

Superconductivity in Hole-Doped Diamond

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Diamond is usually considered the prototype of band insulators: it came as a big surprise, therefore, when it was shown that, under extremely high boron doping (*i.e.* 3 %), diamond undergoes a superconducting transition with a critical temperature of 4 K [1]. After the initial report in polycrystalline samples, the result has also been confirmed in thin films, with T_c 's as high as 11 K. Besides creating an obvious technological interest, as diamond is a promising material for application in electronics, these findings posed fundamental questions concerning the superconducting mechanism and the possibility of observing superconductivity in other doped semiconductors. Our investigations based on first-principles electronic structure calculations suggest that the observed superconductivity in hole-doped diamond is due to an electron-phonon mechanism. We assume that at these doping concentrations, which are one order of magnitude larger than those at which an insulator-metal transition takes place, B-doped diamond can be described as a degenerate metal. A similar point of view has been adopted in several other subsequent works [2], while in Ref. [3] a purely electronic mechanism valid for impurity bands was proposed. Our results not only show that electron-phonon is a very likely explanation for the observed superconductivity, but also allow us to discover an unexpected similarity between hole-doped diamond and the record electron-phonon superconductor MgB₂.

We have performed first-principles calculations of the electronic and phononic properties of hole-doped diamond and other tetrahedral group-IV semiconductors, silicon and germanium, using Savrasov Linear Response LMTO program. In the following we shall focus mainly on diamond, but, unless differently stated, the arguments and results apply to all the tetrahedral semiconductors studied. To model the effect of doping we used the Virtual Crystal Approximation (VCA): we approximated the real lattice, in which a fraction x of Carbon atoms is randomly replaced by Boron atoms, with a regular lattice of *virtual atoms* with a non-integer number of protons (Z_{virt}), which is a weighted average of those of Carbon and Boron: $Z_{\text{virt}} = (1-x)Z_C + xZ_B$. This allowed us to evaluate the physical properties of hole-doped diamond, silicon and germanium for different doping, up to $x = 0.1$.

Even at $x = 0.1$, the band structure of hole-doped diamond, shown as solid blue lines in Fig. 1, is still almost identical to that of the pure material: the 4 sp^3 hybrids on each C atom form 4 bonding (valence) and 4 anti-bonding (conduction) bands, separated by a large gap. The exceptional hardness of diamond derives from the

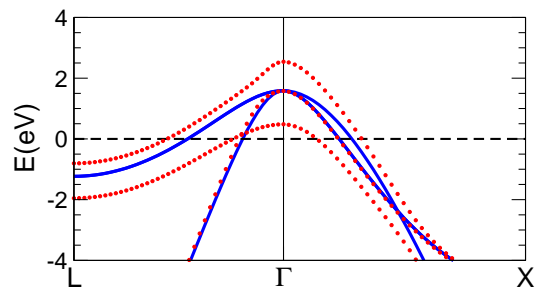


FIG. 1: The band structure of hole-doped diamond in the VCA approximation (*blue solid line*) is almost identical to that of the pure material, even at $x = 0.1$; however, boron doping drives holes into the valence band, which couple strongly to the bond-stretching phonon at $q \simeq 0$. The red dotted line shows the effect of a frozen optical zone-center phonon on the band structure.

fact that the only states which are full are all of σ bonding character, and these form bonds which are among the strongest in nature.

With boron doping, electrons are removed from the crystal and holes form at the top of the triply-degenerate valence band: diamond becomes metallic, with the holes forming three distorted spherical Fermi surfaces around the center of the Brillouin zone. The average radius of the spheroids grows with doping as $k_F \simeq (x/3)^{1/3}k_{BZ}$; the Density of States (DOS) has a typical $3d$ behaviour, and its value at the Fermi level, $N(\varepsilon_F)$, grows as $x^{2/3}$. **This picture has recently been confirmed by the ARPES measurements of B-doped diamond films by Yokoya *et al.*[1], who have shown that around E_F the band structure of B-doped diamond is very similar to that of the pure material, with E_F moving to lower energies with doping.**

