The electron-phonon coupling of a theoretically devised carbon phase made by assembling the smallest fullerenes $C_{20}$ is calculated from first principles. The structure consists of $C_{20}$ cages in an $fcc$ lattice interlinked by two bridging carbon atoms in the interstitial tetrahedral sites ($fcc-C_{22}$). The calculation of the equation of state of $C_{20}$ is reported in Fig. 2. The system is an insulator with a slightly indirect transition temperature ($T_c=10-40$ K) has attracted much attention on these materials as representatives of a new class of superconductors [11-14]. Superconductivity, albeit at lower temperature ($T_c=7$ K), has been recently observed in another member of this class, $C_{70}$, which indicates the possibility that other fullerenes might also become superconducting [15]. In this respect, the smaller fullerenes are the most interesting since the electron-phonon coupling (and hopefully $T_c$) has been calculated to become larger with increasing curvature of the molecule [16-18]. Therefore, the recent synthesis of the smallest fullerene, having the largest curvature, $C_{20}$, starting from the stable $C_{60}H_{20}$ molecules [19] represents a step further along the way towards high-$T_c$ superconductivity in carbon-based materials. Experimental evidence for the realization of the next step, the formation of a crystalline solid based on $C_{20}$ clusters, has been recently provided as well [20]. Crystalline micro-domains of the new carbon phase have been detected by Transmission Electron Microscopy (TEM) in carbon films deposited on a nickel substrate by the ultraviolet laser ablation of diamond. A face-centered-cubic ($fcc$) structure comprises $C_{20}$ cages in a $fcc$ lattice interconnected by two bridging atoms per unit cell in the tetrahedral interstitial sites (Fig. 3). Hereafter it is referred to as $fcc-C_{22}$, the unit cell containing 22 atoms.

In this letter, we report on the ab-initio study of the electronic properties of $fcc-C_{22}$ doped with alkali metals (Na, Li) in the search for metallization and superconductivity. The calculated electron-phonon coupling constant $\lambda$ for the alkali-doped $fcc-C_{22}$ is found to be substantially enhanced compared to $C_{60}$ leading to the possibility of larger $T_c$ than in alkali-doped fullerite.

We use density functional theory in the local density approximation (LDA), norm-conserving pseudopotentials and plane-wave expansion of the Kohn-Sham orbitals up to a kinetic cutoff of 40 Ry [21]. Non-linear-core corrections have been added within the linear response theory [12, 13]. This approach has been successfully applied to the calculation of phonon dispersion relations in insulator and metals [22-24] and of the electron-phonon coupling constant $\lambda$ in simple and transition metals [25]. Brillouin Zone (BZ) integrations are performed using Hermite-Gaussian smearing of order one [26] with a linewidth of 0.01 Ry and 18 special points in the irreducible wedge of the BZ (IBZ).

The calculation of the equation of state of $fcc-C_{22}$ yields a cohesive energy of 0.63 eV/atom lower than that of diamond and a lattice constant of 8.61 Å. The density is 1.78 g/cm$^3$, close to that of fullerite (1.68 g/cm$^3$), but the bulk modulus is as large as 239 GPa due to the presence of covalent interlinks between adjacent $C_{20}$ cages. The crystal belongs to the Fm3 space group and contains only three independent atoms in the unit cells, the other being obtained by symmetry operations. Their coordinates in units of the lattice constant are $A \equiv (0.25, 0.25, 0.25)$, $B \equiv (0.148, 0.148, 0.148)$, $C \equiv (0.078, 0.217, 0.0)$ [8, 10, 16]. (Fig. 1). Eight atoms out of twenty of the cage (atoms $B$ and the interstitial carbon atoms $A$) are $sp^3$ hybridized. The other twelve atoms of the cage ($C$) are $sp^2$ hybridized forming $C=C$ ethylenic bonds. There are three bond lengths in the crystal: the single $sp^3$-like $B - C$ bond in the pentagonal ring (1.531 Å), the $C=C$ ethylenic-like bond (1.346 Å) long and the single $sp^3$-like bond between a cage (equivalent to $B$) and an interstitial atom ($A$) (1.517 Å).

