

CONFERENCES AND SYMPOSIA

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Scientific session of the Physical Sciences Division of the Russian Academy of Sciences "Room temperature superconductivity" (4 October 2007)

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On 4 October, 2007, the scientific session of the Division of Physical Sciences of the Russian Academy of Sciences on room-temperature superconductivity was held at the conference hall of the Lebedev Physics Institute, Russian Academy of Sciences. The following reports were made at this session:

1. **Maksimov E G** (Lebedev Physics Institute, Russian Academy of Sciences, Moscow). "Room-temperature superconductivity: myth or reality?";

2. **Božović I** (Brookhaven National Laboratory, USA). "Experiments with atomically smooth thin films of cuprate superconductors: strong electron – phonon coupling and other surprises";

3. **Antipov E V, Abakumov A M** (Moscow State University, Chemical Department, Moscow). "Structural design of superconductors based on complex copper oxides";

4. **Kopaev Yu V, Belyavskii V I, Kapaev V V** (Lebedev Physics Institute, Russian Academy of Sciences, Moscow). "With cuprate luggage to room-temperature superconductivity."

An abridged version of these reports is given below.

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Room-temperature superconductivity: myth or reality?

E G Maksimov

The problem of high-temperature superconductivity (HTSC) is considered to have appeared following the pioneering works by Ginzburg [1] and Little [2], who showed the possibility of nonphonon superconductivity mechanisms due to the interaction of electrons with electron excitations (excitons). The energy of these excitations is much higher than the phonon energy, which can result in substantially higher superconducting transition temperatures. Although this work attracted the particular interest of experts in the superconductivity physics, it did not cause a serious boom in HTSC investigations. Moreover, a number of prominent scientists demonstrated scepticism about Ginzburg's and Little's ideas, and some of them published works (see, e.g., [3]) stating that high values of T_c cannot be reached in principle for any superconductivity mechanism at all. This statement followed from the inequality for static permittivity $\varepsilon(\mathbf{q}, 0) > 0$, which was regarded in [3] as a system stability criterion. However, Kirzhnits [4] long ago rigorously proved that the condition $\varepsilon(\mathbf{q}, 0) > 0$ is not a stability criterion if charge density waves occur in the system. The corresponding condition is written as the inequality $1/\varepsilon(\mathbf{q}, 0) < 1$, which demonstrates that the situation where $\varepsilon(\mathbf{q}, 0) > 1$ or $\varepsilon(\mathbf{q}, 0) < 0$ can occur in a stable system. Nevertheless, Anderson [5] again repeats the erroneous arguments regarding the possible nature of high-temperature superconductivity related to the inequality $\varepsilon(\mathbf{q}, 0) > 0$. In the report presented in the session, this issue was discussed in detail; however, we do not dwell on this point, since we have recently published the relevant paper in *Physics – Uspekhi* ([6]).

Generally speaking, the appearance of the problem of high-temperature superconductivity should be dated 1946 rather than 1964. In that year, Ogg from Stanford University [7] detected superconductivity at a temperature $T_c \approx -90\,^\circ\mathrm{C}$. His work was titled "Bose – Einstein Condensation of Trapped Electron Pairs. Phase Separation and Superconductivity of Metal – Ammonia Solutions." If the last words in this title were substituted, for instance, by superconducting cuprates or high-temperature superconductors, that work would be similar to numerous recent HTSC studies. According to a legend existing in the physics community, Ogg's works were neither recognized nor supported by most of his colleagues. The degree of this nonrecognition was such that, according to this legend, Ogg committed suicide. It is now clear with some degree of certainty that Ogg was likely to have observed the transformation of a metal – ammonia solution into a metallic state (in which the resistance decreased by several orders of magnitude) rather than into a superconducting state. Another point is more important: in 1946, long before the appearance of works by Bardeen, Cooper, and Schrieffer [8] and Schafroth's group [9] regarding the formation of real electron pairs followed by Bose condensation, Ogg proposed a plausible explanation of superconductivity in metallic systems.