The effect of doping on the phonon spectrum is shown in Fig.2: there is a sizeable reduction (softening) of the frequency of the zone-center optical phonon; as x is increased, the softening increases and extends to a larger region in \mathbf{q} -space. This effect can easily be understood in terms of the standard electron-phonon theory: in metals, the interaction of conduction electrons with a phonon causes a reduction of its frequency, which grows with the strength of the interaction; also, the theory shows that only phonons with $q < 2k_F$ are allowed to couple. Fig. 2 thus shows that in this system only the optical mode is coupled, with a strength increasing with doping. A simple physical argument explains why in this material electrons couple strongly to some lattice vibrations: the

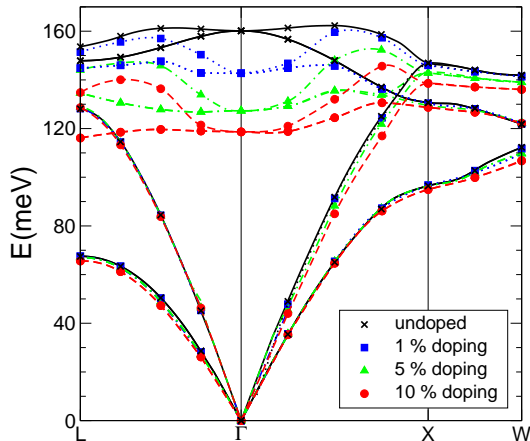


FIG. 2: Phonon dispersion of pure and hole-doped diamond for different values of boron concentration x : we observe a pronounced softening of the frequency of the zone-center optical phonon with respect to the pure case, which increases as a function of x .

optical phonon, which at the zone-center has the same symmetry as the electronic states at the top of the valence band, is a bond-stretching mode which distorts the stiff σ bonds. In fact, when the ions are moved along the eigenvector of the Γ optical mode, the triple degeneracy of the top of the σ band at the Γ point is removed, with one band moving to lower and one to higher energies, the third band being fixed (dotted red lines in Fig. 1 correspond to a frozen distortion of reduced amplitude $u = 0.05\text{\AA}$). As discussed by Cardona [2], this mechanism is also responsible for the zero-point renormalization of the optical gap in pure semiconductors. The same, strong coupling between bond-stretching phonons and holes at the top of doubly-degenerate σ bonding bands is at the basis of the exceptional superconducting properties of Magnesium Diboride. Hole-doped diamond is, after five years of intense theoretical and experimental research in the field of MgB_2 , the first example of an existing material which is similar to MgB_2 that the theoretical knowledge derived there can be applied and tested.

In MgB_2 a surprisingly close estimate of the total electron-phonon coupling λ , is given by the Hopfield formula, which is exact for parabolic bands with $k_F \ll k_{BZ}$:

$$\lambda = \frac{N(\varepsilon_F)D^2}{M\omega^2}, \quad (1)$$

where $N(\varepsilon_F)$ is the density of σ states at the Fermi level, M is the reduced mass of the optical bond-stretching phonon, and Du is the energy splitting of the doubly-degenerate top of the σ band produced by the displacement $\mathbf{e}u$ of the same bond-stretching phonon, with normalized eigenvector \mathbf{e} . There is a feedback effect between λ and the phonon frequency, since ω is renormalized with respect to its *bare* value ω_0 by the interaction with electrons: $\omega^2 = \omega_0^2/(1 + 2\lambda)$.

Once ω and λ are known, the critical temperature can be evaluated using the formula:

$$T_c = \omega \exp\left(\frac{-1}{\frac{\lambda}{1+\lambda} - \mu^*}\right) \quad (2)$$

These results can be generalized to diamond, with a few differences due to dimensionality. MgB_2 is in fact a layered material very similar to graphite, the 2D form of carbon, which unlike diamond is based on sp^2 bonding. Instead of four σ bands, there are three σ and one π band; the top of the σ band, which contains the superconducting holes, is doubly degenerate, with the same symmetry as the bond-stretching phonon mode. In MgB_2 all the σ electrons couple to each of the degenerate phonon vibrations, whereas in diamond only 2 bands out of 3 are coupled to each degenerate phonon vibration. Therefore, the formula for the renormalization of the phonon frequencies in diamond reads: $\omega^2 = \omega_0^2/(1 + 2(\frac{2}{3})\lambda)$.

