Normal and superconducting state properties of B-doped diamond from first-principles

Lilia Boeri\textsuperscript{a,}\textsuperscript{*}, Jens Kortus\textsuperscript{b}, Ole Krogh Andersen\textsuperscript{a}

\textsuperscript{a}Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany
\textsuperscript{b}Institut für Theoretische Physik, TU Bergakademie Freiberg, Leipziger Str. 23, D-09599 Freiberg, Germany

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Abstract

In this paper we give a theoretical description of the superconducting and normal-state properties of hole-doped diamond based on ab initio calculations. Our aim is to provide a useful reference to compare the theoretical predictions with the experimental data. We also discuss the advantages and drawbacks of the virtual crystal approximation (VCA), which we adopted to model the boron doping, comparing our results with supercell calculations.

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1. Introduction

The unexpected discovery of superconductivity with a critical temperature $T_c$ of 4 K in heavily boron-doped diamond \cite{1}, about one year ago, has raised considerable interest. The bulk superconductivity initially observed in polycrystalline samples \cite{1,2} has been reproduced by other groups \cite{3} and $T_c$'s as high as 11 K have been reported in CVD films \cite{4}.

Soon after the report of superconductivity, two main superconducting mechanisms were proposed: a purely electronic one \cite{5,6} and a conventional electron–phonon one \cite{7–12}. While the resonant valence bond mechanism of Refs. \cite{5,6} assumes that the superconducting carriers are contained in an isolated, narrow boron impurity band, the electron–phonon mechanism relies on the assumption that the boron concentrations at which superconductivity takes place are high enough that the boron-derived states overlap with the valence band of diamond, forming a degenerate metallic band which couples to phonons.

In this work we assume that superconductivity in boron-doped diamond is mediated by phonons, and apply the conventional Migdal–Eliashberg (ME) theory for electron–phonon superconductors to evaluate normal and superconducting state properties of this material, using as input the Eliashberg spectral functions calculated from first-principles \cite{7,13}.

The combination of ab initio calculations and ME theory has been successfully applied in the past to a number of elemental superconductors and simple alloys \cite{14}, and recently it has permitted to unravel the reasons for the extraordinary superconducting properties of MgB$_2$ \cite{15–19}.

However, the description of the electron–phonon interaction from first-principles in B-doped diamond is more complicated than in these materials, since an approximation has to be chosen to model the effect of the boron atoms, which have a low concentration and are randomly distributed.

The two approaches adopted so far, the Supercell (SC) and virtual crystal approximation (VCA), both have advantages and drawbacks: the SC approximation is in principle more accurate, as it permits to capture the local nature of the boron impurity states, both in the electronic and in the vibrational properties, but it completely neglects...
the effect of disorder, which is certainly present in the sample and is described in an average way using the VCA. The coherent potential approximation (CPA) adopted in Ref. [20] permits to describe accurately both disorder and local effects, however, so far the authors of [20] described only electronic properties and not phonons.

While the band structure and Fermi surfaces predicted by the three above methods are in good agreement, there is a quantitative discrepancy in the phonon spectra and electron-phonon coupling. All data indicate that the electron-phonon coupling strength grows with doping, with SC calculations giving larger values than the VCA, apart from Ref. [8]. The values of $\lambda$, ranging from 0.2 to 0.56, are sufficiently high to yield the experimental $T_c$, using standard McMillan expressions. The increasing coupling strength with increasing doping matches the experimental observation [3,4] sufficiently well.

The results presented here are based on VCA calculations [7,13]: in the first section we give an overview of the electronic and vibrational properties of hole-doped diamond in this approximation, in the second section we solve ME equations and in the last section we compare our results with the experimental data and other first-principles calculations, discussing the limits of our approximation.

### 2. First-principles calculations

The results presented here were obtained using Savrasov’s linear response full-potential LMTO [21] program [14]. Very similar results were independently obtained by Lee and Pickett [8], using frozen-phonon calculations with the LAPW method and later by Ma et al. [12] using pseudopotentials. The latter work also extends the linear-response treatment to high pressure and electron doping.

To describe the effect of doping we employed the VCA: the real lattice, in which a fraction $x$ of carbon atoms is randomly replaced by boron atoms, is approximated with a regular lattice of virtual atoms with a non-integer number of protons ($Z_{\text{virt}}$), which is a weighted average of those of Carbon and Boron:

$$Z_{\text{virt}} = (1-x)Z_C + xZ_B.$$  

Since the sites in the crystal are all equivalent to each other, atom-dependent, localized electronic and vibrational states cannot be described in any way.

