Lattice of superconducting multilayer nanotubes as ideal high-temperature superconductor

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Abstract: Combining Little's and Ginzburg's ideas with recent progress in nanotubes research, a novel type of material is advanced as a perspective high-\(T_c\) superconductor on base of a close-packed lattice of quasi-1D superconducting nanotubes. Idea is offered that superconducting coaxial multilayer nanotubes of the correlation length in diameter is an ideal and natural trap for pinning of Abrikosov vortex. Nanotube should be layered superconductor, such as LuNiBC. Mechanism of superconductivity was proposed and substantiated quantitatively on base of a whispering mode, which is shown to be responsible for a strong enhancement of electron-phonon interaction and for an increase of critical temperature. Nanocomposite built from such quasi-1D nanotubes when coinciding with vortex lattice provides ideal conditions for the pinning, resonance, distortion, ordering and Little-Parks effects, the joint action of which is suggested to result in synergistic effect increasing the superconductivity. Such quasi-1D nanotubular crystal is proposed to synthesize by template approach using zeolite-like membrane.

Keywords: high-\(T_c\) superconductivity, nanotube, whispering mode, nanocomposite.

Paper received 24.07.00; revised manuscript received 08.09.00; accepted for publication 12.12.00.

1. Introduction

Breakthrough in the challenging problem of high-temperature superconductivity (HTSC) has been triggered by Bednorz and Muller’s discovery of layered LBSCO ceramics. Just so a next step toward in the room-temperature superconductivity requires a synthesis of new materials. For this purpose a leading idea is requested. In Ginzburg opinion «layered compounds and sandwiches of dielectric - metal - dielectric type are the most perspective in respect to HTSC. To produce them is natural to use an atomic layer-by-layer technique» [1].

What all the HTSC ceramics, such as perovskites, borocarbide intermetallides, and intercalated dichalcogenides have in common is that they consist of alternated atomic both super-conducting (SC) layers (CuO\(_6\), NiB\(_6\), MoS\(_2\), etc.) and metallic (La, K, etc.) or dielectric (LuC, etc.) layers, which are the genuine atomic-scale sandwiches. Hence the anisotropic layered 2D structure appear to play a key role in HTSC, ensuring both a strong electron correlation in the SC-layers to create a coherent quantum states, and a weak interaction between superconducting and dielectric layers to prevent a SC-state destroying.

Long years ago Little and Parks have shown that in thin SC-cylindric Sn quasi-1D tube of diameter \(d\) in comparison with plane Sn 2D film of the same thickness \(h\) a critical temperature \(T_c\) raises on some oscillated value \(\Delta T_c(H)\) provided that \(d \leq \xi(T)\) and \(d \leq \lambda(T)\), where \(\xi\) is the electron correlation length and \(\lambda\) is the field penetration depth [2].

This effect depends on the diameter as \(\Delta T_c \sim 1/d\) pointing on small nanotube (NT) as promising high-\(T_c\) superconductor. Synthesis of carbon NT (C-NT) by Iijima [3] in a substance enough to use for further studies has stimulated great interest in its electronic and SC-properties.

Recently Bockrath \textit{et al.} [4] and Tans \textit{et al.} [5] measuring electroconductivity of C-NTs and their bundles have shown that electrons in NTs are spatially extended over an appreciable length along the tube indicating the nanotubes by ~1\(\mu\)m and more length as beautiful quantum wires (see Deccer’s review [6]), that is necessary (but not sufficient) condition for electron pairing. Bachtiold \textit{et al.} [7] have found the oscillating behavior of magnetoresistance in N-NT to be phase dependent and caused by a quantum interference between partial electron waves encircling NT circle in opposite directions (the Aaronov-Bohm effect). Chernoza-
V.V. Pokropivny et al.: Lattice of superconducting multilayer nanotubes ...