	$N(\varepsilon_F)$	D	ω	λ_0	λ	λ_{num}
MgB_2	0.15	12.4	536	0.33	1.01	1.02
C	0.00	21.6	1292	0	0	0
3%C	0.07	21.1	1077	0.21	0.30	0.30
5%C	0.08	20.8	1027	0.25	0.37	0.36
10%C	0.11	20.4	957	0.32	0.57	0.56
Si	0.00	6.8	510	0	0	0
5%Si	0.17	6.3	453	0.13	0.16	0.30
10%Si	0.24	6.1	438	0.17	0.22	0.40
Ge	0.00	5.8	317	0	0	0
10%Ge	0.20	4.4	282	0.08	0.09	0.32

TABLE I:

Values of the parameters which determine the total electron-phonon coupling λ according to the Hopfield formula (1). $N(\varepsilon_F)$ is in states/eV/spin/f.u., D is in eV/ \AA and ω in cm^{-1} . The total electron-phonon coupling obtained by the numerical integration of the full Eliashberg function (λ_{num}) is also reported.

Eq.1 shows that the total electron-phonon coupling is determined by material-dependent parameters, such as the density of states at the Fermi level and the deformation potential, and to a large extent by the phonon softening, which in turn is dominated by dimensionality. To discriminate between these two effects, it is useful to introduce a bare electron-phonon coupling $\lambda_0 = N(\varepsilon_F)D^2/M\omega_0^2$, which only contains material-dependent parameters: while D is a measure of the geometrical distortion of the electronic bands due to phonons, ω_0 measures the hardness of the material. The total electron-phonon coupling is then $\lambda = \frac{\lambda_0}{1 - 2\alpha\lambda_0}$, with $\alpha = 1$ in 2D and $2/3$ in 3D. Tab. I contains the values entering the definition of λ according to Eq.1 for MgB_2 , diamond, Si and Ge and the relative λ_0 . It can be noticed that, even if

at $x = 0.1$ due to the compensating effect of a larger deformation potential and phonon frequency, diamond has the same λ_0 as MgB_2 , its effective electron-phonon coupling is much lower (0.6 instead of 1.0); this reduction is completely due to dimensionality effects, represented by the factor α . The value of λ in diamond grows sensibly with doping, following the increase of $N(\varepsilon_F)$.

In the same table, the value of λ obtained by the numerical integration of the total Eliashberg function $\alpha^2 F(\omega)$, evaluated on a very fine $(1/12)^3$ grid in \mathbf{q} -space is also reported (λ_{num}). In diamond, the agreement between the approximate Hopfield formula and the numerical result, which takes into account the full complexity of the electronic and vibrational spectrum, is striking. In fact, the shape of the Eliashberg function indicates that the electron-phonon coupling is actually concentrated in the bond-stretching phonon branch.

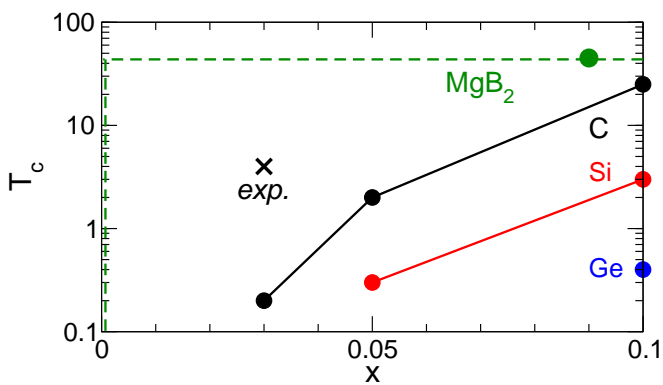


FIG. 3: Critical temperature T_c (Eq.1) as a function of x for hole-doped diamond, Si and Germanium, in comparison to MgB_2 .

As far as the other tetrahedral semiconductors are concerned, their bare and total electron-phonon coupling parameters are always lower than the corresponding ones of diamond, mainly because the deformation potentials are lower. Furthermore, in this case the agreement between the Hopfield formula and the numerical estimate of λ is less good, as the Eliashberg function shows that other phonon branches are involved in the coupling.

Finally, Fig.3 shows the critical temperatures for hole-doped diamond, silicon and germanium given by formula 2; given the approximations in the formula for T_c and in the determination of doping, the results for diamond are in reasonable agreement with the experiment, indicating that electron-phonon coupling is a likely mechanism for the superconductivity in this system. Our results show that, unless very high doping levels can be obtained, it is very unlikely to observe superconductivity in Si or Ge.

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