J Supercond Nov Magn (2013) 26:1915–1919
DOI 10.1007/s10948-012-2054-7

ORIGINAL PAPER

Generalized Bose–Einstein Condensation Formalism and BCS Theory

M. Grether · M. de Llano · V.V. Tolmachev

Received: 7 November 2012 / Accepted: 4 December 2012 / Published online: 29 December 2012

Abstract Reexamining BCS theory leads one to formulate a generalized BEC formalism (GBEC) that is essentially a boson–fermion (BF) model with not two but *three* constituents, two bosonic being two-electron Cooper pairs (2eCPs) plus two-hole CPs (2hCPs), along with unpaired electrons. This ternary BF model contains three new ingredients: (i) CPs as real bosons in contrast to BCS pairs, which are at best so-called "hard-core bosons," (ii) 2hCPs explicitly accounted for on an equal footing with 2eCPs, and (iii) *four* BF vertex interactions (analogous to electron-phonon vertices) describing the formation and dissociation of both 2eCPs and 2hCPs. The two pure gauge-invariant GBEC phases (of a total of four including the trivial normal phase) that result exhibit substantially higher T_cs than BCS theory. In addition, in contrast to the well-known BCS *exponential* rise of T_c from zero, the GBEC scheme exhibits the *linear* rise as function of doping typically observed in high-T_c superconductors.

Keywords Bosonic Cooper pairs · Bose–Einstein condensation · Superconductivity

M. Grether
Facultad de Ciencias, Universidad Nacional Autónoma de México, 04510 México, D.F., Mexico

M. de Llano (✉)
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 70-360, N.E., 04510, México, D.F., Mexico
e-mail: dellano@unam.mx

V.V. Tolmachev
Baumann State Technical University, 107005, 2-ja Baumanscaja St., 5, Moscow, Russia

1 Introduction

Boson-fermion (BF) models of superconductivity were apparently introduced by Ranninger and Robaszkiewicz as early as 1985 [1]. Soon, a BF field theory with a Bose–Einstein condensation (BEC) by Friedberg and T.D. Lee appeared [2]. Both of these efforts, however, were *binary* BF models as they neglected the possibility of two-*hole* Cooper-pair (CP) bosons. Inclusion of 2hCPs leads to a generalized BEC (GBEC) formalism [3] describing a *ternary* BF model leading to gauge-invariant condensed phases. This formalism relies on 2e/2hCP energies $E_{\pm}(K)$ *phenomenologically*, where K is the CP center-of-mass momentum (CMM) wavenumber. A (generalized) BEC (or macroscopic occupation of a given state that appears below a certain fixed absolute temperature $T = T_c$) was found [3] numerically a posteriori from the GBEC formalism. The latter boils down to three coupled transcendental equations for the condensate densities $n_0(T)$ of 2eCPs and $m_0(T)$ of 2hCPs, as well as the electron chemical potential $\mu(T)$, all three as functions of T. As usual, elimination of $\mu(T)$ permits obtaining the two condensate densities of equilibrium thermodynamic states associated with two pure and a mixed phase, with BCS theory corresponding to a half-and-half mixture.

2 Distinction Between Cooper and BCS Pairs

Whether the pairwise interfermion interaction is between charge carriers or between neutral atoms, a CP state of energy $E_{\pm}(K)$ will clearly be characterized *only by a definite* center-of-mass momentum wavevector $\mathbf{K} \equiv \mathbf{k_1} + \mathbf{k_2}$ but *not* definite relative momentum wavevector $\mathbf{k} \equiv \frac{1}{2}(\mathbf{k_1} - \mathbf{k_2})$.

This is because, e.g., for two-electron CPs $E_+(K)$ itself is extracted from the Cooper eigenvalue equation

$$V\sum_{\mathbf{k}}{}'\left[\hbar^2k^2/m+\hbar^2K^2/4m-2E_F-E_+(K)\right]^{-1}=1 \quad (1)$$

which involves a sum over $\mathbf{k}$ with the prime over the summation sign signifying exclusion of states below the Fermi surface as they are already occupied. Hence, an indefinitely large number of CPs depending only on $\mathbf{K}$ implies that they satisfy Bose statistics. *Although deceptively simple, this is an elementary but crucial point in all that follows;* for a survey see [4].

