TOPICAL REVIEW

Selected topics related to the transport and superconductivity in boron-doped diamond

Jiří J Mareš, Pavel Hubík, Jozef Kríštofik and Miloš Nesládek

Institute of Physics of the ASCR, v. v. i., Na Slovance 2, 182 21 Prague 8, Czech Republic
E-mail: semicon@fzu.cz

Received 30 September 2008
Accepted for publication 11 November 2008
Published 28 January 2009
Online at stacks.iop.org/STAM/9/044101

Abstract
This contribution deals with a few topics closely related to the superconductivity in the heavily boron-doped diamond which are, in our opinion, not properly treated in the current literature. Attention is paid especially to the classification of metallic and insulating state, selection of pairing mechanism, limits of weak coupling approximation and to the influence of granularity on the superconducting transition.

Keywords: boron-doped diamond, metal-insulator transition, superconductivity

1. Introduction

Boron doped diamond (BDD), prepared either by high pressure high temperature technique (HPHT) [1, 2], by plasma enhanced chemical vapour deposition (PECVD) [3–5] or by hot filament assisted CVD [6, 7], is a unique material which provides the playground for various quantum transport phenomena, such as hopping, weak localization, ballistic transport, unconventional superconductivity and Josephson’s effects [8–12]. The growth techniques mentioned above provide boron-doped diamond samples not essentially differing from one another. Typically they contain a random subsystem of boron atoms and reveal granular structure, usually with grain size from ∼100 nm (nanocrystalline diamond) up to ∼10 µm. The boron doping concentration, achievable without appreciable segregation, can reach ∼10^{27} m\(^{-3}\) in both types of samples. Besides, PECVD technique enables one to prepare single-crystalline epitaxial layers [13, 14]. In this contribution, we deal both with common properties of all types of BDD and with special features of boron-doped nanocrystalline diamond (B-NCD).

It has already been found that quantum transport effects observed in BDD are related to the peculiar structure of this interesting material. There is, however, no perfect consensus concerning the interpretation of the fairly consistent experimental data provided by different laboratories. Therefore, we have chosen a few somewhat controversial topics, which are, in our opinion, not properly treated in the literature. The emphasis is put mainly on the correct application of fundamental concepts to the special case of BDD/B-NCD. Presented discussion also reflects our current understanding of the subjects which has slightly developed comparing to the previous works (e.g. [15]). The topics selected for our discussion are: the classification of metallic and insulating state of BDD, possible mechanisms of superconductivity in BDD, applicability of weak coupling approximation to the superconducting transition in BDD and effect of granularity of B-NCD on the superconducting transition.

2. Weak definition of metal and insulator

Since the beginning of the 18th century, when electrical conduction was discovered, solids have been classified as conductors (metals) and insulators. Nevertheless, such a
classification, which is very useful for practical purposes, was found to be enormously difficult to reformulate in terms of theory, so that the problem has not been satisfactorily solved yet. In the theoretical literature dealing with this subject, the definitions and the concepts of a metal and an insulator are confined to the absolute zero temperature [16]. As, however, the absolute zero temperature, corresponding to an improper point of hotness manifold [17], does not exist at all, such a definition bears a somewhat metaphysical character. For authors, it is a very strange fact that Planck’s warning ‘all thought experiments which are making use of absolute zero should be avoided’ [18] is ignored in the theory quite generally. The consequence of such an approach is, among others, the impossibility to distinguish between metal and insulator experimentally. Therefore, as we are convinced, it is necessary to abandon all the ‘strong’ definitions based upon the non-existing concept of absolute zero temperature and formulate operational criteria enabling us to distinguish between metal and insulator experimentally at finite temperatures.

Relatively simple and effective is the so-called gap criterion [16] which is usable for conductors controlled by single-particle excitations. Moreover, it is advantageous for application of this criterion that it can be decided, by means of auxiliary experiments, whether or not the conductivity is due to single-particle excitations. As usually, by gap $\Gamma$ we mean the energy difference between the Fermi level and the mobility edge where the single-particle excitations become macroscopically extended, i.e. where they correspond to the charge-carrying states. Assuming further that the effective gap, which controls the thermal activation of the carriers, is temperature dependent, the temperature dependence of resistivity may be written in quite a general form

$$R/R_0 = \exp(\Gamma(T)/kT),$$

where the factor $R_0(T)$ is a weak function of $T$. The parameter $\Gamma(T)$ setting the energy scale of the activation process of charge carriers, can be experimentally determined from the local slope (taken with minus sign) of the temperature dependence of the resistivity plotted in the Arrhenius coordinates (i.e. log $R$ versus $1/T$). This fact enables one to recast the gap criterion into the weak definition of metal and insulator applicable within a certain finite interval of temperatures $J$, namely:

If for every $T \in J$, $\Gamma(T) \leq kT$ the conductor is called metal with respect to $J$.

