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Superconductivity in doped clathrates, diamond and silicon

Supraconductivité dans des clathrates dopés, du diamant et du silicium

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ABSTRACT

We review in the present article recent work pertaining to the superconducting transition in boron-doped silicon and diamond in their well-known ambient pressure and temperature cubic diamond structure. Thanks to recent developments in chemical vapor deposition techniques, high-temperature–high-pressure experiments, or laser assisted non-equilibrium doping approaches, it is indeed now possible to dope these standard semiconductors and insulators up to the few percent range, that is way beyond the impurity solubility limit and the insulator–metal transition doping threshold. We discuss in particular the microscopic origin of the superconducting transition, emphasizing the role of first-principles calculations in directing the interpretation to a phonon-mediated scenario for these degenerate compounds with no impurity band. A large variety of ab initio calculations predict superconducting transition temperatures larger than that of MgB_2 if diamond doping can be increased up to about 30%. The case of intercalated semiconducting clathrates is discussed, not only as a precursor to the superconductivity in silicon, but also as a prototype system offering directions to significantly increase T_C in doped diamond and silicon.

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R É S U M É

Nous présentons dans cet article une analyse de la transition supraconductrice induite par dopage au bore du diamant et du silicium dans leur phase cristallographique usuelle aux conditions ambiantes. Grâce aux progrès réalisés dans les techniques de croissance par dépôt en phase vapeur et les techniques de synthèse par les voies hautes températures-hautes pressions, ou encore les approches « hors d'équilibre » assistées par laser, il est aujourd'hui possible de doper ces phases denses bien au delà non seulement de la limite de solubilité pour l'impureté choisie, mais également au delà du seuil de transition isolant–métal. Nous discutons du mécanisme microscopique à l'origine de cette transition sur la base en particulier de simulations ab initio mettant en relief l'importance du couplage électron–phonon dans ces semiconducteurs dégénérés ne présentant pas de bande d'impureté. De nombreuses prédictions suggèrent des températures de transition supérieures à celle de MgB_2 sous condition que le taux de dopage puisse être augmenté vers les 30%. Nous discuterons également des clathrates de silicium et de carbone, précurseurs dans la famille des semiconducteurs sp^3 de la colonne IV présentant une transition supraconductrice sous dopage, et offrant des perspectives pour l'augmentation de la température critique dans le diamant et le silicium.

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1. Introduction

It may seem surprising to find diamond and silicon sharing a few pages with compounds such as high- T_C cuprates, pnictides, or heavy fermions uranium-based systems, in a book devoted to “exotic superconductivity”. As a matter of fact, it is certainly difficult to find systems less exotic than silicon and diamond which are probably the most common materials in condensed matter physics. Silicon in its standard form (the diamond structure) has been extensively studied by scientists and engineers as the building material for most electronic devices, and diamond is the prototype insulator and hardest material used for e.g. tools’ coating. Nevertheless, silicon and diamond have been recently found to undergo a type-II superconducting transition under p -type boron doping in the few percent range [1,2]. It is certainly the very common nature of such “perfect” semiconductors and insulators that endows them with a flavor of exoticity in the world of the superconducting materials.

The superconductivity in doped, or uncompensated, semiconductors or insulators, is not a novel subject. It has been first discussed in the early 1960s at the theoretical level [3], and rapidly confirmed experimentally in the case of reduced SrTiO₃ crystals [4] and in Ge_{1-x}Te alloys [5]. Further, in the world of superconductivity, diamond can be incorporated in the family of the “covalent metals” [6] to which belong very well-known systems such as the fullerenes [7,8], MgB₂ [9], CaC₆ or YbC₆ [10,11] intercalated graphites, which are all characterized by light elements, strongly covalent C–C or B–B bonds, and an insulating character in the absence of doping or intercalation.