Clearly, as a "Cooper pair" depends *only* K and it contrasts sharply with a "BCS pair" defined [5] as a dimer with fixed $\mathbf{K}$ *and* $\mathbf{k}$ (or equivalently fixed $\mathbf{k}_1$ and $\mathbf{k}_2$), even though only the case $K=0$ is considered in [5]. The BCS-pair annihilation and creation operators for any $K>0$ can be defined quite generally as $b_{\mathbf{kK}}\equiv a_{\mathbf{k}_2\downarrow}a_{\mathbf{k}_1\uparrow}$ and $b^\dagger_{\mathbf{kK}}\equiv a^\dagger_{\mathbf{k}_1\uparrow}a^\dagger_{\mathbf{k}_2\downarrow}$ where $a^\dagger_{\mathbf{k}_1 s}$ and $a_{\mathbf{k}_1 s}$ are fermion operators, and as before $\mathbf{k}\equiv\frac{1}{2}(\mathbf{k_1}-\mathbf{k_2})$ and $\mathbf{K}\equiv\mathbf{k_1}+\mathbf{k_2}$ are the relative and CMM wavevectors, respectively, associated with two fermions with wavevectors $\mathbf{k}_1=\mathbf{K}/2+\mathbf{k}$, $\mathbf{k}_2=\mathbf{K}/2-\mathbf{k}$. One finds [6] that $[b_{\mathbf{kK}},b^\dagger_{\mathbf{k'K}}]=(1-n_{\mathbf{K}/2-\mathbf{k}\downarrow}-n_{\mathbf{K}/2+\mathbf{k}\uparrow})\delta_{\mathbf{kk'}}$ and $[b^\dagger_{\mathbf{kK}},b^\dagger_{\mathbf{k'K}}]=[b_{\mathbf{kK}},b_{\mathbf{k'K}}]=0$ where $n_{\mathbf{K/2}\pm\mathbf{k}s}\equiv a^\dagger_{\mathbf{K}/2\pm\mathbf{k}s}a_{\mathbf{K}/2\pm\mathbf{k}s}$ are fermion number operators. Clearly, these are not the usual Bose commutation relations. Because two BCS pairs cannot exactly overlap in real space without violating the Pauli principle, they are often referred to as "hard-core bosons," albeit with hard-core radii of 0^+ sufficing to obey this principle.

3 Generalized BEC Formalism (GBEC)

The GBEC formalism is described in detail in [7, 8]; here we summarize its main equations. It applies in d dimensions and is defined by a Hamiltonian of the form $H=H_0+H_{\rm int}$. Here,

$$H_0=\sum_{\mathbf{k}_1,s_1}\epsilon_{\mathbf{k}_1}a^+_{\mathbf{k}_1,s_1}a_{\mathbf{k}_1,s_1}+\sum_{\mathbf{K}}E_+(K)b^+_{\mathbf{K}}b_{\mathbf{K}}-\sum_{\mathbf{K}}E_-(K)c^+_{\mathbf{K}}c_{\mathbf{K}} \quad (2)$$

where $\mathbf{K}$ is the previously-defined CMM wavevector of the pair, while $\epsilon_{\mathbf{k}_1}\equiv\hbar^2k_1^2/2m$ are the single-electron, and $E_\pm(K)$ the 2e-/2h-CP *phenomenological*, energies. Here, $a^+_{\mathbf{k}_1,s_1}$ ($a_{\mathbf{k}_1,s_1}$) are creation (annihilation) operators for fermions, and similarly $b^+_{\mathbf{K}}$ ($b_{\mathbf{K}}$) and $c^+_{\mathbf{K}}$ ($c_{\mathbf{K}}$) for 2e- and 2h-CP bosons, respectively. These b and c operators depend only on $\mathbf{K}$ and so are *distinct* from the BCS-pair operators depending on both $\mathbf{K}$ *and* the relative $\mathbf{k}\equiv\frac{1}{2}(\mathbf{k_1}-\mathbf{k_2})$. They are stated in [5] Eqs. (2.9) to (2.13) for the particular case of $\mathbf{K}=0$ and stressed there *not* to satisfy the ordinary Bose commutation relations. In contrast, by inspection, CPs do obey Bose–Einstein statistics, which is all that is required to ensure a BEC (or macroscopic occupation of a given state that appears below a certain fixed $T=T_c$). This was found [7, 8] numerically a posteriori in the GBEC formalism that starts from (2) as a zeroth-order picture consisting of an *ideal* ternary BF gas.