If for every $T \in J$, $\Gamma(T) > kT$ the conductor is called insulator with respect to $J$.

Note that the confinement of the weak definition to an interval $J$ makes, in contrast to the standard strong definition, the metal-insulator classification experimentally provable. In order to comprehend this important fact, the typical $R(T)$ curves are depicted in figure 1. There the dashed border line, corresponding to the condition $\Gamma(T) = kT$ unambiguously separates, within the interval $J$, metallic and insulating regions.

![Figure 1](image_url)

**Figure 1.** Various types of $R(T)$ curves are sketched corresponding to insulator (INS), disordered metal (DM), real metal (M) and ideal metal (IM). Dashed curve represents the border line between metals (underneath the curve) and insulators (above the curve).

Let us now classify various forms of BDD according to our weak definition of metallic and insulating state using the experimental data taken from the literature [19, 20]. The most conspicuous experimental observation is that the metal-insulator transition, characterized in accordance with our definition by the condition $\Gamma \approx kT$ takes place just in close vicinity of Mott’s critical concentration $N_C \approx 6 \times 10^{26} \text{ m}^{-3}$ given by the semi-empirical formula [10, 21]

$$a_B N_C^{1/3} \approx 1/(2\pi)^{1/3} \approx 0.26 \pm 0.01,$$

where $a_B \approx 3.1 \times 10^{-10} \text{ m}$ is the effective Bohr radius of boron in diamond. The identity of Mott’s criterion with the gap criterion in BDD has, however, far reaching consequences not fully recognized and respected in the current literature. For example, the interpretation of temperature dependence of conductivity above Mott’s threshold (Mott’s metal, $\Gamma < kT$) in terms of hopping is absolutely misleading, in spite of ‘successful’ fitting to say $T^{1/4}$ law. Hopping requires that the transport is controlled by the tunnelling between strongly localized sites, but such a conductor, controlled by strong localization (i.e. $\Gamma > kT$), is per definition insulator and not metal!

Another, rather frequent misinterpretation of experimental data involves treating any increase of resistivity with decreasing temperature as a symptom of insulating state. In fact, such a behaviour, which is rather a symptom of localization, may be observed in metal and insulator as well. In case of metal where $0 < \Gamma < kT$ however, the localization cannot bear a character of strong localization characterized by exponential damping of wave-functions [21], but is appropriately called weak localization. The only known microphysical model of such a type of localization is based on quantum interference of electrons in disorder-induced potential. Therefore, we have a right to use for such a system the term ‘disordered metal’. It is a remarkable experimental fact that in various highly doped BDD samples, as far as we know, disappearance of the effective gap ($\Gamma \approx 0$, as in ordinary metals) has never been observed.
An example of actual behaviour of a B-NCD sample having the boron doping concentration of $\sim 1.7 \times 10^{27} \text{ m}^{-3}$ which is well above $N_C$, is depicted in figure 2. It is apparent that the effective energy gap in the range between on-set $T_C \approx 2.4 \text{ K}$ and $\sim 350 \text{ K}$ is everywhere smaller than $kT$. Using then our weak definition of metal, one can unambiguously claim that this material is, in the temperature range $2.4-350 \text{ K}$, a disordered metal controlled by weak localization.

The experimental data concerning the low-temperature transport in BDD, with regard to our classification, can be thus summarized as follows. For boron concentrations $N_B < N_C \approx 6 \times 10^{26} \text{ m}^{-3}$, BDD is disordered insulator where hopping transport mechanism prevails, while for concentrations $N_B > N_C$ this material is disordered metal controlled by weak localization. It is an experimental fact that only the latter, metallic form of BDD undergoes the superconducting transition. Moreover, at sufficiently high temperatures ($>150 \text{ K}$) and $N_B < 10^{25} \text{ m}^{-3}$, an activated transport is usually observed with activation energy converging to $\Gamma \approx 0.37 \text{ eV}$ with decreasing $N_B$ [13].

