Superconductivity from doping boron icosahedra.

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We propose a new route to achieve the superconducting state in boron-rich solids, the hole doping of B$_{12}$ icosahedra. For this purpose we consider a prototype metallic phase of B$_{13}$C$_2$. We show that in this compound the boron icosahedral units are mainly responsible for the large phonon frequencies logarithmic average, $\langle 65.8 \rangle \text{meV}$, and the moderate electron-phonon coupling $\lambda = 0.81$. We suggest that this high $T_c$ could be a general feature of hole doped boron icosahedral solids. Moreover our calculated moderate value of $\lambda$ excludes the formation of bipolarons localized on the icosahedral length scale as suggested by previous authors.

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I. INTRODUCTION

Low atomic number elements have been intensively investigated in the attempt of finding electron phonon mediated superconductors with high critical temperatures ($T_c$). Boron rich solids are eminent examples. The high energy phonon frequencies of metallic boron layers in the structure of magnesium diboride \cite{1} are mainly responsible for the 39 K $T_c$. Intercalation of these boron layers with lithium and boron substitution with carbon are currently under study in the quest of even higher $T_c$. Elemental boron becomes metallic (in a non-icosahedral structure) and superconducting at 160 Gpa, with a $T_c$ which increases up to 11.2 K at 250 Gpa. A 23 K $T_c$ has recently been discovered in intermetallic, yttrium palladium boron carbides \cite{5}. High temperature superconductivity has been found in alkali intercalated fullerene (C$_{60}$) and theoretically suggested in other intercalated carbon polyhedrons, C$_{27}$\cite{6}, C$_{28}$\cite{7}, or C$_{38}$\cite{8}. C$_{60}$ is a band insulator under normal conditions but the intercalation with alkali atoms does generate a metallic state and a consequent superconducting state with $T_c$ up to 40K\cite{9}. Superconductivity is mainly sustained by the high frequency intramolecular phonons so that most of the physical properties of alkali doped fullerenes can be understood from the solid C$_{60}$ electronic and phonon structures. In particular it is seen that the small radius of the molecule substantially increases the electron-phonon coupling with respect to the case of the unrolled graphite layer\cite{10}. The study of solids made of light atoms is then interesting since they can satisfy the two important requirements of having large phonon frequencies and fairly high electron-phonon coupling.

In this work we propose a new route to achieve the superconducting state in boron-rich solids, the hole doping of B$_{12}$ icosahedra. For this purpose we consider a prototype metallic phase of B$_{13}$C$_2$ (sec. II) for which we predict a $T_c$ comparable to that of MgB$_2$. We show (sec. III) that in this compound the boron icosahedral units are the main responsible for the predicted large $T_c$. Thus this high $T_c$ is a general feature of hole doped boron icosahedral solids.

II. CRYSTAL STRUCTURE

We consider the hole doping of boron carbide B$_{12}$C$_3$ (or B$_4$C), a wide gap band-insulator. Its crystal structure consists of an arrangement of B$_{11}$C distorted icosahedra
III. CALCULATIONS AND RESULTS

In $B_{13}C_2$ a metallic phase could be achieved either by obtaining clean samples or by applying a small pressure. In DFT, already at room pressure, the ground state is metallic. Therefore we use DFT to study the superconducting properties of the hypothetical metallic state of $B_{13}C_2$. Electronic structure calculations and geometrical optimization are performed using DFT in the local density approximation. We use norm conserving pseudopotentials with a non local part. The wavefunctions are expanded in plane waves using a 40 Ry cut-off. For the electronic structure we sample the Brillouin zone (BZ) using a 4$^3$ Monkhorst-Pack grid (10 $k$-points in the irreducible BZ wedge) and first order Hermite-Gaussian smearing of 0.03 Ry. From geometrical optimization we obtain the values of $a = 9.686$ (a.u.) and $\alpha = 66.05$ (deg.) for the cell parameters of the rhombohedral unit cell, very close to the experimental values ($a = 9.823$ a.u. and $\alpha = 65.62$ deg.).