The interaction Hamiltonian $H_{\rm int}$ in the expression $H=H_0+H_{\rm int}$ describes the formation and disintegration of CPs, respectively, from and into unpaired electrons and unpaired holes. It is further simplified by dropping all $K\neq0$ terms. In [9, 10], the nonzero-CMM CPs were explicitly considered via two-time Green functions [11–13] and this leads to a *pseudogap* opening up at temperatures higher than T_c, but below a so-called "depairing" or pseudogap critical temperature $T^*\geq T_c$.

The simplified GBEC $H_{\rm int}$ consists of four distinct BF interaction vertices each with two-fermion/one-boson creation and/or annihilation operators. These vertices depict how unpaired electrons (subindex $+$) [or holes (subindex $-$)] are involved in the formation and disintegration of the 2e- (and 2h-) $K=0$ CPs in the d-dimensional system of size L, specifically

$$H_{\rm int}=L^{-d/2}\sum_{\mathbf{k}}f_+(k)\left\{a^+_{\mathbf{k},\uparrow}a^+_{-\mathbf{k},\downarrow}b_{\mathbf{0}}+a_{-\mathbf{k},\downarrow}a_{\mathbf{k},\uparrow}b^+_{\mathbf{0}}\right\}+L^{-d/2}\sum_{\mathbf{k}}f_-(k)\left\{a^+_{\mathbf{k},\uparrow}a^+_{-\mathbf{k},\downarrow}c^+_{\mathbf{0}}+a_{-\mathbf{k},\downarrow}a_{\mathbf{k},\uparrow}c_{\mathbf{0}}\right\}. \quad (3)$$

The interaction vertex form factors $f_\pm(k)$ in (3) are essentially the Fourier transforms of the 2e- and 2hCP intrinsic wavefunctions, respectively, in the relative coordinate of the two fermions. The grand (sometimes also called the Landau) thermodynamic potential Ω associated with the full Hamiltonian $H=H_0+H_{\rm int}$ given by (2) and (3) is then constructed as $\Omega(T,L^d,\mu,N_0,M_0)=-k_BT\ln[{\rm Tr}\exp\{-\beta(H-\mu\hat{N})\}]$ where "Tr" stands for "trace" and $\beta\equiv1/k_BT$. It is related to the system pressure P, internal energy E and entropy S via $\Omega=-PL^d=F-\mu N\equiv E-TS-\mu N$, where F is the Helmholtz free energy. Following the well-known Bogoliubov prescription [14], one sets $b^+_{\mathbf{0}}$, $b_{\mathbf{0}}$ equal to $\sqrt{N_0}$ and $c^+_{\mathbf{0}}$, $c_{\mathbf{0}}$ equal to $\sqrt{M_0}$ in (3), where $N_0(T)$ is the T-dependent number of zero-CMM 2eCPs and $M_0(T)$ likewise for 2hCPs. This allows *exact* diagonalization for any coupling, through a Bogoliubov transformation of the a^+, a fermion operators. One introduces $N(\epsilon)$ and $M(\varepsilon)$ as respectively the electronic and bosonic density of states. Finally, an electron dispersion energy $E(\epsilon)$ emerges as

$$E(\epsilon)=\sqrt{(\epsilon-\mu)^2+\Delta^2(\epsilon)} \quad (4)$$

$$\equiv\sqrt{(\epsilon-\mu)^2+n_0f_+^2(\epsilon)+m_0f_-^2(\epsilon)} \quad (5)$$

since $\Delta(\epsilon) \equiv \sqrt{n_0} f_+(\epsilon) + \sqrt{m_0} f_-(\epsilon)$ and $f_+(\epsilon) f_+(\epsilon) \equiv 0$ where $f_+(\epsilon)$ and $f_+(\epsilon)$ can be constructed as in [7], while $n_0(T) \equiv N_0(T)/L^d$ and $m_0(T) \equiv M_0(T)/L^d$ are the 2eCP and 2hCP number densities, respectively, of BE-condensed CP (i.e., with $K = 0$) bosons.