The boom in the problem of high-temperature superconductivity began with the work by Bednortz and Müller [10], in which they detected superconductivity in $La_{1-x}Ba_xCuO_4$ compounds at a temperature $T_c \approx 30$ K. The discussion of the consequences of this boom for the problem of HTSC is beyond the scope of this work; such a discussion is given in our review [11], for example. Here, we only dwell on some conclusions that are important for the

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problem of room-temperature superconductivity. First, this concerns the nature of the superconducting state in cuprates. In most metals, the transition to a superconducting state is known to be well described in terms of the Bardeen – Cooper – Schrieffer (BCS) model [8]. This means that electrons near the Fermi surface are coupled into Cooper pairs, which form something that resembles Bose condensation, due to the electron – electron attraction. After discovering superconducting cuprates with the transition temperature $T_c \approx 30$ K, researchers proposed a number of scenarios in which a superconducting state appears due to various mechanisms other than the formation of Cooper pairs. We do not discuss these mechanisms here because it is now obvious that superconductivity in cuprates is based on the same phenomenon as the appearance of Cooper pairs. This was most clearly demonstrated by angle-resolved photoemission spectroscopy [12]. The authors of [12] proved that the electron excitations in the superconducting state of these systems represent so-called Bogoliubov quasiparticles, i.e., a coherent mixture of electrons and holes, which follows from the BCS model. Of course, the superconductivity in HTSC cuprates is not described by the simple BCS model, which uses well-determined electron quasiparticle excitations weakly interacting with each other. Superconducting cuprates have a system of strongly interacting electrons subjected to damping. The wave function of electron pairs is anisotropic, in contrast to the wave function of the simple BCS model, which involves the isotropic s pairing. These differences should be taken into account in calculating or estimating T_c, but they are not critical for the purposes of this report.

The only question that is challenging for both the problem of superconductivity in cuprates and the discussion of the possibility of room-temperature superconductivity is the nature of the interaction that results in electron pairing into Cooper pairs. Broadly speaking, only two possibilities exist. First, these can be the well-known electron – phonon and electron – exciton interactions. The other possibility is provided by magnetic interactions between electrons. Such interactions, for example, can result in various magnetically ordered states. The critical magnetic transition temperatures can be rather high: in many cases, they are well above both the superconducting transition temperature T_c in cuprates and room temperature. In discussing the possibilities of achieving high T_c for a superconducting transition due to magnetic interactions, the following points must be taken into account. The magnetic transition temperature T_M depends on the electron – electron exchange interaction constant J,

$$T_M \approx J . \tag{1}$$

But the superconducting transition temperature depends directly not on J but on the dimensionless constant $g = N(0)J$, where $N(0)$ is the density of electron states at the Fermi surface. The corresponding dependence has the form

$$T_c = \varepsilon_F \exp\left(-\frac{1}{N(0)J}\right), \tag{2}$$

where ε_F is the Fermi energy.

In the Hubbard model, which is often used to describe systems with strong exchange – correlation effects, the exchange constant can be written as

$$J = t\,\frac{t}{U}, \tag{3}$$

where t is the overlap integral and U is the on-site Coulomb repulsion. According to estimates obtained for the compound La_2CuO_4, which is an insulator and antiferromagnet in the undoped state, the exchange constant is $J \approx 0.1$ eV ≈ 1000 K. It is then not surprising that the antiferromagnetic transition temperature in this compound is relatively high ($T_M \approx 230$ K). The dimensionless coupling constant g in this model can be written as

$$g = N(0)\,t\,\frac{t}{U} \approx \frac{t}{ZU}, \tag{4}$$

where Z is the number of the nearest neighbors. In this case, g is of the order of 0.1, and the resulting value of T_c is well below 100 K and, all the more, below room temperature at any reasonable value of the prefactor in Eqn (2) ($\varepsilon_F \sim t$). Therefore, hereafter, we restrict ourselves to the discussion of the possibilities of room-temperature superconductivity in terms of the standard electron – phonon interaction (EPI) and the BCS model. As Kikoin once wrote, [1]

Until a single vibration
Exists in earthly world
And powerful workstation
Gives us its wireless cord,
Until our Troika lashes,
Until our brains progress,
The pairs will couple in Russia
By means of BCS!

The maximum value of T_c characteristic of a system with the electron – phonon superconducting mechanism was found in the compound MgB_2 (≈ 40 K). The question arises: Is it possible to increase this value of T_c in terms of the electron – phonon mechanism? The modern theory of solids can answer this question using a rigorous quantitative analysis of electron – phonon interaction effects in metals. For this analysis, the electron-density functional method can be used to calculate the electron and phonon spectra of metals and matrix elements of the electron – phonon interaction. The corresponding calculations are described in detail, for example, in our reviews [13, 14] published in *Physics – Uspekhi*.