The electronic band structure of $fcc-C_{22}$ is reported in Fig. 2. The system is an insulator with a slightly indirect $XL$ band gap of 2.47 eV. Projection of the Kohn-Sham states on the minimal atomic basis set shows that the lowest conduction bands and the highest valence bands are mainly formed by $\pi^*$ and $\pi$ states of the ethylenic-like bonds.
It is suggestive to wonder if doping might turn fcc-C_{22} metallic by electron transfer into the molecular-like lowest conduction bands, as occurs for instance in fullerite. The analogy with C_{60} is evident by considering that both C_{60} molecules in fullerite and C_{20} cages in fcc-C_{22} form a fcc lattice. In the A_{3}C_{60} (A=K, Cs, Rb) compounds the three alkali metal ions per unit cell occupy the two tetrahedral sites and the octahedral site. In fcc-C_{22} the two tetrahedral sites are occupied by the interstitial carbon atoms, but the octahedral site is empty and might host a guest ion. In the search for metallization we inserted a Na atom per unit cell in the octahedral site. Calculation of the equation of state of the compound NaC_{22} shows an increase in the lattice parameter (a=8.765 Å) with respect to the pure phase and a larger (2 %) increase in the C=C bond length due to population of antibonding π∗ states. In fact, Na is ionized by donating its outermost electron to the host which becomes metallic. The Na-host interaction is weak and the band structure of NaC_{22} is very close to that of the pure system, but for the shift of the Fermi level inside the lowest conduction bands (Fig. 2b). Therefore the rigid band approximation holds to a large extent in the description of Na insertion in fcc-C_{22}. Although the lowest conduction band is 3-fold degenerate at the Γ point (Fig. 2a), the Fm3̅m symmetry is preserved in NaC_{22} and no static Jahn-Teller distortion is observed. This is due to the fact that the minima of the lowest conduction bands are located at the X and L points where the degeneracy is already lifted.

To study the superconducting properties we have computed the electron phonon coupling constant λ as

\[
\frac{\lambda}{N(0)} = \sum_{\alpha} \int \frac{dq}{\Omega_{BZ}} \frac{1}{2} \delta(E_{k\alpha}) \langle \delta(E_{k+q\alpha}-E_{k\alpha}) \rangle \frac{\pi}{N^{2}(0)} | \langle u_{k+q\alpha,m} | M^{-1} \lambda \alpha q \nabla \epsilon_{eff}^{q} | u_{k\alpha,m} \rangle |^{2}
\]