tonsky has suggested idea of giant resonance in quantum NT rings, when the quantized geometric electron movement around a ring is covered by a quantized electron movement in magnetic field [8]. Ordering both of vortices and artificial pinning centers is a factor favored superconductivity, as for example, in quasi-1D crystal of plane-packed TCNO molecules columns. Critical current density \( J_c \) in superconducting Pb/Ge multilayers is also strongly enhanced by perforating of submicron holes in kind of anti-pinning lattice of parameter \( L/L^\ast \gg 1 \) [9]. \( T_c \) of superconducting \( \text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4 \) film in comparison with volume one was shown to increase twice, from 25K to 49K, that is explained by distortion of deformed unit cells in film [10]. Search in ISI Database at the end of 1999 year has given zero documents on the key words «superconducting nanotube» and 9 papers on the key words «nanotube and superconductivity». Proximity induced superconductivity in both single C-NTs and their crystalline ropes below 1K was observed [11]. The highest citation index of ref. Lee et al.[12] indicate that doping of C-NTs bundles by metals (K, Ta, etc.) is generally accepted as perspective and promising direction. For example, TaC nanorodeds encapsulated in C-NTs of ?14 nm in diameter were fabricated with \( T_c = 9.7 \)K [13] but no essential difference from the volume \( T_c \) was obtained. One can observe an intensive search of SC-NTs but without pure success until now.

In this paper we advanced a principally new direction in HTSC based on a lattice of quasi-1D nanotubes rather then thin but still 3D nanorodes.

2. Nanotube composite

Accounting a geometrical similarity between Abrikosov vortex and NT one can conclude that nanotube is genuine trap for ideal pinning of vortices[14]. Layered 2D structure mismatches geometrically with a 1D vortex lattice, although intuitively it is necessary. So the idea arrive to wrap HTSC-sandwich into the cylindric multilayer HTSC-nanotube, the examples of which is presented in Fig. Also we may expect an amplification of superconductivity due to ordering of SC-NTs into a close packed triangular lattice. Free energy minimum condition of interacting vortices lattice gives the minimum distance between vortex, \( L \equiv 2\lambda \). The distortion effect is expected to reveal itself in the bending layers of SC-NTs too due to the difference between inner and outer radius of SC-layer \( \Delta R = c \), where \( c \) is a parameter of unit cell.

Summary analysis of the specified effects gives the basis to assume, that the composite structure in kind of the close-packed triangular lattice (with lattice parameter \( L \approx 2\lambda \)) of the super-conducting sandwich-type coaxial multilayer nanotubes by diameter \( d \approx \xi \) can serve as ideal trap for pinning of an equilibrium vortex lattice. In addition, a joint action of the pinning, resonance, ordering, distortion and Little-Parks effects in the quasi-1D HTSC-nanotubular crystal should cause a synergetic effect increased the superconductivity current \( J_c \) and the critical temperature \( T_c \) [14].

We shall notice that usual objection concerning impossibility of 1D superconductivity is not so hard. Even «for wires of ~10nm thickness a fluctuating break of chain is practically impossible and SC-current would not decay» [1,15]. Furthermore «nanotubes appear to be only weakly sensitive to local defects because its disordering effect will be averaged out over the whole tube circumference due to the doughnut-shaped electron wave functions» [6]. Such a nanocomposite combine three classes of perspective superconductors, namely: HTSC-ceramics, quasi-1D fibers proposed by Little [2] and quasi-2D sandwiches proposed by Ginzburg [1,15].

3. HTSC mechanism on whispering mode

Main change under wrapping of layer in tube lie in a lowering of dimensionality 2D31D followed by a change of symmetry, that causes reorganization of electron and phonon spectra. In phonon spectrum of NTs a peculiar gallery of circular modes came into existence. For example, a breathing \( A_{1g} \) mode and whispering \( E_{2g} \) mode with frequencies \( \omega_{A_{1g}} = 165 \) cm\(^{-1} \) and \( \omega_{E_{2g}} = 22 \) cm\(^{-1} \) respectively arises instead of \( A_{2g} \) and \( E_{1u} \) modes in graphite under the change of \( D_{sh} \) [4] symmetry of graphite into \( D_{6h} \) or \( D_{4h} \) symmetry of N-NT on evidence derived by Ecklund et al.[16] from NTs Raman spectra. The frequencies of these modes are few order of magnitude less than other optical modes and its intensity strongly depends on diameter of NT under law \( \sim 1/d \).

In electron spectrum of nanotubes a series of narrow spikes in electron density of states \( N(E) \) appears below \( (E_{\tilde{1}}, E_{\tilde{2}},...) \) and higher \( (E_{\tilde{2}}, E_{\tilde{2}},...) \) of Fermi level \( E_F \) separated by gap \( \Delta \sim 1 \) eV [4, 6]. Sharp Van Hove singularities show up in the \( N(E) \) of NT. As stressed by Bok and Bouvier [17] the model of 2D itinerant electrons in presence of the singularities already explained a certain number of experimental facts in HTSC, i.e. high-\( T_c \), anomalous isotope effect, marginal Fermi liquid effects and the very small values of \( \lambda \). Diameter-selective resonant Raman scattering is a direct consequence of the 1D electronic quantum-confinement in NT. Numerous Raman peaks were identified with vibrational modes pointing on its phonon nature. In particular the lowest energy transition \( E_{\tilde{1}} \rightarrow E_{\tilde{2}} \) is associated with the lowest frequency of nanotube vibrations \( \omega_{E} \) [16], which in a language of vibrational theory corresponds to a whispering mode.