In a system with electron – phonon interaction, the superconducting transition temperature can be written as

$$T_c = \frac{\omega_{ln}}{1.4}\,\exp\left(\frac{1+\lambda}{\lambda-\mu^*}\right), \tag{5}$$

where μ^* is the Coulomb pseudopotential that describes the contribution of the Coulomb interaction to superconductivity. In most standard metals, this contribution is rather small ($\mu^* \approx 0.1$) and may be neglected when the problem of EPI-induced high-temperature superconductivity is considered. The electron – phonon coupling constant λ and the prefactor ω_{ln} are expressed using the Eliashberg function $\alpha^2(\omega)F(\omega)$ as

$$\lambda = 2\int_0^\infty \frac{\alpha^2(\omega)F(\omega)}{\omega}\,\mathrm{d}\omega, \tag{6}$$

and

$$\omega_{ln} = \frac{2}{\lambda}\int_0^\infty \alpha^2(\omega)F(\omega)\ln(\omega)\,\mathrm{d}\omega . \tag{7}$$

[1] Translated by K A Kikoin, the author of the poem "How Hi T_c was searched for in Russia," published in Russian in: *The Seminar: Papers and Reports*, compiled by B M Bolotovskii and Yu M Bruk (Moscow, Izd. Fiziko-Matematicheskoi Literatury, 2006), p. 245.

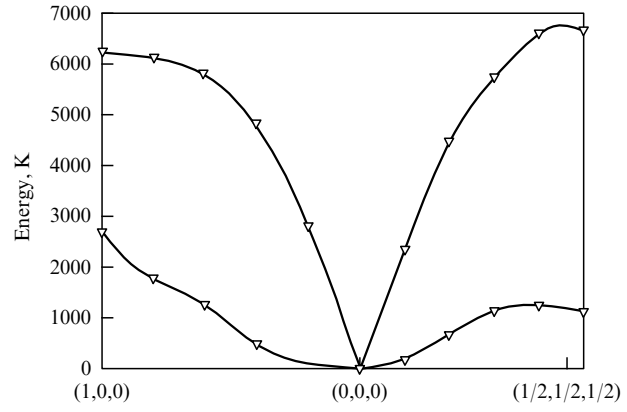

Figure 1. Calculated phonon frequencies of metallic fcc hydrogen at $r_s = 1$.

In turn, the Eliashberg function can be represented in the form

$$\alpha^2(\omega)\,F(\omega) = \frac{1}{N(0)} \sum_{k,q,i} \frac{|\,g^{\lambda,i}_{k,k+q}|^2}{\omega_{q\lambda} M_i}\, \delta(\varepsilon_k - \varepsilon_F) \times \delta(\varepsilon_{k+q} - \varepsilon_F)\,\delta(\omega - \omega_{q\lambda})\,, \qquad (8)$$

where $g^{\lambda,i}_{k,k+q}$ is the EPI matrix element, λ is the phonon mode index, and i is the atom number in the unit cell. All the quantities entering the expression for $\alpha^2(\omega)\,F(\omega)$ are calculated using the density functional method; hence, T_c can easily be calculated without using any fitting parameters.

As an example of this analysis, we note paper [15], where the properties of metallic hydrogen at high pressures were calculated. Figure 1 shows the phonon frequencies calculated in a face-centered cubic (fcc) structure at the pressure $p \approx 20$ Mbar. The energy of the transverse acoustic mode is seen to be substantially lower than that of the longitudinal mode; i.e., the transverse mode is rather 'soft.' The importance of soft modes for high values of T_c was repeatedly discussed in works dealing with superconductivity physics. This can be understood from Fig. 2, which shows the spectral density of the electron–phonon interaction (Eliashberg function). It is seen that the Eliashberg function intensity at the energies corresponding to the transverse mode (1000–2000 K) is significantly higher than in the longitudinal-mode energy range (near 6000 K). The conclusion regarding the importance of soft modes for high values of T_c was previously deduced from the formula

$$\lambda = \frac{N(0)\langle I^2\rangle}{M\langle\omega^2\rangle} \qquad (9)$$

for the electron–phonon coupling constant λ. As follows from this formula, λ increases with decreasing $\langle\omega^2\rangle$, i.e., for soft phonon modes. We note that the transverse mode is soft only in a conventional sense, because it is small compared to the longitudinal mode, but its absolute values ($\sim$ 1000–2000 K) are not small compared to room temperature. Our calculations with Eqns (5)–(7) for metallic hydrogen give $\lambda = 6.1$ and, correspondingly, $T_c = 600$K, which is well above room temperature [15]. Of course, it is impossible to use the superconductivity of metallic hydrogen in practice, and a pressure of 20 Mbar cannot be generated under laboratory conditions.