We review in the present article what is known to date about the superconducting nature of doped diamond and silicon. We introduce the field by the case of the silicon clathrates, a low density semiconducting sp^3 silicon network showing a rather large superconducting transition temperature under intercalation doping. We focus mainly on the microscopic mechanisms at the origin of the superconducting transition, as supported both by state-of-the-art ab initio calculations and experimental results. As emphasized below, it is believed that a conventional phonon-mediated BCS picture [12] holds for this family of compounds. In these conditions, standard first-principles calculations, which are known to yield a fair account of both electronic and vibrational modes in such systems, can indeed be of much help in providing a reliable description of which electronic and phonon modes are contributing to the transition, and what is the strength of the effective electron–electron “glueing potential”. Such informations, when used in conjunction with existing theories such as the Eliashberg formalism [13], treating the phonon-mediated electron–electron interaction thanks to many-body perturbation techniques [14], can directly relate to the superconducting transition temperature.

2. Ab initio approaches to phonon-mediated superconductivity

Silicon and diamond are quite well described by the standard “band structure” ab initio theories within modern mean-field approaches such as the density functional theory (DFT). Bond lengths are calculated within a fraction of a percent, vibrational modes within a few percent, and, apart from the “band gap problem”, the dispersion of the valence bands is quite well reproduced. As such, when doping is large enough so that we are beyond the Mott insulator–metal transition (MIT), with the Fermi level entering the valence bands (under p -type doping), that is in the absence of a “flat” impurity band, there is little doubt that mean-field DFT calculations will provide a fair account of the electronic and vibrational modes of the system.

Assuming the validity of Migdal theorem [15] (see conclusion below), the Eliashberg equations [13,14,16,17] offer a straightforward connection between ab initio calculations and the superconducting properties. The knowledge of the electronic and phonon states indeed allows one within perturbation theory to evaluate the effective attractive potential V_{ep} between two electrons within a Cooper pair under the mediation of phonons. With $N(E_F)$ the density of states at the Fermi level, the adimensional coupling constant $\lambda = N(E_F)V_{ep}$ reads:

$$\lambda = N(E_F)V_{ep} = 2N(E_F) \sum_{\mathbf{q},\nu} (|g_{\mathbf{q},\nu}|^2) / \hbar\omega_{\mathbf{q},\nu}$$

$$(|g_{\mathbf{q},\nu}|^2) = \int \frac{d^3k}{\Omega_{BZ}} \sum_{n,n'} |g_{\mathbf{q},\nu}(\mathbf{k}; n, n')|^2 \frac{\partial(\varepsilon_{\mathbf{k}+\mathbf{q},n'})\partial(\varepsilon_{\mathbf{k},n})}{N(E_F)^2}$$

$$g_{\mathbf{q},\nu}(\mathbf{k}; n, n') = \left(\frac{\hbar}{2M\omega_{\mathbf{q},\nu}} \right)^2 \langle \psi_{\mathbf{k},n}^0 | \epsilon_{\mathbf{q},\nu} \cdot \frac{\partial V}{\partial \hat{u}_{\mathbf{q},\nu}} | \psi_{\mathbf{k},n'}^0 \rangle$$

where $(\varepsilon_{\mathbf{k},n}, \psi_{\mathbf{k},n}^0)$ are eigenstates of the (DFT) Hamiltonian (with wavevector \mathbf{k} and band index n), and $\partial V / \partial \hat{u}_{\mathbf{q},\nu}$ is the (normalized) variation of the total potential (ionic, hartree, exchange and correlation) seen by the electrons upon activation of a phonon with wavevector \mathbf{q} . Such a variation is closely related to the so-called deformation potentials that quantify the changes in the band structure upon deformation of the atomic network.

Under a few assumptions on the isotropy of the electron–phonon and electron–electron coupling, the Eliashberg equations reduce to the celebrated McMillan formula [18]:

$$T_C = \frac{\hbar\omega_{log}}{1.2k_B} \exp \left[\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]$$

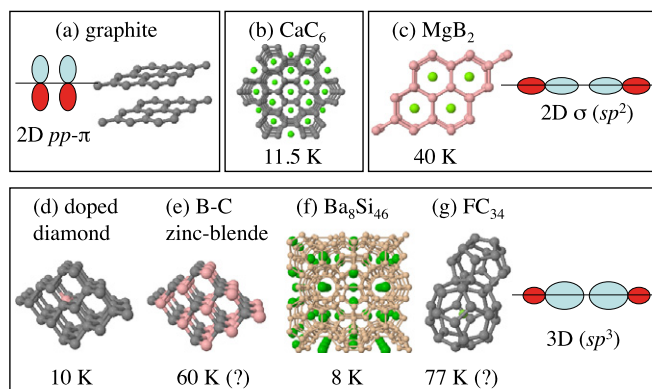


Fig. 1. (Color online) Symbolic representation of a few “covalent metals” with their superconducting transition temperature. Question marks in parentheses indicate theoretical predictions. The nature of the bonding is sketched on the right-hand side of the picture. Adapted from Ref. [24].

