.S. Bethune, G. Meijer, W.C. Tang, H.J. Rosen, W.G. Golden,

H. Seki, C.A. Brown, and M.S. de Vries, Chem. Phys. Lett. **179**, 181 (1991).

[36] Z.H. Wang, M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, Phys. Rev. B **48**, 16881 (1993).

[37] Similar values of T_c are obtained using Allen's solution (Refs. 38 and 39) of Eliashberg equations.

[38] P.B. Allen and R.C. Dynes, Phys. Rev. B **12**, 905 (1975).

[39] P.B. Allen and B. Mitrovič, *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic Press, New York, 1982), Vol. 37, p. 1.

[40] While no clear evidences have been found in carbon cluster beams for a particularly abundant bare C_{20} cluster, the fully hydrogenated $C_{20}H_{20}$ molecule, dodecahedrane, turns out to be stable (Ref. 41).

[41] L.A. Paquette, R.J. Ternansky, D.W. Balogh, and G.J. Kentgen, J. Am. Chem. Soc. **105**, 5446 (1983).