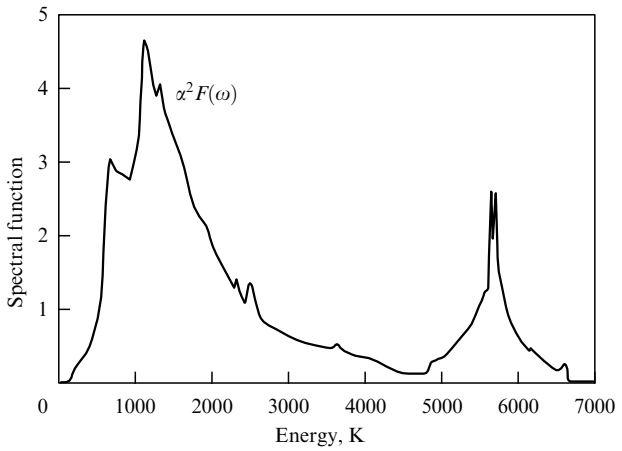

Figure 2. Calculated spectral density of the electron–phonon interaction in metallic fcc hydrogen at $r_s = 1$.

Pickett [16] comprehensively analyzed the possibilities of a significant increase in T_c due to the electron–phonon interaction in systems such as MgB_2 and boron-doped diamond. The analysis results for MgB_2 demonstrate that electrons in this compound strongly interact with only two phonon modes (i.e., bending modes with $\omega_a \approx 20$–25 meV) of the nine modes existing in this compound. Moreover, this interaction is bounded by small values of wave vectors **q** (12% of the total Brillouin zone). Nevertheless, $T_c = 40$ K for MgB_2! The question arises: What values of T_c could be achieved if the interaction of electrons with all modes was strong? In this case, the EPI constant could be $\lambda = 22.5$. In the limit of high values of λ, T_c can be written as

$$T_c = 0.18\sqrt{\lambda\langle\omega^2\rangle} = 0.18\int_0^\infty \omega\alpha^2(\omega)\,F(\omega)\,\mathrm{d}\omega\,. \qquad (10)$$

As was shown in [16], at $\lambda = 22.5$ K, temperature T_c would reach 300–430 K! The expression for $\lambda\langle\omega^2\rangle$ can be rewritten as

$$\lambda\langle\omega^2\rangle = \sum_i \frac{N_i(0)\langle I_i^2\rangle}{M_i}\,, \qquad (11)$$

where $\langle I_i^2\rangle$ is the EPI matrix element on the Fermi surface,

$$\langle I_i^2\rangle = \sum_{n,k} \left|\left\langle nk\left|\frac{\partial V_{ie}(\mathbf{r}-\mathbf{R}_i)}{\partial \mathbf{R}_i}\right|nk\right\rangle\right|^2 \delta(\varepsilon_k - \varepsilon_F)\,. \qquad (12)$$

Here, $V_{ie}(\mathbf{r} - \mathbf{R}_i)$ is the self-consistent ion potential. Pickett [16] also showed that the situations with superconductivity in MgB_2 and boron-doped diamond have many common features. Both systems have strong covalent bonds, which result in large values of $\langle I_i^2\rangle$; moreover, small ionic masses in these systems also favor an increase in the coupling constant λ. The substantial difference between these systems consists in the fact that the electron system of MgB_2 is two-dimensional and that of boron-doped diamond is three-dimensional. This leads to a small density of electron states in boron-doped diamond.