where \(N(0)\) is the electronic density of states at the Fermi level (zero of energy) per spin and per cell, \(\lambda\alpha q/N(0)\) is the partial electron-phonon coupling due the \(\alpha\)-th phonon at the point \(q\) in the BZ (of volume \(\Omega_{BZ}\)), \(\epsilon_{\alpha q}\) is the phonon polarization vector, \(M\) is the atomic mass matrix, \(n\) and \(m\) are electronic band indices, \(u_{k\alpha,m}\) is the periodic part of the Kohn-Sham state with energy \(E_{k\alpha}\), and \(\nabla \epsilon_{eff}^{q}\) is the derivative of the Kohn-Sham effective potential with respect to the atomic displacement caused by a phonon with wavevector \(q\). We replaced the \(\delta\)-functions in Eq. 2 with Hermite-Gaussian forms of 0.01 Ry linewidth. The BZ integration over \(k\) is performed on a grid of 18 special points in the IBZ. We computed \(\lambda\alpha q/N(0)\) for \(q\) along the high symmetry directions \([100]\) and \([111]\). The integration over \(q\) in Eq. 2 is performed over a uniform mesh in the IBZ by assigning to each point the value of \(\lambda\alpha q/N(0)\) computed for the closest point along a high symmetry direction \([17]\). Finally, for NaC_{22} we obtain \(\lambda/N(0)=0.28\) eV, \(N(0)=4.0\) states/eV/spin/cell (as computed by the tetrahedron method with 213 points in the IBZ) and \(\lambda=1.12\). A similar calculation for the charged fullerite C_{60} at the Γ point only in the molecular-like approximation \([18]\) gives \(\lambda/N(0)=0.076\) eV, in agreement with previous works \([2\) (or 0.064 eV by including the set of phonons considered in table IV of Gunnarsson’s review \([3]\)). Therefore, although fcc-C_{22} is not strictly a fullerite, the C_{20} clusters being covalently interlinked via interstitial atoms, the solid retains some features of its molecular building blocks, giving rise to a substantial enhancement of \(\lambda/N(0)\) with respect to C_{60} as expected from the larger curvature of C_{20} \([8\). The persistence of molecular features in the crystal is also confirmed by the calculation of \(\lambda/N(0)\) in the molecular-like approximation \([15\) for the pure fcc-C_{22} doped with an additional electron (equally shared by the three lowest \(t_{u}\) states). This latter calculation gives \(\lambda/N(0)=0.31\) eV, a value very close to the result for NaC_{22} at convergence in BZ integration (0.28 eV) \([20\). A tight-binding calculation of the electron-phonon interaction in the isolated C_{20} cluster gave a somehow lower value \(\lambda/N(0)=0.18\) eV \([21\) which may be partially due to the semiempirical method used.

In order to identify the phonons which mostly contribute to the electron-phonon coupling, we report in Table I the partial electron-phonon coupling constants \(\lambda_{\alpha}/N(0)\) of the individual \(\alpha\)-th phononic band, obtained by averaging \(\lambda\alpha q/N(0)\) over the BZ. The frequency and symmetry of the \(\alpha\)-th phononic bands at the Γ point are also given in Table I for the pure fcc-C_{22} and NaC_{22} phases. Although the phonons with the largest matrix elements in Eq. 2 correspond to the stretching modes of the C=C ethylenic bonds (1359-1362 cm^{-1}), their contribution to \(\lambda\) is attenuated by the factor \(1/\omega^2\). As a consequence the largest \(\lambda_{\alpha}/N(0)\) is due to the \(E_g\) mode at 334 cm^{-1} (cfr. Table I); its displacement pattern (Fig. 3b) produces the largest modulation of the dihedral angles which control the π conjugation of the ethylenic bonds. This is at variance with C_{60} where the largest electron-phonon coupling constants are due to the phonons with the highest frequencies \([3\].

In system where the superconductivity is driven by the electron-phonon interaction an estimate of \(T_c\) can be obtained by making use of the McMillan’s solution \([20\, 21\) of the Eliashberg equations:

\[
T_c = \frac{\omega_{ln}}{1.2} \exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right)
\]
where \( \omega_{ln} \) is the weighted logarithmic average of the phonon frequencies [20, 21] (470 cm\(^{-1}\) in NaC\(_{22}\)) and \( \mu^* \) is the Coulomb pseudopotential \( \mu = UN(0) \) renormalized by retardation effects. \( U \) is a typical screened Coulomb interaction among states at the Fermi level [21]. Latest estimates give \( \mu^* \sim 0.3 \) for C\(_{60}\) although, due to the similarity between the electronic bandwidth (0.5 eV) and phonon energies (up to 0.2 eV), the applicability of Eq. 2 is questionable for fullerite [2]. We have not attempted to estimate numerically \( \mu^* \) for NaC\(_{22}\), so our discussion now turns on a very speculative level. Although \( U \) might be larger in NaC\(_{22}\) than in fullerite due to the smaller size of C\(_{20}\), \( N(0) \) turns out to be lower (4.0 and 6.6-9.8 states/eV/spin/cell in NaC\(_{22}\) and K\(_3\)C\(_{60}\) from band structure calculations [2], respectively) due to the larger dispersion of the conduction bands, three times larger than in C\(_{60}\) due to the larger bandwidth. Thus, if we assume that the value of 0.3 estimated for fullerite is an upper bound for \( \mu^* \) in NaC\(_{22}\) we obtain \( T_c=15 \) K from Eq. 2 and \( \lambda=1.12 \). For the more optimistic case of \( \mu^* \) in the range 0.1-0.2 typical of simple and transition metals [20, 21], we obtain the remarkable result of \( T_c=55-33 \) K (\( T_c \) changes linearly with \( \mu^* \) in this range).