which relates T_C to λ and an average phonon frequency ω_{log} , both calculated ab initio (no adjustable parameter), plus the “screened and retarded” Coulomb repulsion parameter μ^* that counterbalances the effect of λ . The simplification of the microscopic Eliashberg equations into the McMillan formula is not mandatory (see [19] in the case of MgB_2) and other formulas have been used in the case e.g. of diamond exhibiting a single coupling phonon mode (an Einstein-like model) [20,21]. However, such variations are rather marginal in the present case of doped diamond or silicon and the main difficulty in the field lies in the value of μ^* which is usually used as an adjustable parameter “within reasonable bounds”, namely around 0.10–0.15 for “good metals”. As such, these approaches are not strictly speaking ab initio when it comes to predict the exact value of T_C , and the goal of this class of work is rather to decide if phonon-mediated scenarios are likely, and if so, which modes are involved. It is to be noted however that a fully ab initio density functional theory-like approach for phonon-mediated superconductivity has been developed recently with excellent results when applied to simple metals or MgB_2 [22]. The future will say if such a breakthrough approach may be used for a large variety of materials.

3. Silicon and carbon clathrates

Nearly one decade before the discovery of a superconducting transition in highly-doped diamond and silicon, a superconducting transition in (Na,Ba)-doped silicon clathrates was observed [23]. Silicon clathrates are three-dimensional (3D) networks composed of face-sharing Si_n ($n = 20, 24, 28$, etc.) cages (see Fig. 1(f) for intercalated clathrates). All atoms are four-fold coordinated within a slightly distorted tetrahedral environment, sharing therefore with the standard Si-diamond phase (Si-2) the local sp^3 hybridization. Satisfying the octet rule, Si clathrates are semiconducting with a ~ 1.8 eV band gap [25–27], a gap larger than that of Si-2 due to the presence of pentagons in the network that frustrate the bonding character of the sp occupied bands, inducing a contraction of the valence bands [28]. However, in contrast with the Si-2 phase, the cage structure leads to a low density network with the possibility of intercalating during synthesis atoms within the cages. Intercalation by sodium, barium, etc. leads to n -type endohedral doping with typical stoichiometry of 8 guest atoms per 46 Si host atoms in the so-called type-II simple cubic clathrates.

With such a large intercalation ratio, way beyond the critical concentration for inducing an insulator–metal transition (MIT), semiconducting Si-clathrates become degenerate semiconductors with the Fermi level (E_F) entering the conduction bands. Such a metallic behavior leads to the possibility of a superconducting transition with a critical temperature depending on the intercalated atoms. The first observation on (Na,Ba)-intercalated clathrates revealed a transition temperature T_C of about 4 K [23], while barium doping only increases T_C to about 8 K [29] due to the hybridization at E_F of Ba $5d$ states with Si sp bands resulting in a large density of states $N(E_F)$ [30]. Both experimental isotopic effect analysis [29] and theoretical ab initio calculations [31] of the electron–phonon coupling constant λ lead to the interpretation that the superconducting transition in such systems was phonon-mediated with a remarkable agreement between theory and experiment on the electron–phonon coupling constant λ and the (screened and retarded) Coulomb repulsion coefficient μ^* , with $0.8 < \lambda_{exp} < 1.0$ and $0.23 < \mu_{exp}^* < 0.31$ experimentally, and $(\lambda_{theo}, \mu_{theo}^*) \sim (1.0, 0.3)$.¹ Further, the comparison of theory and experiment concerning the decrease of T_C under applied pressure [31] confirmed that the superconducting scenario was probably phonon-mediated and well described by the standard Eliashberg formalism and the simplified McMillan formula.