3. Possible mechanisms of superconductivity in BDD

Let us first recall the conditions which are essential for superconductivity in general. There is a consensus that in a solid state, any attractive interaction near the Fermi level dominating the Coulomb interaction can lead to the charge carrier pairing. Such paired fermions (Cooper’s pairs) may occupy, in contrast to the single fermions, the common, ‘collective’ ground state which is separated from the sea of excited single fermions by a finite energy gap $\Delta(T)$. The very property of the Cooper pairs occupying the ground state is that they are indistinguishable by any quantum measurement. Consequently, in case where the ground state is extended from one side of a macroscopic sample to its other side, the transfer of paired carriers via this state is inevitably non-dissipative, i.e. the sample can be regarded superconducting with respect to the transport properties. The aim of any research into the superconductivity may thus be reduced to the identification of pairing mechanism and to the specification of the symmetry of the corresponding ground state.

At present, three types of competitive theories are used for the explanation of the superconductivity in heavily BDD. The main stream is represented by various modifications of classical Bardeen–Cooper–Schrieffer (BCS) theory based on phonon-mediated pairing [22–29]. A review discussing this theory both for BDD and for other semiconductors can be found in [30]. The second approach, correctly describing most of the experimentally observed features, is ‘correlated impurity band theory’ of Baskaran [31]. The third variant of the theory accounting for superconductivity in B-NCD, which is due to the authors of this review, is based on the spin-flip-driven pairing of holes weakly localized in the vicinity of the Fermi level [11, 32]. The simultaneous existence of different, more or less equally justified theories makes it obvious that the a-priori choice of a pairing mechanism followed, e.g. by the ‘derivation of correct value of $T_C$’ cannot serve as a proof of a particular theory. The problem is more complex, requiring the seeking of supplementary experimental indications discriminating some of the pairing mechanisms. An example of a successful identification of pairing mechanism is BCS theory applied to such ordinary metals and alloys as Sn, Pb, Nb,Ge and others. In that case, isotope effect [33, 34] eliminated any pairing not related to the phonons. A very similar idea is also behind recent attempts at proving that the pairing mechanism in heavily boron-doped diamond is phonon mediated [2, 35]. The authors of these important papers report that the $T_C$ is changed $\sim 0.2 \text{ K}$ [2] or $\sim 0.5 \text{ K}$ [35] if the host lattice is composed of $^{13}\text{C}$ instead of $^{12}\text{C}$. Contrary to the case of an ordinary homogeneous metal, the physical meaning of such experiments in BDD is, in our opinion, somewhat ambiguous. In BDD, the superconducting transition is controlled rather by the properties of the inhomogeneous boron subsystem, and the effect of the composition of the host lattice is hardly distinguishable from the influence of granularity, local deformations and of the filamentary structure of the superconducting channels. Moreover, a characterization of the doping level by a change of lattice parameter [35] is yet unreliable, e.g. because a portion of electrically active boron atoms can vary in dependence on used technology (cf seemingly inconsistent values of $T_C$ and lattice parameter when comparing $^{13}\text{C}$ samples investigated in [1] and [35]). We thus claim that the reliable experimental proof determining the pairing mechanism in superconducting BDD is lacking at present.

4. An example of selection of pairing mechanism

In order to confirm or eliminate a particular pairing mechanism in BDD, a pragmatic method of trial and error may
be used, consisting of combining experimental observations with some arbitrary construction. Resulting picture and its consequences are then compared with reality, and its plausibility is tested. Let us now illustrate application of this method to the spin-flip pairing model [32], with which the authors of this contribution are well acquainted.

The most exhausting summary of experimental observations related to the superconductivity in BDD, formulated in terms introduced above, is the following: BDD revealing the superconducting transition is disordered Mott’s metal controlled above $T_C$ by weak localization. An arbitrary element added is the effects dominating the transport above $T_C$ play the dominant role in superconducting transition. (Note that the same conjecture is valid for the superconducting transition in ordinary metals treated within the BCS theory. Indeed, in ordinary metals, the transport above $T_C$ is dominated by electron-phonon interaction, as well as the superconducting transition.) These two statements provide basis for the following chain of deductions [10, 32]: in disordered Mott’s metal, the Coulomb and exchange interactions at distances larger than the Bohr radius $a_B$ cease to play a substantial role. Simultaneously, the effect of weak localization gives rise to the temporarily stable coherent single-electron (hole) interference patterns having intrinsic extent $\xi = \hbar \nu_F / 4 k T$, where $\nu_F$ is the Fermi velocity, and characteristic Orstein’s coherence time $\tau = \hbar / 2 k T$ [36]. Respecting then our conjecture, the attraction between oscillating weakly localized carriers mediated by a periodic polarization of the host lattice (i.e. electron-phonon mediated interaction), should be confined to the energy band of width $\approx \hbar / \tau$. On the other hand, the direct Heitler–London electron–electron interaction is, of course, because of the said screening, reduced to the attractive spin–spin interaction represented by the energy gap [10]