Minimizing F with respect to N_0 and M_0, while simultaneously fixing the total number N of electrons by introducing the electron chemical potential μ in the usual way, requires

$$\frac{\partial F}{\partial N_0} = 0, \qquad \frac{\partial F}{\partial M_0} = 0 \quad \text{and} \quad -\frac{\partial \Omega}{\partial \mu} = N. \tag{6}$$

This ensures an *equilibrium thermodynamic state* of the system with volume L^d at temperature T and chemical potential $\mu(T)$. The constancy of total electron number N imposed via the third relation in (6) guarantees gauge invariance, in contrast to BCS theory based as it is on an electron-*non*conserving variational trial wavefunction. Evidently, N includes both paired and unpaired CP electrons. The following relies on a so-called pseudo-Fermi energy $E_f \equiv \frac{1}{4}[E_+(0) + E_-(0)]$ implying $E_\pm(0) = 2E_f \pm \delta\varepsilon$ with $\delta\varepsilon$, usefully identified as the Debye energy $\hbar\omega_D$ in dealing with the well-known BCS two-parameter model interaction. The E_f merely serves as a convenient energy scale; it is not to be confused with the usual Fermi energy $E_F = \frac{1}{2} m v_F^2 \equiv k_B T_F$ where v_F and T_F are respectively the Fermi velocity and Fermi temperature. If n is the total number density of charge-carrier electrons of effective mass m, the Fermi energy $E_F = (\hbar^2/2m)(3\pi^2 n)^{2/3}$ in 3D, while E_f is similarly related to another density n_f, which serves to scale the ordinary electron number density n. The two quantities E_f and E_F, and consequently also n and n_f, coincide *only* when perfect 2e/2h-CP symmetry holds as in the BCS theory instance.

Some algebra then leads to the three coupled integral transcendental Eqs. (7)–(9) in [7]. These expressions can be rewritten [15] as two *"gap-like equations"* plus the single *"number equation"*

$$2n_B(T) - 2m_B(T) + n_f(T) = n \tag{7}$$

which guarantees charge conservation and thus gauge invariance. Here,

$$n_f(T) \equiv \int_0^\infty d\epsilon N(\epsilon) \left[1 - \frac{\epsilon - \mu}{E(\epsilon)} \tanh \frac{1}{2}\beta E(\epsilon)\right] \tag{8}$$

is the number density of unpaired electrons, $n \equiv N/L^d$ that of *all* electrons while $n_B(T)$ and $m_B(T)$ are, respectively, the number densities of 2e and 2hCPs in *all* bosonic states (both $K = 0$ as well as $K > 0$). The "complete" number equation (7) can be displayed more explicitly as

$$2n_0(T) + 2n_{B+}(T) - 2m_0(T) - 2m_{B+}(T) + n_f(T) = n \equiv N/L^d. \tag{9}$$

Here, $n_B(T) \equiv n_0(T) + n_{B+}(T)$ with

$$n_{B+}(T) \equiv \int_{0+}^\infty d\varepsilon M(\varepsilon) \big[\exp\beta\big\{E_+(0) + \varepsilon - 2\mu\big\} - 1\big]^{-1}$$

and similarly for $m_B(T)$. Clearly, $n_{B+}(T)$ and $m_{B+}(T)$ are precisely the number of "preformed" $K > 0$ 2eCPs and 2hCPs, respectively, entirely neglected in BCS theory. These CPs are noncondensed in contrast with the $K = 0$ CPs, which are BE condensed. The original crossover picture for unknowns $\Delta(T)$ and $\mu(T)$ is now supplemented by the central relation that unifies BCS and BEC

$$\Delta(T) = f\sqrt{n_0(T)} = f\sqrt{m_0(T)}.$$

All three functions $\Delta(T)$, $n_0(T)$ and $m_0(T)$ turn out to be familiar "half-bell-shaped" forms. Namely, they are zero above a certain critical temperature T_c, and rise monotonically upon cooling (lowering T) to maximum values $\Delta(0)$, $n_0(0)$ and $m_0(0)$ at $T = 0$. One clearly has the normalized relation

$$\Delta(T)/\Delta(0) = \sqrt{n_0(T)/n_0(0)} = \sqrt{m_0(T)/m_0(0)} \tag{10}$$

so that being BF-dynamics (i.e., in f) independent it applies to *either* superconductors or ultracold fermionic-atom superfluids.