The idea that superconductivity in such systems is phonon-mediated quickly led theoreticians to play with carbon clathrates’ structure with the idea that the isotope effect may dramatically increase T_C . Further, the exceptional mechanical properties of these cage-like systems [31–33] and their affiliation with doped fullerides, were other strong incentives to try to predict the properties of carbon clathrates which, unfortunately, have not been synthesized so far. As expected, transition

¹ The theoretical μ^* is the value needed to get the experimental T_C using the McMillan formula and the calculated λ and ω_{log} coupling constant and average phonon frequency.

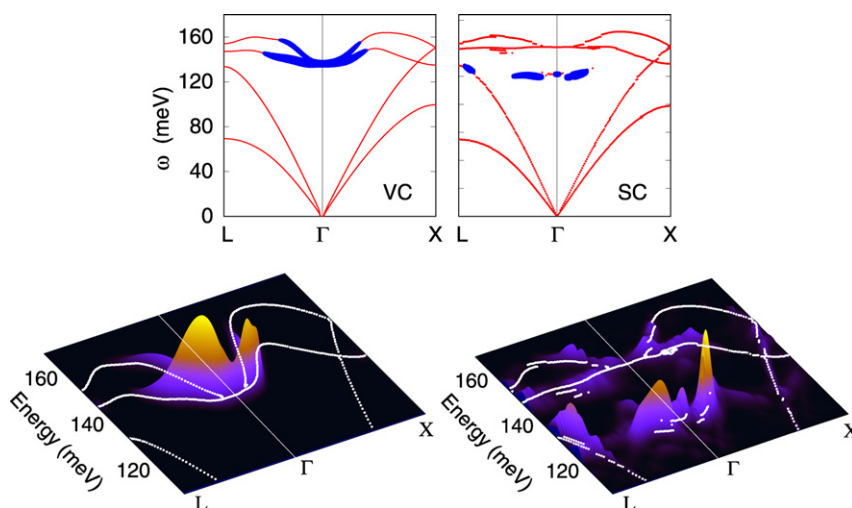


Fig. 2. Doped diamond: (thick blue lines and color intensity maps) calculated phonon width Γ_{qv} , related to the imaginary part of the electron–phonon self-energy operator. (Left) Virtual crystal approximation showing the importance of zone-center optical modes. (Right) Supercell calculations showing the importance of B–Si stretching modes. In thin full lines (red), the calculated phonon band structure. Note the important softening of the optical modes in the virtual crystal approach. From Ref. [38].

temperatures as large as ~ 77 K were predicted for halogen-intercalated carbon clathrates [34] on the basis of ab initio calculations within the Eliashberg/McMillan framework (see Fig. 1(g)). Even though highly hypothetical, we will show below that several studies lead to predicted T_C larger than that of MgB_2 in doped covalent carbon systems.

4. Superconductivity in doped diamond, silicon, and related systems

4.1. Doped diamond: experiments, theory and prospects

The physics of the superconducting transition in highly-doped column IV semiconductors remained a curiosity until the discovery of a superconducting transition in B-doped diamond [1] with $T_C \sim 4$ K for doping concentration of a few percent. Soon after, various samples synthesized through high-temperature–high-pressure (HPHT) techniques or CVD [35] approaches were found to be superconducting with T_C up to 10 K. It is worthwhile underlining that progresses in increasing the doping rate greatly benefited from the activity of a community attempting to synthesize ultrahard materials with various B:C:N stoichiometry [36]. Even though difficult to quantify, it is tempting to suggest that the strongly covalent nature of the bonding in diamond is responsible for both its exceptional mechanical properties and the very large electron–phonon coupling that enhances T_C in such materials.

Ab initio calculations within various supercell [21,37,38], virtual crystal (VCA) [39,20,40] or coherent-potential (CPA) [41] approximations, aiming at accounting in an approximate way for doping randomness, consistently predicted that in the few percent doping range, there are no impurity bands and the Fermi level enters the conduction bands. This degenerate scenario was confirmed by experimental angle-resolved photoemission spectroscopy [42], X-ray emission and absorption spectroscopy [43], answering the question: “Where are the electrons?” [44]. As a result, the proposed resonant valence bond (RVB) model [45] assuming that the Fermi level is in a well defined narrow impurity band remained rather marginal and a standard phonon-mediated scenario has now the favor of the community.