Since \( \lambda/N(0) \) is mainly a molecular property, we have also attempted to increase \( \lambda \) by increasing \( N(0) \) with a lattice expansion. This has been achieved by substituting C by Si in the interstitial sites producing the compound NaSi\(_2\)C\(_{20}\). This latter system has a substantially expanded lattice parameter (\( a=9.49 \) Å, \( N(0)=4.44 \) states/eV/spin/cell) but only a marginally enhanced \( \lambda=1.49 \) with respect to NaC\(_{22}\). In fact the increase in \( N(0) \) is lower than expected from the lattice expansion due to the reduction of bands at the Fermi level from two in NaC\(_{22}\) (cfr. Fig. 2) to one in NaSi\(_2\)C\(_{20}\). Moreover, a decrease in \( \omega_{ln} \) due to the lattice expansion compensates the increase in \( \lambda \) and finally yields a \( T_c \) close (within 10 K) to that of NaC\(_{20}\). However, further increase in \( \lambda \) is foreseeable for the compounds NaGe\(_2\)C\(_{20}\) and NaSn\(_2\)C\(_{20}\).

In summary, we have carried out ab-initio calculations on the electronic and superconductive properties of a new carbon phase \textit{fcc-C\(_{22}\)} formed by assembling C\(_{20}\) clusters in a \textit{fcc} lattice. The system is insulating but can be made metallic by doping with interstitial alkali metals. Although the structure is not a molecular crystal, the C\(_{20}\) cages being covalently interlinked via interstitial carbon atoms, the crystal retains some molecular features. In fact, as expected from the molecular properties of the isolated C\(_{20}\) cluster, the compound NaC\(_{22}\) exhibits a large electron-phonon coupling constant \( \lambda/N(0) = 0.28 \) eV, strongly enhanced with respect to C\(_{60}\) due to the larger curvature of C\(_{20}\). Estimate of \( N(0) \) from band structure calculation yields \( \lambda =1.12 \) which allows a rough estimate of \( T_c \) from McMillan’s formula. For \( \mu^* \) in the reasonable range of 0.3-0.1 we predict \( T_c=15-55 \) K for NaC\(_{22}\). Although a more precise estimate of \( T_c \) requires the difficult calculation of \( \mu^* \), the results presented here shows that NaC\(_{22}\) is a potentially interesting superconductor. We hope that these theoretical results could stimulate further experimental work on the synthesis and characterization of this new structure.