$$\Delta = 2 \mu_0 \mu_B^2 / \hbar^3.$$  \hfill (3)

Here $b$ is the inter-atomic distance in the host lattice, $\mu_0$ the permeability of vacuum and $\mu_B$ the Bohr magneton ($b \approx 1.54 \times 10^{-10} \text{m}$, $\Delta \approx 3.7 \times 10^{-4} \text{eV}$). Obviously, both types of attractive interactions, i.e. the electron–phonon mediated and the direct spin–spin interaction may operate simultaneously or cooperate in creating Cooper pairs. Taking, however, into account the fact that for temperatures just above the superconducting transition (say for $T \lesssim 2 \text{K}$), it must be $\hbar / \tau = 2 k T \approx 3.4 \times 10^{-4} \text{eV} < 3.7 \times 10^{-4} \text{eV} \approx \Delta$, which means that the spin–spin interaction is the most robust attractive interaction present. Moreover, in contrast to the electron-phonon mediated interaction, the spin-flips are unavoidable for the establishment of proper symmetry of the ground state satisfying the Pauli exclusion principle. Applying the philosophy of Occam’s razor, one has to believe in spin-flip model of pairing mechanism in BDD.

5. Law of corresponding states

For the discussion of the superconductivity in a given system, the preliminary consideration of various energy scales involved is important. The upper cut-off energy for phonons is set by the Debye energy $k \theta_D$. In diamond, the Debye temperature $\theta_D = 2230 \text{K}$ and $k \theta_D = 0.192 \text{eV}$. Analogous cut-off energy for holes is the Fermi energy [37]:

$$E_F = 9.57 (h^2 / 2m) N_B^{2/3},$$  \hfill (4)

where $N_B$ is the concentration of electrically active boron acceptors. For Mott’s metal of concentration $N_B \approx 2 \times 10^{22} \text{m}^{-3}$, the Fermi energy $E_F$ formally amounts to $\approx 0.58 \text{eV}$. The energy scales in a metallic BDD may thus be in the vicinity of the transition temperature $T_C$ ordered as follows: $\hbar / \tau \approx \Delta < k \theta_D < E_F$. This means that the quantities relevant to the superconducting transition are much smaller than other energies characterizing the system as a whole. This circumstance, largely simplifying the theoretical description of the superconducting transition, is the essence of the so called weak coupling approximation originally developed within the BCS theory [38, 39]. On the basis of quite general thermodynamics arguments, this approximation leads to the universal scaling relation connecting $\Delta$ and $T_C$, which has the character of the ‘law of corresponding states’, namely:

$$\Delta = 1.76 k T_C.$$  \hfill (5)

It is worth noting that relation (5) is very often erroneously used as a fingerprint of phonon-driven pairing mechanism. Whereas, it is merely the direct consequence of weak coupling approximation, which is also valid for our spin-flip pairing model. Moreover, the experimentally confirmed validity of scaling law (5) excludes any pairing mechanism exploiting high-frequency phonons having energy comparable, e.g. with the Debye energy. These very facts should be considered seriously before accepting a theoretical approach for interpretation of experimental data.

Anyway, the usefulness of relationship (5) is quite obvious. For example, it enables the assessment of change of $T_C$ due to the increase of the gap $\Delta$ in consequence of host lattice deformation. Indeed, combining equations (3) and (5) and computing the derivative with respect to parameter $b$, we obtain a relation

$$d T_C = - \left(1.14 \mu_0 \mu_B^2 / \hbar b^4\right) d b.$$  \hfill (6)

Inserting $b = 1.54 \times 10^{-10} \text{m}$, we obtain $d T_C = -4.76 \times 10^{10} \text{db}$. Effective local lattice deformation due to the substitution of C atom by B atom will increase the distance between the nearest neighbouring atoms by an amount of $db \approx 1.1 \times 10^{-11} \text{m}$. (Note that the covalent radii of carbon and boron are $7.7 \times 10^{-11} \text{m}$ and $8.8 \times 10^{-11} \text{m}$ respectively.) According to formula (6), the $T_C$ has to decrease about $\approx 0.5 \text{K}$; we thus predict the existence of a maximum in the dependence of $T_C$ on boron concentration followed by a decrease of $T_C$ at appreciably high concentrations [28].