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, even at $x = 0.1$: the 4 $sp^3$ hybrids on each C atom form 4 bonding (valence) and 4 anti-bonding (conduction) bands, separated by a large gap. 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 [13]. The average radius of the spheroids grows with doping as $k_F = (x/3)^{1/3}k_{\text{BZ}}$: the density of states (DOS) has a typical 3D behavior, and its value at the Fermi level, $N(0)$, grows as $x^{2/3}$. The effect of doping on the phonon spectrum is shown in the left panel of Fig. 2: there is a sizeable reduction (softening) of the frequency of the zone-center optical phonon, while the rest of the spectrum is unchanged. In the figure we only show the results for $x = 0$ and 0.03, but as $x$ is increased the qualitative behavior remains unchanged, and the softening increases and extends to a larger region in 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. The left panel of Fig. 2 thus shows that in this system only the optical phonon is coupled.

On the right panel of the same figure, we show as dashed lines the Eliashberg spectral function $x^2F(\omega)$, which is a weighted density of phonon states $\omega_q$, where the weights are given by the so-called phonon linewidths $\gamma_q$,

$$x^2F(\omega) = \frac{1}{2\pi N(0)} \sum_{q,\omega} \frac{\gamma_q}{\omega_q} \delta(\omega - \omega_q)$$  

and

$$\gamma_q = \frac{1}{2\pi N(0)} \sum_{k,\omega} |g^q_{k\omega}|^2 \delta(\omega_k) \delta(\omega_{k+q}).$$  

The total electron-phonon coupling constant $\lambda$ can then be obtained as

$$\lambda = 2 \int \frac{x^2F(\omega)}{\omega} \, d\omega.$$  

At variance with other elemental superconductors, in which $x^2F(\omega)$ basically follows the phonon DOS $F(\omega)$, here there is a single peak centered around the value of the renormalized zone-center frequency. In the figure we show the results for a 3% hole concentration: similar behavior is
observed at higher dopings, with the peak moving to lower frequencies due to the larger phonon softening [7]. This picture confirms the idea that in hole-doped diamond the coupling is concentrated in optical bond-stretching phonons.

A simple physical argument explains why diamond, which is an insulator, acquires a large electron–phonon coupling when doped with holes: the 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 atoms are moved along the eigenvector of the $\Gamma$ optical mode, the triple degeneracy of the top of the σ band 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 distortion of reduced amplitude $u = 0.05$ Å). Both Refs. [7,8] have pointed out that the same kind of coupling, involving bond-stretching phonon modes and holes at the top of σ bands, is the origin of superconductivity in the record electron–phonon superconductor MgB$_2$ [15]. The comparison between the two materials, and their implications on superconductivity, are extensively discussed in these two works, and we refer the reader to them for further details.

In the above papers the authors also derived simple analytical expressions to estimate the total electron–phonon coupling and hence critical temperature of hole-doped diamond from frozen-phonon calculations like those depicted in Fig. 1.

In the next section, we will instead use the full information contained in the electron–phonon spectral function to solve the ME equations.

3. Superconducting and normal-state properties

The derivation of ME equations from a Hamiltonian of electrons interacting with phonons can be found in several textbooks, [22] with different degrees of approximation. In the end, one obtains a set of coupled equations for the superconducting gap $\Delta$ and the electronic renormalization function $Z$, which, apart from very simple cases, have to be solved numerically.

In the case of hole-doped diamond, we can use the following expressions, which assume that the electronic bandwidth is large compared to phonon frequency and that the coupling is isotropic.

$$\Delta_n Z_n^S = \pi T \sum_m (\lambda(n-m) - \mu^*) \frac{\Delta_m}{\sqrt{\omega_m^2 + \Delta_m^2}},$$

$$Z_n^S = 1 + \pi T \sum_m \frac{\lambda(n-m)}{\omega_n} \frac{\omega_m}{\sqrt{\omega_m^2 + \Delta_m^2}},$$

$$\lambda(\nu) = 2 \int_0^{\infty} \frac{\nu^2 F(\Omega)}{\Omega^2 + \omega_0^2} d\Omega,$$

where $\Delta_n = \Delta(i\omega_n)$ and $Z_n = Z(i\omega_n)$ are the band gap and electronic renormalization function at Matsubara frequencies $(\omega_n = (2n + 1)\pi T)$. These equations hold both in the superconducting and in the normal state, where $\Delta_n = 0$.

At variance with the other variables, which can be calculated from first-principles, $\mu^*$ is an empirical parameter that can be adjusted to reproduce the experimental $T_c$ [23,24]. Typical values for $\mu^*$ for normal metals are in the range $0.1–0.2$. 