Theoretical studies all pointed to the same key features in doped diamond: a dramatically large electron–phonon potential $V^{ep} = \lambda/N(E_F)$, but a density of states which remains small due the low doping rate and the 3D nature of the system. In particular, the deformation potential associated with the zone-center optical modes was predicted [39,20] to be 50% larger than that associated with the E_{2g} mode in MgB_2 , another covalent phonon-mediated superconductor. However, the largest T_C in diamond (10 K) remains smaller than that of MgB_2 (39 K) which benefits from a much larger density of states at the Fermi level related in particular to its 2D-like underlying structure. As a result, λ remains limited in diamond to about 0.4–0.5 in the experimentally achieved few percent doping range. First-principles calculations explored the properties of diamond in the limit of extremely large doping [46,47], with doping rate of up to 50% (alloying should then be used rather than doping). The analysis of the density of states and a quantity known as the effective McMillan–Hopfield parameter [46] led to the conclusion that, in randomly substituted B_xC compounds in the diamond phase, T_C could increase with doping up to 60 K for $x \sim 0.3$ in a rigid band model and assuming that $\mu^* \sim 0.12$. Similarly, it was also predicted [47] that T_C could be equivalent to that of MgB_2 in the cubic BC_5 structure recently synthesized [48] in search, again, for an ultrahard material. Previous ab initio calculations [49] suggested that carbon-doped boron icosahedra could be very good candidates for large T_C s. The actual stability of these systems, and potential synthesis techniques, are of course not provided by computer simulations.

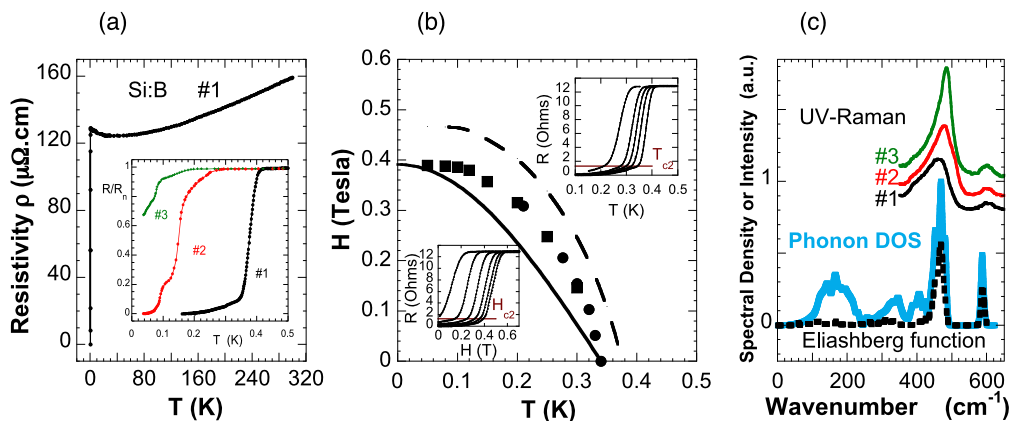


Fig. 3. (Color online) Superconducting boron-doped silicon: (a) Temperature dependence of the a.c. resistivity for different boron samples. (b) Temperature dependence of the upper critical field H_{c2} . (c) Experimental Raman spectra for 3 different samples and calculated vibrational spectral density and Eliashberg function (dotted line). The structure at 590–600 cm^{-1} is related to the B–Si stretching modes. Adapted from Ref. [2].

The answer to the question “Where are the phonons?”, that is namely which phonons contribute mainly to the coupling with electrons, is still somehow opened. While VCA calculations, with a “smeared jellium-like” doping model, clearly identified the role of the zone-center diamond optical modes [39,20,40], supercell approaches, with actual boron atoms in substitution but periodically arranged, consistently pointed out to the importance of the local vibrational modes of the dopant [21,38] (see Fig. 2). Further isotope effect experiments, changing both the C and B isotopes, are awaited for straightening out this point [50]. As yet another puzzling question stands the difficulty of relating the dopant content, as determined e.g. through SIMS analysis, and the density of free carriers. Samples with the apparent same doping content may in particular show very different T_C s. First-principles calculations showed that in degenerate conditions of high doping, it is thermodynamically favorable for B atoms to cluster into B-dimers which are electronically neutral (not ionized) [51,52], a picture confirmed by a dramatic change of the kinetic order for boron incorporation across the MIT transition [52].