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[17] To check the convergence of our results, we have considered that \( \lambda / N(0) \) represents a double average over the BZ of the matrix elements in Eq. 2 weighted by the function \( f_{nm}(q, k) = \delta(E_{kn})\delta(E_{k+q,m})/N^2(0) \), which is normalized to one at convergence in the BZ integration. By normalizing the double integral in Eq. 2 by the factor \( \sum_{n,m} \int dq dk f_{nm}(q, k)/N^2(0) \), we achieve a faster convergence with respect to \( q \) and \( k \) sums and gaussian spreading. We estimate a total error in \( \lambda / N(0) \) below 10%.
[18] In the molecular-like approximation, valid for flat electronic and phononic bands, the electron-phonon coupling constant is \[ \frac{\lambda}{N(0)} = \sum_{\alpha} \frac{1}{\omega_{\alpha} g^2} \sum_{n,m} | \langle u_m | M^{-\frac{1}{2}} \epsilon_{\alpha} \nabla V_{eff} | u_n \rangle |^2 \]
where the sum over \( \alpha \) and \( n, m \) run over the phonons and the \( g \) degenerate electronic states at the Fermi level at the \( \Gamma \) point.
[19] We have also found \( \lambda / N(0) = 0.32 \) eV for the compound LiC_{22} (a= 8.59 Å) as computed in the molecular-like approximation for a cubic supercell with four formula units. For this preliminary calculation we have used the code CPMD version 3.4, developed by J. Hutter et al., Max–Planck–Institut für Festkörperforschung and IBM Research Laboratory (1990–2001). In this latter case the phonons and the quantity \( \nabla V_{eff} \) have been computed by finite differences.
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TABLE I: The partial electron-phonon coupling constant $\lambda_\alpha/N(0)$ (eV) of the individual $\alpha$-th phononic band, obtained by averaging $\lambda_{\alpha q}/N(0)$ over the BZ. The frequency and symmetry of the $\alpha$-th phononic bands at the $\Gamma$ point are also given for the pure $fcc$-$C_{22}$ and $NaC_{22}$ phases. Only the phononic bands with $\lambda_\alpha/N(0)$ larger than 5 meV are reported. $T_u(1)$ correspond to the acoustic bands. $T_u(2)$ correspond to translational modes of Na ions.

| Modes | C$_{22}$ | NaC$_{22}$ | $\lambda_\alpha/N(0)$ |
|-------|-----------|------------|----------------------|
| $T_u$(1) | - | - | 0.010 |
| $T_u$(2) | - | 271 | 0.022 |
| $T_g$(1) | 281 | 282 | 0.046 |
| $T_u$(2) | 490 | 445 | 0.038 |
| $E_u$(1) | 492 | 334 | 0.072 |
| $T_u$(3) | 576 | 482 | 0.019 |
| $T_u$(4) | 626 | 609 | 0.008 |
| $T_g$(3) | 701 | 637 | 0.008 |
| $T_u$(5) | 731 | 697 | 0.007 |
| $E_u$(1) | 754 | 719 | 0.005 |
| $T_u$(4) | 857 | 823 | 0.005 |
| $T_u$(6) | 948 | 927 | 0.006 |
| $T_u$(10) | 1559 | 1362 | 0.010 |
| $E_u$(3) | 1574 | 1359 | 0.005 |
FIG. 1: The face-centered-cubic structure of the \textit{fcc-}C_{22} crystal. The conventional unit cell with four formula units is shown. The crystal belongs to the Fm\overline{3} space group and the coordinates of the three independent atoms in units of the lattice constant are $A \equiv (0.25, 0.25, 0.25)$, $B \equiv (0.148, -0.148, 0.148)$, $C \equiv (0.078, -0.217, 0.0)$. The atoms $C$ and $C'$ and the other 10 of the cage equivalent by symmetry are linked by an ethylenic-like bond 1.346 Å long. In the NaC$_{22}$ compound the alkali atom occupy the octahedral site of the \textit{fcc} lattice.
FIG. 2: Band structure around the Fermi level of the pure fcc-C\textsubscript{22} (a) and NaC\textsubscript{22} (b) crystals. The zero of energy is the Fermi level of NaC\textsubscript{22}. The top of the valence bands of the two compounds is aligned. The two lowest conduction bands at the Γ points have t\textsubscript{\alpha} symmetry. The electronic density of state of NaC\textsubscript{22} is also reported (c), as computed by the tetrahedron method with 213 points in the IBZ.

FIG. 3: Displacement pattern of the $E_g(1)$ phonon at 334 cm\textsuperscript{-1} (cfr. Table I).