In superconducting NT only subbands crossed Fermi level influence on a density of electronic state at Fermi level \( N(0) \) and \( \Delta_{ab} \). Hence the whispering mode is precisely the phonon vibration, which is responsible for superconductivity in framework of a phonon mechanism of pairing.

Whispering modes actually are very suitable for the phonon pairing electrons because: 1) their frequency is relatively lower (with two vibration periods per circle), 2) their decay is relatively the lowest (given the largest signal from resonant Raman scattering [16]), and 3) their coherent vibration of atoms on diameter-opposite walls of the NT correspond ideally for formation of coherent states of electron pairs with opposite momenta \((\mathbf{k}, \mathbf{k})\). Furthermore if we assume a macroscopic wave function of the Cooper pair is of whispering mode type, \( \psi = A \sin(2\phi) = \)
\[ = A \cdot \exp(i \ 2\phi), \] then a slow variation of amplitude \( A \) and angle \( \phi \) in electronic scale along NT-ring means simply a condition of the Bose-Einstein condensation.

Moreover, the low-frequency whispering mode expected in 1D HTSC-nanotubes one can consider as softening of phonon spectrum, which results in increasing of a constant of electron-phonon (e-p) interaction \( \lambda_{ph} = N(0) V \), where in accordance with McMillan relation \( V = < F_0 > / M < a^2 > \) is the energy of \( e-p \) interaction of the Cooper pair, \( F_0 \) is a matrix element of electron-ion interaction, \( M \) is an ion mass, and \( < a^2 > \) is a mean square of phonon frequency [15].

The original mechanism of HTSC on the whispering mode is possible to suggest. Relatively low-frequency whispering vibrations provide a relatively high-energy interaction of Cooper pair \( V \). Furthermore coherent vibrations are responsible for symmetric dynamics distortion of crystal structure, the elastic energy of which is compensated by arising of charge or spin density waves and narrow subbands. The overlapping of the subbands give rise to augmentation of the electron density \( N(0) \). As a consequence both factors will cause the constant of \( e-p \) interaction \( \lambda_{ph} \) and hence the critical temperature \( T_c \), to increase.

Nanotube diameter is an additional to other parameters which governs both the phonon spectrum [16] and the density of electron states giving rise to increase \( T_c \) and \( J_c \).

Chiral angle of NT may be the another one. In chiral NTs a transport of the Cooper pair is possible along the NT axis. It is quite possible that the chiral high-\( T_c \) SC-NTs should be the most effective superconductors.

4. \( T_c \) estimation

We estimate the effect of a critical temperature increase expected under wrapping of high-\( T_c \) SC-film into high-\( T_c \) SC-nanotube in framework of a phonon mechanism of Cooper pairing.

For illustration we choose the new class of a borocarbide HTSC intermetallics of a LuNiB_2C type with \( T_c = 16.6 \) K synthesized by Cava et al. [18] The LuNiBC comprises alternated SC-layers of covalent-bonded NiB_4 tetrahedrons and dielectric ion-bonded LuC layers of a NaCl type. Mattheiss et al. [19] by tight binding method has shown that superconductivity of LuNiBC is caused by interaction of electrons with optical breathing phonons of \( A_{1g} \) symmetry. Pickett and Singh [20] have shown that superconductivity arises from the formation of a mixed conduction band with peak of Ni d-electron density at Fermi level \( N(0) \), which results in enhancement of \( e-p \) interaction. However the frequency of Raman active \( A_{1g} \) mode 855 cm\(^{-1}\) do not agree with estimated value of the constant \( \lambda_{ph} = 2.6 \), that requires a more soft mode [20].

Let’s estimate the frequency of a whispering mode in classical approach for a monolayer of normal HTSC nanotubes by thickness of \( h = n = 7.75 \) Å and by radius of \( R = 41 \) Å (Fig.). For thin cylinder by thickness \( h \) and radius \( R \) the frequency of a whispering mode was determined in early 1871 by Hoppe [21], \( \omega_0 = h / R^2 \cdot \sqrt{95 E(p)} \), where \( E \) is Young’s modulus, \( \rho \) is a density. Supposing \( E \equiv 500 \text{GPa} \) and \( \rho = 8974 \text{kg/m}^3 \) we shall receive \( \omega_0 \equiv 15.4 \text{cm}^{-1} \equiv 1.91 \text{meV} \).