4.2. From silicon clathrates to silicon in the diamond phase

A few years after the discovery of the superconductivity in B-doped diamond, highly B-doped silicon in its diamond phase (the “standard” structure) was also found to undergo a superconducting transition [2,24]. As expected from standard BCS theory with phonon mediation, the larger mass of Si and softer vibrational modes should lead to a smaller T_C . Indeed, a T_C of ~ 0.35 K was measured for boron content of about 10% ($\sim 4 \times 10^{21}$ at cm^{-3}). Such a result is certainly now not surprising and the real challenge lied in the synthesis techniques for achieving such a doping rate which is well above the thermodynamic solubility limit ($\sim 10^{20}$ at cm^{-3}) and the MIT critical concentration (a few 10^{18} at cm^{-3}). Among the various out-of-equilibrium techniques developed to overcome this limitation, laser-assisted processes are well adapted to silicon, germanium and their alloys. As such, gas-immersion laser doping (GILD), consisting in a rapid melt and quench of a Si surface covered by impurity carrying molecules [53], was successfully used for introducing silicon to the family of superconducting materials.

Ab initio calculations in the VCA [20] or supercell [2,54] approaches confirmed the picture of a degenerate semiconductor with an electron–phonon coupling mediated mainly by zone-center optical modes. In the case of silicon, the local B–Si vibrational modes are located too high in energy to significantly contribute to λ (see Raman and theoretical peak at ~ 590 – 600 cm^{-1} in Fig. 3c) which amounts to 0.2–0.3 in the accessible doping range. Again, the low density of states at the Fermi level can explain why T_C in B:Si diamond is much smaller than the ~ 8 K found experimentally for barium-doped Si clathrates. As emphasized above, the presence of the Ba 5d states at E_F in $\text{Ba}_8\text{Si}_{46}$ significantly contributes to increasing T_C . Doping silicon in its diamond phase with other elements than boron is currently under investigation.

We briefly conclude this study of column IV sp^3 covalent superconductors by the case of B-doped SiC carbide which was found to be superconducting with $T_C \sim 1.4$ K for a boron content estimated to be in the 2.2–3.9% range [55,56]. The samples consisted mainly of cubic 3C-SiC and boron is expected to substitute carbon atoms. Again, calculations suggest that a standard phonon-mediated scenario is likely to be at the origin of the transition [57,58]. Contrary to diamond and Si-2 silicon, the large difference in mass between Si and C leads to the observation that not only optical modes, but also acoustic phonons, significantly contribute to the electron–phonon coupling.

5. Conclusions

Beyond the problems related to material sciences, and in particular the challenges in increasing the doping content in these rather dense phases, our understanding of the superconducting transition in such systems remain to be strengthened, in particular in the low-doping limit, just after the onset of the MIT transition. Important complications may change the

picture conveyed by the theoretical and experimental work published so far, considering namely that (a) doping induces disorder in the system, an aspect hardly accounted for in VCA or supercell calculations, and (b) the Fermi energy is of the order of a few tenths of an electronvolt, that is not significantly larger than the energy of the optical phonon modes in diamond contributing to the coupling. This last point may suggest that the Migdal theorem does not hold, with strong non-adiabatic effects and deviations from the standard Bardeen–Cooper–Schrieffer (BCS) theory. Accurate dynamical mean-field theory calculations for fullerenes, presenting a similar ratio of electron to phonon energy, led however to the conclusion that for λ parameters lower than ~ 0.5 , the standard Migdal–Eliashberg approach provides equivalent results to more accurate many-body treatments of electron–electron and electron–phonon interactions [59]. Further, scanning tunneling spectroscopy measurements on superconducting diamond revealed a $2\Delta(T)/k_B T_C$ ratio thermal dependence in excellent agreement with the weak coupling BCS limit [60]. It remains, however, that the observed T_C seems to remain anomalously large in the low doping limit close to the MIT transition [61], in contrast to the exponential dependence with λ in the standard Eliashberg/McMillan approach. A recent theory predicted that close to a mobility edge, T_C may only drop as a power law of λ as a consequence of disorder [62]. The simultaneity of the two transitions (MIT and superconductivity) in doped diamond may offer new opportunities to study this issue in detail.

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