This $\Delta(T)$ turns out to be [15] *precisely* the BCS energy gap, Eq. (3.27) in [5],

$$1 = \lambda \int_0^{\hbar\omega_D} d\xi \frac{1}{\sqrt{\xi^2 + \Delta^2(T)}} \tanh \frac{1}{2}\beta\sqrt{\xi^2 + \Delta^2(T)} \tag{11}$$

if the boson-fermion coupling f is made to correspond to $\sqrt{2V\hbar\omega_D}$ within the GBEC formalism. Here, $\xi \equiv \epsilon - \mu$, and $\lambda \equiv N(E_F)V = f^2 N(E_F)/2\delta\varepsilon$ while $\delta\varepsilon = \hbar\omega_D$ and provided $N(\epsilon)$ can be taken outside the integral sign in (11). Equation (11) follows from the GBEC formalism *provided one picks* $E_f = \mu$. This choice *cannot* be justified, to our knowledge, without assuming within the GBEC that $n_{B+}(T) = m_{B+}(T)$ *as well as* $n_0(T) = m_0(T)$, i.e., by explicitly recognizing the existence of 2hCPs along with 2eCPs and taking them in equal or half-and-half proportions.

4 Condensation Energy

The $T = 0$ condensation energy per unit volume according to the GBEC theory is

$$\frac{E_s - E_n}{L^d} = \frac{\Omega_s(T = 0) - \Omega_n(T = 0)}{L^d} \tag{12}$$

since for any T the Helmholtz free energy $F \equiv E - TS = \Omega + \mu N$, with S the entropy, and μ is the same for either superconducting s or normal n phases with internal energies E_s and E_n, respectively. Some algebra then allows one to show ([15], Sect. 6) that the GBEC formalism condensation

energy is *identical* for *any* coupling to that of BCS theory, Eq. (2.42) of [5], namely

$$\frac{E_s - E_n}{L^d} = N(0)(\hbar\omega_D)^2\left[1 - \sqrt{1 + (\Delta/\hbar\omega_D)^2}\,\right] \underset{\lambda\to 0}{\longrightarrow} -\frac{1}{2}N(0)\Delta^2\left[1 - \frac{1}{4}\left(\frac{\Delta}{\hbar\omega_D}\right)^2 + O\left(\frac{\Delta}{\hbar\omega_D}\right)^4\right] \tag{13}$$

whenever there is perfect 2e- and 2h-CP symmetry. The energy E_s, associated with the expectation value of the BCS trial wavefunction gives a rigorous upper bound to the exact ground-state energy of the BCS Hamiltonian. This equivalence indicates that, as in the GBEC formalism, there are no pair-pair interactions in the BCS theory either; this is evident from Hamiltonians (2) and (3) as well as the well-known BCS Hamiltonian.

5 Results

Numerical elimination of $\mu(T, n)$ has shown that, in addition to a normal phase defined by $n_0(T, n) = m_0(T, n) = 0$ at high T, *three* gauge-invariant condensed phases appear at lower temperatures: two pure phases of 2eCP- and 2hCP-BE-condensed states and one mixed phase with arbitrary proportions of both kinds of BE-condensed CPs. Figure 1 shows the phase boundaries for several sets of BCS interaction parameters, including the set $\lambda = 1/2$ and $\hbar\omega_D = 10^{-3}E_F$ used extensively in [7, 8]. Clearly, the pure 2eCP-GBEC phase rises *linearly* abruptly from zero in sharp contrast to the well-known *exponential* rise of BCS theory; inset of Fig. 1.

Finally, the GBEC results would seem to suggest, at least for $n/n_f \geq 1$, a possible explanation, to be explored in the near future, for the intriguing experimental fact emphasized by Hirsch ([16], § 6) that regardless of whether charge carriers *above* T_c are holes or electrons, they are always electrons *below* T_c.

6 Conclusions

The GBEC formalism introduced gives four gauge-invariant phases, three condensed along with the normal one, and predicts the observed *linear and abrupt* rise of T_c with charge-carrier density (e.g., doping, as in cuprates) in contrast with the *exponentially smooth* rise of BCS theory. The hopefully practical outcome of the BCS-BEC unification ensuing from that formalism is *enhancement* in T_c by up to *four* orders-of-magnitude in 3D. These enhancements fall within empirical ranges for 2D and 3D "exotic" SCs [17, 18], whereas BCS T_c values remain much lower. The latter are within the empirical ranges for conventional, elemental SCs using