6. Reduction of the number of degrees of freedom at low temperatures

A somewhat neglected aspect of common B-NCD is its granularity. As the typical grain size is of the order of $\approx 100 \text{nm}$, one has to expect that the quantum processes in this
material should be, due to the spatial confinement, affected significantly. Our recent study [12] dealing with the effect of granularity of B-NCD on ballistic transport and Josephson noise is by no means exhaustive. It can be shown that also the spectrum of acoustic phonons, which is believed to play an important role in the superconducting transition, should be essentially modified in grained structure. Indeed, applying Planck’s condition [18] to the upper cut-off frequency of phonon spectrum of a diamond grain with size \(d\), we estimate the temperature \(T_K\), below which the phonons and other associated effects must be appreciably modified by the presence of grain boundaries. Let us take a cubic diamond grain of size \(d \approx 100\) nm. Considering that there are 8 carbon atoms per diamond cubic cell of side \(a \approx 3.57 \times 10^{-10}\) m, we obtain that such a grain contains \(n \approx 1.76 \times 10^9\) atoms. Assuming further that the average number of degrees of freedom per atom \(f\) is known (e.g. \(f \approx 6\)), Planck’s condition may be written as

\[ T_K \approx \theta_0 (4\pi/3nf)^{1/3}. \]  

(7)

Inserting then the above figures into formula (7), we obtain \(T_K \approx 3.52\) K which is close to the temperature of superconducting transition \(T_C\) experimentally observed in B-NCD. In such a case, however, any phonon-driven mechanism of superconducting transition, especially that using weak coupling approximation (i.e. involving prevailingly long-wave phonons) should be enormously sensitive to the extent of the grains in the aggregate. (cf. also the predicted effect of the grain size on the stability of superconductivity due to the thermal noise [40].) Strong dependence of \(T_C\) on the grain size might thus serve as an auxiliary support for the phonon-driven mechanism of superconductivity. Systematic study in this direction is vigorously recommended.

7. Conclusions

In this short review, a non-systematic exposition is given of some controversial points related to the superconductivity in boron-doped diamond. We do not pretend to provide the final solutions, but are rather trying to turn attention of the ‘diamond community’ to lesser known aspects of these problems.

The items discussed in this contribution may be summarised as follows: we provide an original ‘weak’ definition of metal and insulator, applicable to experimental data observed in finite temperature intervals, and its relation to Mott’s criterion. Possible mechanisms of superconductivity in BDD are shortly outlined. On a special case of spin-flip pairing, a general method for selection of a particular mechanism is illustrated. The proper significance of weak coupling approximation for interpretation of the superconductivity in BDD is pointed out. Attention is paid to the reduction of the number of degrees of freedom in grains of B-NCD and to its possible consequences.

Acknowledgment

This work was supported by the Czech Science Foundation Contract No 202/06/0040, by the Grant Agency of ASCR Contract No A1010404 and by Institutional Research Plan of Institute of Physics No AVOZ10100521.