The DFT band structure of $B_{13}C_2$ is shown in fig. 2 and is in good agreement with ref. 22. It displays a metallic behaviour. The Fermi level is close to the top of the valence band and it is crossed by several bands. We calculated the electronic density of states (see fig. 3) of $B_{13}C_2$, using a mesh of $N_k = 14^3$ inequivalent $k$-points. The mesh is generated by taking the mesh centered at the $\Gamma$ point and shifting it by a random vector. The density of states at the Fermi level is $N(N) = 3.6$ states/eV/unit cell. We decompose the $N(N)$ in icosahedral and chain density of states, by projecting the $ab$ initio $B_{13}C_2$ wavefunction on the basis formed by the respective atomic pseudo-wavefunction (Lowdin population). At the Fermi level the icosahedral states are responsible for 88% of the total density of states ($N_{ico}(0) = 3.2$). In particular the boron atoms in the polar sites have the largest contribution to $N_{ico}(0)$, namely $N_{polar}(0) = 2.3$ and the contribution due to the equatorial sites is smaller, $N_{eq}(0) = 0.9$. Thus, most of the electrons involved in conduction processes resides in icosahedral states and only a small part in chain states, ($N_{chain}(0) = 0.4$).

We compute the harmonic phonon frequencies $\omega_{q,\nu}$ using Density Functional Perturbation Theory in the linear response. We use a $N = 4^3$ Monkhorst-Pack $q$-points mesh, $q$ being the phonon wavevector. The total phonon density of states, $F(\omega)$, together with the phonon density of states restricted to the icosahedral and chain phonon modes are shown in fig. 4. The large number of peaks in $F(\omega)$ is determined by the large number of phonon modes present in the system.

The icosahedral phonon modes are responsible for most of the weight between 0 and 140 meV. The vibrations of the atoms in the chain explain the high energy feature at 193 meV (both B and C vibrations) and part of the feature at 129 meV (C vibrations). The structures in the chain restricted $F(\omega)$ between 25 and 55 meV are mainly due to B vibrations, while the remaining weight between...
60 and 106 meV is due to C vibrations.

The electron-phonon interaction for a phonon mode $\nu$ with momentum $q$ can be written as:

$$\lambda_{q\nu} = \frac{4}{\omega_{q\nu} N(0)} \sum_{k,n,m} |g_{k,n,k+q,m}^\nu|^2 \delta(\varepsilon_{kn}) \delta(\varepsilon_{k+q,m})$$

where the sum is carried out over the BZ, and $\varepsilon_{kn}$ are the energy bands measured with respect to the Fermi level at point $k$. The matrix element is $g_{k,n,k+q,m}^\nu = \langle kn|\delta V/\delta u_q|^k+q,m\rangle/\sqrt{2\omega_{q\nu}}$, where $u_q$ is the amplitude of the displacement of the phonon $\nu$ of wavevector $q$, $V$ is the Kohn-Sham potential and $N(0) = 3.6$ states/eV/unit cell is the electronic DOS at the Fermi level. The electron-phonon coupling $\lambda$ is then calculated as an average over the $N$ $q$-points mesh and over all the modes, $\lambda = \sum_{q\nu} \lambda_{q\nu}/N = 0.81$.

The modes responsible for superconductivity can be identified from the Eliashberg function $\alpha^2 F(\omega)$

$$\alpha^2 F(\omega) = \frac{1}{2N} \sum_{q\nu} \lambda_{q\nu} \omega_{q\nu} \delta(\omega - \omega_{q\nu})$$

The Eliashberg function is depicted in fig. 5. Most of the contribution to $\lambda$ comes from the region from 60 to 105 meV, mainly related to the icosahedral phonon modes.

The critical superconducting temperature is estimated from the calculated phonon frequencies and electron-phonon coupling using the McMillan formula:

$$T_c = \frac{\langle\omega\rangle}{1.2} \exp\left(\frac{1}{1.04(1+\lambda) - \mu^*(1 + 0.62\lambda)}\right)$$

where $\mu^*$ is the screened Coulomb pseudopotential which takes into account the Coulomb repulsion between the electrons dressed by retardation effects due to the phonons and $\langle\omega\rangle = 65.8$ meV is the phonon frequencies logarithmic average. The calculated values of $T_c$ for $\text{B}_13\text{C}_2$ as a function of $\mu^*$ are illustrated in table I. The critical temperature for metallic $\text{B}_13\text{C}_2$ is comparable to the one obtained for MgB$_2$ and, using the McMillan formula, ranges between 15.8 K and 36.7 K.