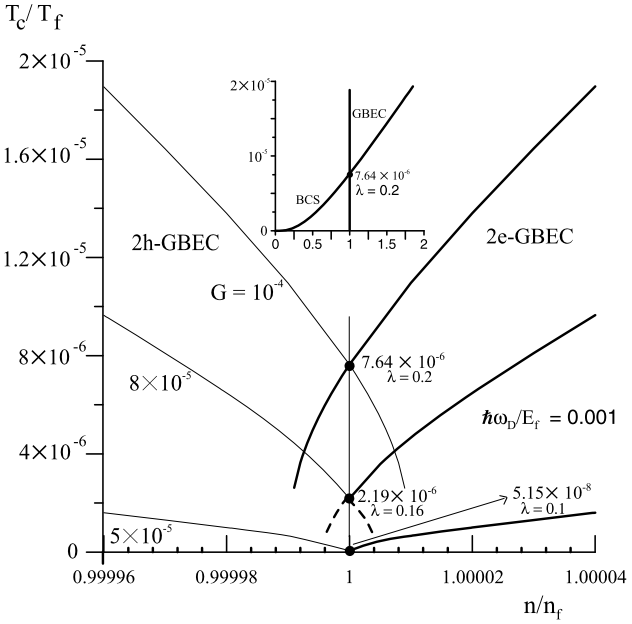

Fig. 1 Phase boundaries of pure GBEC of 2hCPs (*thin curve*) and of 2eCPs (*thick full curve*) for several values of BCS model-interaction coupling λ that creates the CPs. Note linear abrupt rise of T_c in dimensionless charge-carrier densities n/n_f with n_f as defined in text, contrasted with the exponential rise in n/n_f of BCS theory, *Inset*. *Dots* represent BCS T_c values calculated with BCS weak-coupling expression $T_c = 1.134\hbar\omega_D \exp(-1/\lambda)$

standard interaction-parameter values. Lastly, room temperature superconductivity is possible [19] for a material with a Fermi temperature $T_F \leq 10^3 K$, with the *same* electron-phonon model-interaction parameters used in BCS theory for conventional SCs.

Acknowledgements MdeLl thanks UNAM-DGAPA-PAPIIT (Mexico) for its support via Grant IN102011.

References

1. Micnas, R., Robaszkiewicz, S., Bussmann-Holder, A.: Struct. Bond. **13**, 114 (2005) and refs. therein
2. Friedberg, R., Lee, T.D., Ren, H.-C.: Phys. Rev. B **45**, 10732 (1992) and refs. therein
3. de Llano, M., Tolmachev, V.V.: Ukr. J. Phys. **55**, 79 (2010) and refs. therein
4. de Llano, M., Annett, J.F.: Int. J. Mod. Phys. B **21**, 3657 (2007)
5. Bardeen, J., Cooper, L.N., Schrieffer, J.R.: Phys. Rev. **108**, 1175 (1957)
6. de Llano, M., Sevilla, F.J., Tapia, S.: Int. J. Mod. Phys. B **20**, 2931 (2006)
7. Tolmachev, V.V.: Phys. Lett. A **266**, 400 (2000)
8. de Llano, M., Tolmachev, V.V.: Physica A **317**, 546 (2003)
9. Mamedov, T.A., de Llano, M.: J. Phys. Soc. Jpn. **79**, 044706 (2010)
10. Mamedov, T.A., de Llano, M.: J. Phys. Soc. Jpn. **80**, 074718 (2011)
11. Zubarev, D.N.: Sov. Phys. Usp. **3**, 320 (1960). English trans. of Usp. Fiz. Nauk **71** (1060) 71

12. Bogoluibov, N.N.: Statistical Physics and Quantum Field Theory. Nauka, Moscow (1972)
13. Tyablikov, S.V.: Methods in the Quantum Theory of Magnetism. Plenum, New York (1967)
14. Bogoliubov, N.N.: J. Phys. (USSR) **11**, 23 (1947)
15. Adhikari, S.K., de Llano, M., Sevilla, F.J., Solís, M.A., Valencia, J.J.: Physica C **453**, 37 (2007)
16. Hirsch, J.: Int. J. Mod. Phys. B **23**, 3035 (2009)
17. Uemura, Y.J.: J. Phys. Condens. Matter **16**, S4515 (2004)
18. Uemura, Y.J.: Physica B **374–375**, 1 (2006)
19. Kresin, V.Z., Wolf, S.A.: Rev. Mod. Phys. **81**, 481 (2009)