References

[1] Ekimov E A, Sidorov V A, Bauer E D, Mel’nik N N, Curro N J, Thompson J D and Stishov S M 2004 Nature 428 542
[2] Dubrovinskaia N, Dubrovinsky L, Papageorgiou T, Bosak A, Krisch M, Braun H F and Wosnitza J 2008 Appl. Phys. Lett. 92 132506
[3] Takano Y, Nagao M, Sakaguchi I, Tachiki M, Hatano T, Kobayashi K, Umezawa H and Kawarada H 2004 Appl. Phys. Lett. 85 2851
[4] Bustarret E, Kačmarčík J, Marcenat C, Gheraeart E, Cyternann C, Marcus J and Klein T 2004 Phys. Rev. Lett. 93 237005
[5] Nesládek M, Tromson D, Mer C, Bergonzo P, Hubik P and Mareš J J 2006 Appl. Phys. Lett. 88 232111
[6] Wu D, Ma Y C, Wang Z L, Luo Q, Gu C Z, Wang N L, Li C Y, Lu X Y and Jin Z S 2006 Phys. Rev. B 73 012501
[7] Fortunato W, Chiupito A J, Galzerani J C and Moro J R 2005 Thin Solid Films 476 246
[8] Sato T, Ohashi K, Sugai H, Sumi T, Haruna K, Maeta H, Matsumoto N and Otsuka H 2000 Phys. Rev. B 61 129701
[9] Mamin R F and Inushima T 2001 Phys. Rev. B 63 033201
[10] Mareš J J, Hubik P, Nesládek M, Kindl D and Kristofik J 2006 Diam. Relat. Mater. 15 1863
[11] Mareš J J, Hubik P, Kríšiofik J, Kindl D and Nesládek M 2008 Chem. Vapor. Depos. 14 161
[12] Mareš J J, Hubik P, Kríšiofik J and Nesládek M 2008 Phys. Status Solidi a 205 2163
[13] Langrange J P, Deneuville A and Gheraeart E 1998 Diam. Relat. Mater. 7 1390
[14] Takano Y, Takenouchi T, Ishii S, Ueda S, Okutsu T, Sakaguchi I, Umezawa H, Kawarada H and Tachiki M 2007 Diam. Relat. Mater. 16 911
[15] Nesládek M, Mareš J J, Tromson D, Mer C, Bergonzo P, Hubik P and Kristofik J 2006 Sci. Technol. Adv. Mater. 7 S41
[16] Gebhard F 1997 The Mott Metal-Insulator Transition (Heidelberg: Springer)
[17] Serrin J 1979 Arch. Ration. Mech. Anal. 70 355
[18] Planck M 1923 Vorlesungen über die Theorie der Wärmestrahlung 5th edn (Leipzig: Barth)
[19] Klein T et al 2007 Phys. Rev. B 75 165313
[20] Winzer K, Bogdanov D and Wild C 2005 Physica C 432 65
[21] Mott N F 1987 Conduction in Non-Crystalline Materials (New York: Oxford University Press)
[22] Giustino F, Yates J R, Souza I, Cohen M L and Louie S G 2007 Phys. Rev. Lett. 98 047005
[23] Ortolani M, Lupi S, Baldassarre L, Schade U, Calvani P, Takano Y, Nagao M, Takenouchi T and Kawarada H 2006 Phys. Rev. Lett. 97 097002
[24] Ma Y, Tse J S, Cui T, Klug D Z, Zhang L, Xie Y, Niu Y and Zou G 2005 Phys. Rev. B 72 014306
[25] Lee K W and Pickett W E 2006 Phys. Rev. B 73 075105
[26] Blase X, Adessi Ch and Connetable D 2004 Phys. Rev. Lett. 93 237004
[27] Boeri L, Kortus J and Andersen O K 2004 Phys. Rev. Lett. 93 237002
[28] Moussa J E and Cohen M L 2008 *Phys. Rev.* B *77* 064518

[29] Hoesch M, Fukuda T, Mizuki J, Takenouchi T, Kawarada H, Sutter J P, TsuTsui S, Baron A Q R, Nagao M and Takano Y 2007 *Phys. Rev.* B *75* 140508

[30] Cardona M 2006 *Sci. Technol. Adv. Mater.* *7* S60

[31] Baskaran G 2008 *J. Supercond. Nov. Magn.* *21* 45

[32] Mareš J J, Nesládek M, Hubík P, Kindl D and Kristofik J 2007 *Diam. Relat. Mater.* *16* 1

[33] Maxwell E 1950 *Phys. Rev.* *78* 477

[34] Reynolds C A, Serin B, Wright W H and Nesbitt L B 1950 *Phys. Rev.* *78* 487

[35] Ekimov E A, Sidorov V A, Zoteev A, Lebed’ Yu B, Thompson J D and Stishov S M 2008 *Sci. Technol. Adv. Mater.* *9* 044210

[36] Ornstein L S 1917 *Versl. Acad. Amst.* *26* 1005

[37] Blakemore J S 1962 *Semiconductor Statistics* (Oxford: Pergamon)

[38] Waldram J R 1996 *Superconductivity of Metals and Cuprates* (London: IOP Publishing)

[39] Tilley D R and Tilley J 1974 *Superfluidity and Superconductivity* (New York: Van Nostrand-Reinhold)

[40] Mareš J J, Hubík P, Nesládek M and Kristofik J 2007 *Diam. Relat. Mater.* *16* 921