Unfortunately, Pickett [16] specified no concrete methods to achieve the above extremely high values of T_c in MgB_2. He only noted the importance of the further search for compounds with a quasi-two-dimensional electron system and

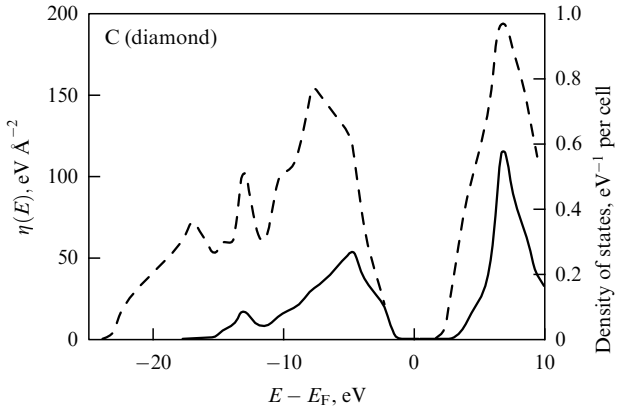

Figure 3. Electron-state density (dashed line) and the Hopfield parameter for diamond (solid line) (borrowed from [18]).

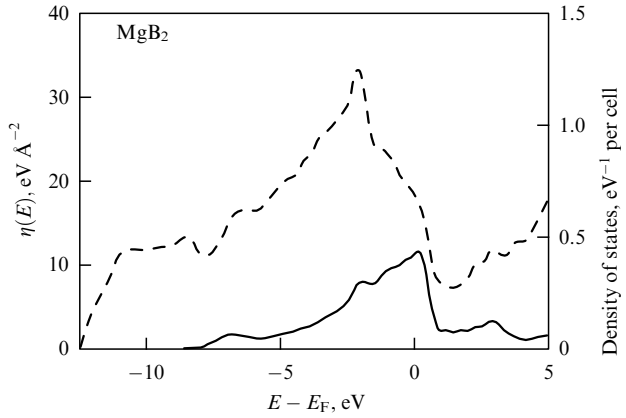

Figure 4. The density of electron states (dashed line) and the Hopfield parameter for MgB_2 (solid line) (borrowed from [18]).

strong covalent bonds. The authors of [17, 18] used another approach to the problem of high-temperature superconductivity in EPI systems. They rewrote $N(0)\langle I_i^2\rangle$ not only for energies at the Fermi surface but also for any energies using the Hopfield parameter η,

$$\eta_i(E) = \sum_{n,k} \left| \left\langle nk \left| \frac{\partial V_{ie}}{\partial \mathbf{R}_i} \right| nk \right\rangle \right|^2 \delta(E - \varepsilon_k + \varepsilon_F) \,. \qquad (13)$$

With the density functional method, the authors of [17, 18] calculated $N(0)\langle I_i^2\rangle$ for a number of systems, including aluminum. The calculation results for diamond and MgB_2 are shown in Figs 3 and 4 borrowed from [18]. As is seen in Fig. 3, the $\eta(E)$ function in doped diamond can reach rather high values if the chemical potential of the system is placed 6 eV below or 6 eV above that in pure diamond. The corresponding values of T_c can be rather high. For example, $T_c^{max} \approx 290$ K in the case of hole doping and $T_c^{max} \approx 420$ K in the case of electron doping. Unfortunately, it is still unclear whether it is possible to produce diamond with such a high level of doping. As regards high T_c, the situation in MgB_2 is much less optimistic (see Fig. 4). In Al, $N(0)\langle I_i^2\rangle$ very weakly depends on energy, and its absolute value is well below that for systems with covalent bonds.

Unfortunately, we cannot now unambiguously answer the question formulated in the title of this report. This is thought to be a dream rather than a myth. In 1976, Ginzburg published a note titled "High-Temperature Superconductivity: A Myth or Reality?" in *Physics – Uspekhi* [19]. Within almost a decade, this dream concerning high-temperature superconductors was achieved. We hope that the same will be true of room-temperature superconductivity.

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Experiments with atomically smooth thin films of cuprate superconductors: strong electron – phonon coupling and other surprises

I Božović

This paper is based on a presentation prepared for the Scientific Session of the Physical Sciences Department of the Russian Academy of Sciences held on October 4, 2007, in honor of 90th birthday of Academician V L Ginzburg. A short review is presented of our own work only, including some very recent experiments, on molecular beam epitaxy of thin films of high-temperature superconductors (HTS). We have developed a technique to fabricate HTS heterostructures with atomically smooth surfaces and interfaces. This has enabled a series of novel or improved experiments that