Our calculation of the electron-phonon coupling gives also new insight on the possible occurrence of a bipolaronic insulating state in $\text{B}_13\text{C}_2$, as suggested by other authors. In icosahedral boron compounds the bipolaron could be localized on two length scales: the icosahedron length scale or a smaller one, of the order of the bond length. If the bipolaron were localized on the icosahedron length scale (as most of the bipolaronic literature seems to suggest) the bipolaronic distortion could
be seen as a small perturbation to the metallic state. In this case the bipolaron could be described within a model considering a linear electron-phonon coupling perturbation to the harmonic Hamiltonian in the metallic phase. Such a model is the one used in the present paper to study the superconducting properties. Our calculated value of $\lambda$ is too small to justify a bipolaronic insulating state for $\text{B}_{13}\text{C}_2$. On the contrary our calculation cannot exclude the occurrence of a bipolaron localized on the bond-length scale. In this scenario the bipolaron would involve a substantial deformation of our crystal structure (e.g. the breaking or formation of chemical bonds). Such a strong deformation could not be seen as a weak perturbation to the harmonic Hamiltonian in the metallic state and could not be described by the approach used in the present paper.

### IV. CONCLUSIONS

In this work we have studied the possible occurrence of superconductivity from hole doping boron icosahedra. We found the possibility of having high superconducting critical temperatures in these systems. As a possible physical realization of a metallic state we have considered $\text{B}_{13}\text{C}_2$, which is formed from $\text{B}_{12}$ icosahedral units with one hole per icosahedra. Using ab-initio calculations we have determined its normal state properties, finding a moderate electron-phonon coupling and a large phonon logarithmic average to the phonon frequencies. We have demonstrated that both properties are connected to the $\text{B}_{12}$ building blocks. Indeed the local density of state at the Fermi level and the phonon modes strongly coupled with electrons are localized on the icosahedra. As a consequence our findings are not restricted to $\text{B}_{13}\text{C}_2$ compounds but can be applied to other metallic compounds composed by B rich icosahedra. For example another possibility to achieve a metallic state is the substitution of $\text{P}$ with $\text{Si}$ in $\text{B}_{12}\text{P}_2$ or of $\text{As}$ with $\text{Si}$ in $\text{B}_{12}\text{As}_2$. $\text{B}_{12}\text{P}_2$ and $\text{B}_{12}\text{As}_2$ are band insulators composed by $\text{B}_{12}$ icosahedra and 2-atom $\text{P}_2$ or $\text{As}_2$ chains. The substitution of pentavalent atoms like $\text{As}$ and $\text{P}$ with a tetravalent $\text{Si}$ introduces a hole in the system. $\text{B}_{12}\text{P}_2-x\text{Si}_x$ wafer resistivity measurements show a low electrical conductivity. If such conduction were related to bipolaron formation then a metallic state could be achieved applying pressure. An advantage of the 2-atom chain systems ($\text{B}_{12}\text{P}_2-x\text{Si}_x$ or $\text{B}_{12}\text{As}_2-x\text{Si}_x$) respect to the 3-atom chain systems ($\text{B}_{13}\text{C}_2$) is the lack in the formers of an internal soft degree of freedom, the chain bending. Probably this feature makes the 2-atom chain structures more stable under pressure.

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| Material | $\mu^*$ | $\langle \omega \rangle$ (meV) | $\lambda$ | $T_c$ (K) |
|----------|--------|-------------------------------|---------|---------|
| $\text{B}_{13}\text{C}_2$ | 0.1   | 65.8                          | 0.81    | 36.7    |
|          | 0.14  | 65.8                          | 0.81    | 27.6    |
|          | 0.2   | 65.8                          | 0.81    | 15.8    |
| $\text{MgB}_2$ | 0.14  | 62.0                          | 0.87    | 30.7    |

TABLE I: Critical temperatures of $\text{B}_{13}\text{C}_2$ and $\text{MgB}_2$. Predicted critical temperatures as a function of the screened Coulomb pseudopotential ($\mu^*$). The critical temperature is estimated using the McMillan formula (eq. 3). The results are compared with $\text{MgB}_2$ (from ref. 3).
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