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**Fig. 2.** Left panel: Calculated dispersions of pure (grey) and 3% hole-doped (black) diamond. The two spectra coincide, apart from the optical frequencies close to zone-center, which are strongly renormalized in hole-doped diamond. Right panel: Phonon DOS ($F(\omega)$) and Eliashberg spectral function ($\nu^2 F(\omega)$) of 3% hole-doped diamond: in contrast to other elemental superconductors, in which the Eliashberg function follows the phonon DOS, in hole-doped diamond it displays a single peak centered around the renormalized zone-center frequency, indicating that the electron–phonon coupling is concentrated in this branch.
The knowledge of $\Delta$ and $Z$ at different temperatures also permits to evaluate the contribution to the free energy of the system due to the electron–phonon interaction $\Omega_{e-p}$. As shown by Golubov et al. [25], this is given by:

$$\Omega_{e-p} = -2\pi N(0) T \sum_n \frac{\omega_n^2 (Z_n^2 - 1) + \phi_n^2}{|\omega_n| + \sqrt{\omega_n^2 Z_n^2 + \phi_n^2}} + \pi N(0) T \sum_n \frac{\omega_n^2 Z_n (Z_n - 1) + \phi_n^2}{\sqrt{\omega_n^2 Z_n^2 + \phi_n^2}}, \quad (6)$$

where $N(0)$ is the electronic DOS at the Fermi level, and we set $\phi_n = A_n Z_n$.

In particular, one obtains that the difference between the free energies in the normal (N) and superconducting (S) states is given by [25]:

$$\Delta\Omega_{N-S} = -2\pi N(0) T \sum_{n=\delta_n}^{\omega_n} \frac{|\omega_n|(Z_n^2 - 1)}{|\omega_n| + \sqrt{\omega_n^2 Z_n^2 + \phi_n^2}} - \frac{2\omega_n^2 (Z_n^2 - 1) + 2\phi_n^2}{|\omega_n| + \sqrt{\omega_n^2 Z_n^2 + \phi_n^2}} + \frac{\omega_n^2 Z_n (Z_n - 1) + \phi_n^2}{\sqrt{\omega_n^2 Z_n^2 + \phi_n^2}}, \quad (7)$$

The first and second derivative of $\Delta\Omega$ with respect to $T$ give the difference between the entropies of the normal and superconducting state and the jump in the specific heat at $T = T_c$, $\Delta\mathcal{C}_p$, which can directly be compared with experiment

$$\Delta\mathcal{C}(T) = \frac{1}{2} T d^2 \Delta\Omega(T)/dT^2. \quad (8)$$

We solved Eqs. (5) and (7) numerically using the Eliashberg functions for $x = 0.03, 0.05$ and $0.10$ and for each temperature $T$ we extracted the value of the gap at zero frequency $\Delta(T)$; the critical temperature $T_c$ was then defined as the temperature for which $\Delta(T) = 0$. The same procedure was repeated for different values of $\mu^*$ in the interval $0 - 0.1$: we found that the experimental $T_c$ of 4 K at 3% doping could be reproduced with $\mu^* = 0.065$.

All the results shown in Fig. 3 were obtained with this value, but the qualitative behaviour of the physical properties did not change for $\mu^*$ in the above interval. In the upper panel of Fig. 3 we show the behaviour of the gap as a function of temperature: in the left plot, we see that for each $x$, decreasing $T$ the gap converges to a value which is very close to the BCS one: $\Delta(0) = 1.767 T_c$.

In the right part of the figure we plot for different concentrations, the $\Delta$ and $T$ values rescaled by the corresponding $\Delta(0)$ and $T_c$: All the data fall on the same curve, as prescribed by BCS theory. Close to $T_c$, we have in fact: $\Delta(T)/\Delta(0) \simeq 1.74(1 - T/T_c)$.

Fig. 3. Superconducting and normal-state properties of hole-doped diamond obtained by the numerical solution of Migdal–Eliashberg equations with $\mu^* = 0.065$ (see text). Upper panel: Calculated superconducting gap $\Delta(0)$ as a function of temperatures for different boron concentrations (left); all the curves fall onto the universal BCS curve (right). Lower panel: Calculated difference between the superconducting and normal state free energy in 10% hole-doped diamond, fitted with a quadratic scaling law close (Eq. (9)) to $T_c$ (left). When the free energy and the temperature are rescaled with respect to $\delta_0$ and $T_c$, respectively, all the data fall onto a universal curve (right).
In the lower part of the same figure, we show the results for the free energy, from which we extracted the specific heat jump reported in Table 1. On the left side we show an example of the difference between the free energies of the normal and superconducting state as a function of temperature (Eq. (7)), corresponding to $x = 0.1$ (we do not show other $x$ on the same figure because the scale is too different, but the behaviour is the same). In order to extract the value of $\Delta C(T)$ at $T_c$ we did not calculate the numerical derivative of the $\Delta \Omega$ curve due to numerical noise. Instead, as suggested in Refs. [25,26], we obtained it from the coefficient $a_0 = T_c \Delta C(T_c)/2$ from a fit close to $T_c$

$$\Delta \Omega(T \rightarrow T_c) = a_0(1 - T/T_c)^2.$$  

(9)

The quality of the fit is very good and, once $a_0$ is known, it can be used together with $T_c$ to rescale the $\Delta \Omega$ data for different $x$, so that they all fall on the same curve, as shown in the lower right panel of Fig. 3.