Constant of \( e-p \) interaction in accord with ref.[20] is equal to \( \lambda_{ph} = \omega_0 / \omega_{ph} \), where the plasmon frequency for LuNiBC equals \( \omega_{ph} = 31 \) meV. In case of the whispering mode \( \omega_{ph} = \omega_0 \) for the taken nanotubes we obtain \( \lambda_{ph} = 268.5 \), that is \( \sim 100 \) times greater than a volume one.

Let’s estimate an increase of \( T_c \). Using again the data \( \theta \equiv 130.4 \) K and \( \mu^{*} = 0.15 \) from ref.[20], we obtain from the Allen and Dynes formula [15] \( T_c = \theta \cdot \exp[-(1 + \lambda_{ph}) / (\lambda_{ph} - \mu^{*})] \equiv 47.8 \) K, and from the modified Eliashberg formula [15] \( T_c = \theta \cdot (\lambda_{ph})^{1/2} \equiv 2137 \) K, that in 1.6 – 71.2 times exceeds the volume one. \( T_c = 30 \) K under \( \lambda_{ph} = 2.6 \).

In spite of tentative approximation of these evaluations nevertheless a main conclusion that transition of SC layer into a nanotubular state results in strong amplification of electron-phonon interaction and in increase of critical temperature seems to be substantiated sufficiently to stimulate interest of technologists in synthesis of such nanocomposites.

5. Fabrication way

At present time noncarbon nanotubes on base of BN, BNC, B_4C, MoS_2, etc. were synthesized except carbon NTs, but no successive attempts are known for us to fabricate superconducting nanotubes up to date. However the principal opportunities exist for this purpose.

Firstly, many physical and chemical vapor deposition techniques have been developed to fabricate SC-films, including laser evaporation or ablation, plasma or ion beam deposition.

\( SQO, 3(4), 2000 \)
sputtering, electron beam or molecular beam epitaxy, thermal evaporation, etc. Secondly, nanotubes and their regular lattices can be prepared on base of metals, semiconductors, and any other materials, using a membrane-based synthetic approach developed by Martin [22]. Perhaps a nanotube lattice on base of superconducting materials may assumed to be made by the same manner.

Nanocomposite shown in Fig. can assumed to be produced by using as a substrate a zeolite-like membrane comprised a lattice of cylindrical nanopores of ~2Å in diameter separated by ~2Å lattice parameter. On the inner surface of the template nanochannels the high-T SC-cover should be deposited. It believed to be growth epitaxially in form of nanotubes. Reality of this approach was demonstrated recently by Tang et al. [23], who have produced single-walled C-NTs within channels of zeolite crystals. Also Li et al. [24] has grown highly-ordered arrays of parallel C-NTs by three-stage fabrication process including (a) anodization of Al in oxalic acid, that forms a hexagonal close-packed nanochannel alumina template; (b) electrochemical deposition of Co catalyst into the bottom of the template channels; (c) growth of C-NTs within the nanochannel by pyrolysis of acetylene.

Relatively weak Coulomb interaction between layers in SC-rare-earth borocarbides promotes an insertion of additional layers resulting in a known series of related homologous compounds of (LuC2)(Ni2B2) type. This key property also permits atoms to easily incorporate in to subsequent outer layer and to form multiwalled NTs with different number of unit cells, as shown in Fig.

Following restrictions is possible to specify for sizes of SC-NTs from below and from above: 1) h > 10 nm to remove (a) influence of fluctuations at 2D → 1D transition, and (b) amorphisation of HTS-lattice at the transition in nanocrystalline state; a greater thickness is not required because only external shells participate in conductivity [7]; 2) L ≈ 2Å to ensure Cooper pairing and do not entail a reverse transition 1D → 2D.

It should be emphasized that quasi-1D lattice of layered SC-nanotubes differs fundamentally both from 2D sandwich film and 3D lattice of cylindrical SC-nanorodes, that is the principal distinguishing feature of SC-nanotube composite proposed here.

Fabrication of such a nanotube composite is extremely difficult, but it is just the difficulty which would be a payment for solution of the paramount importance problem considered.

References