In Table 1, we report the calculated values for $T_c$, $\Delta(0)$, normal state electronic specific heat coefficient ($\gamma_N$) and specific heat jump for different dopings and $\mu^* = 0.065$, together with the predictions of the BCS theory [27]. As we can see, even at $x = 0.1$, the difference between the two sets of values is very small. This is not surprising, since the maximum $\lambda$, for $x = 0.1$, is 0.56: in the VCA approximation, therefore, hole-doped diamond behaves like a standard low-coupling BCS superconductor.

### Table 1

Superconducting and normal state properties of hole-doped diamond, obtained by solving the ME equations (5), (7)

| $x$   | $N(0)^*$ | $\lambda^*$ | $\omega^*$ | $\gamma_N$ | $T_c$ | $\Delta(0)$ | $\Delta\mu^*(0)$ | $\Delta C_P$ | $\Delta C_P^B$ |
|-------|----------|-------------|------------|-------------|-------|-------------|-----------------|-------------|----------------|
| 0.03  | 0.07     | 0.3         | 1077       | 0.21        | 4.22  | 7.44        | 7.42            | 1.25        | 1.29           |
| 0.05  | 0.08     | 0.36        | 1027       | 0.26        | 11.96 | 21.16       | 21.05           | 4.40        | 4.40           |
| 0.10  | 0.11     | 0.56        | 957        | 0.40        | 36.56 | 65.9        | 64.35           | 22.01       | 21.12          |

$N(0)$ is in states/eV/atom, $\omega$ in cm$^{-1}$, $\gamma_N$ is in mJ/mol K$^2$, $T_c$ and $\Delta(0)$ are in K. $\Delta C_P$ is the specific heat jump at $T_c$, in mJ/mol K. Data with an asterisk (*) are from Ref. [7]. The superscript $B$ indicates BCS values obtained according to the formulas in [27].

4. Conclusions and discussion

In this paper we calculated some normal and superconducting state properties of boron-doped diamond, solving Migdal Eliashberg (ME) equations using the VCA spectral function $\pi^2 F(\omega)$ of Ref. [7]. Our results predict that diamond behaves like a standard BCS (low-coupling) superconductor, which seems to be confirmed by experiments. However, the experimental situation is still not clear enough to draw a final conclusion. For example, the gap seems to follow the BCS curve [28], but in some samples it displays a different behaviour. Specific heat measurements [2] find an electronic coefficient of the specific heat in the normal state which is in reasonable agreement with our value. In contrast the ratio $\Delta C_P/C_N$ at $T_c$ is 0.5, that is, about one third of the BCS value. As discussed by the authors, some of these effects are probably related to the presence of impurities in the samples [2]; eventually the samples show inhomogeneous doping which would further complicate an accurate estimate. If this deviation from the BCS behaviour was confirmed, one would have to search for effects which go beyond the standard BCS theory. While strong electron–phonon coupling may explain a larger jump, one would need multiband effects to explain a smaller jump. Further experiments on specific heat appear thus to be very interesting.

In summary, the VCA assumes that in boron-doped diamond there are mobile holes at the top of the valence band which are responsible for the coupling. These holes couple strongly to bond-stretching optical phonons, which get renormalized by the interaction close to the zone-center. This strong coupling between vibrational and electronic states, represented by a large deformation potential, is already present, but dormant, in pure diamond and it is "switched on" as holes are doped into the system. As discussed in Ref. [11], this is the same mechanism that causes the renormalization of the optical gaps of tetrahedral semiconductors via zero-point motion.

Our picture of the electronic structure, already supported by more accurate SC [9,10] and CPA calculations [20], received direct experimental confirmation from ARPES measurements in Ref. [29].

Also the softening of the optical phonon frequencies close to zone-center, predicted by our calculations, has been measured by inelastic X-ray scattering [30]. However, in this case the quantitative agreement of our data with the experiment and other first-principles calculations which employ SCs is less good. In fact, Refs. [9,10] obtained values of $\lambda$ which are larger than ours, and this indicates that the VCA underestimates the electron–phonon coupling strength. This is not surprising, since in their case, besides the optical phonons, which get softened, also some localized boron modes play a role in the superconducting coupling.

Nevertheless, the VCA correctly predicts the main features of electron–phonon coupling in boron-doped diamond, such as the softening of the phonon frequency and the increase of $T_c$ with doping and it offers a very simple and visual explanation for superconductivity in this material. An interesting consequence of our analysis is that it indicates a useful, new path in the search for higher-temperature superconductors by hole doping materials with strong covalent bonds.
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Further readings

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