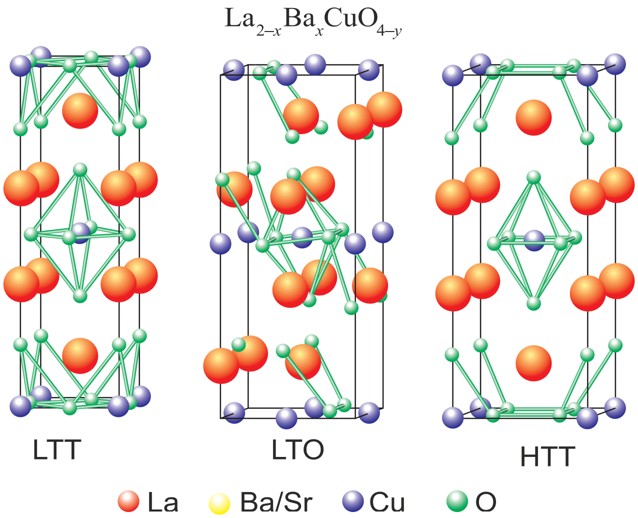
On the 40th anniversary of the discovery of high-temperature superconductivity: History and present



Although 115 years have passed since Kamerlingh Onnes discovered superconductivity with a critical transition temperature of $T_c \approx 4$ K, this macroscopic quantum phenomenon remains a rich field of study and continues to attract the attention of numerous researchers. In this preface, we will outline only the most significant achievements from a historical perspective.

Despite intensive research into superconductivity in various countries, including Ukraine, during the 75 years following its discovery, the critical temperature of the superconducting transition had been raised to only ≈ 23 K (in Nb_3Ge). At the same time, persistent efforts to find high-temperature superconductors (HTSCs) were being pursued everywhere and across a wide range of materials. In the Soviet Union, this work was fostered by Academician V. L. Ginzburg. The group of theorists under his leadership formulated a significant portion of the fundamental theoretical premises regarding high-temperature superconductivity — ideas put forward long before the phenomenon was actually discovered. In particular, it was demonstrated that there are no fundamental limits on the possible value of the superconducting transition temperature T_c, regardless of the microscopic mechanism of Cooper pairing (in principle, superconductivity could take a different form — for instance, the superfluidity of electron-hole pairs in layered structures). In addition, it was shown that high T_c values can be obtained only in systems with strong local-field effects, that is, in systems with strong electron-phonon coupling. According to the Bardeen–Cooper–Schrieffer (BCS) theory, the temperature T_c is exponentially small for small coupling constants λ. Thus, materials with large λ values are required to achieve high T_c values. A more in-depth analysis has shown that a necessary, albeit insufficient condition for the existence of high T_c values is the presence of negative values of the static dielectric permittivity $\varepsilon(\mathbf{q},0) < 0$ at $q \neq 0$. This inequality can be satisfied only when strong electron-phonon coupling is taken into account, as demonstrated within the framework of the Eliashberg–McMillan theory, which serves as a necessary generalization of the semi-phenomenological BCS theory. Theoretical research in this area has continued to the present day, including detailed analyses of the various factors that determine T_c using the phonon mechanism of superconductivity. Unfortunately, a drawback of such studies is the inability to describe both electron-phonon interaction and Coulomb repulsion within a single approximation; in most cases, the latter is replaced by a single constant that is discussed in detail but not explicitly calculated.

Nevertheless, numerous studies have demonstrated the promise of investigating metal oxides, nitrides, and carbides, in which high phonon frequencies can occur due to the low masses of oxygen, nitrogen, and carbon. Similar considerations formed the basis for predictions regarding possible high-temperature superconductivity in hypothetical metallic hydrogen and hydrogen-rich compounds. Indeed, signs of the existence of such superconductivity in palladium hydrides were discovered in 1972 by T. Skośkiewicz of the Institute of Physics of the Polish Academy of Sciences in Warsaw. Currently, several groups claim to have discovered true high-temperature superconductivity at high pressures in hydrogen-rich compounds. However, difficulties encountered in interpreting the results make it impossible to draw definitive conclusions regarding the validity of these achievements.

Unfortunately, during the 1970s and the first half of the 1980s, many scientists abandoned the idea of high-temperature superconductivity for a number of reasons. First, there was a sense of psychological fatigue resulting from long, fruitless attempts to detect the electrical and magnetic manifestations of this phenomenon. Second, some theorists "invented" fundamental obstacles to the existence of high critical temperatures T_c. Although these obstacles were neither fundamental nor universal, proponents of the idea faced ridicule, even in serious scientific papers. A third reason was the prevailing conviction that high-temperature superconductivity required a high density of charge carriers. Therefore, even existing research on superconductivity in narrow-band semiconductors and semimetals (such as $SrTiO_{3-x}$) failed to gain widespread recognition. As a result, research on high-temperature superconductors receded into the background. In the United States, where a pragmatic approach prevailed and the financial aspects of scientific activity were taken into account, virtually all projects addressing this issue were shut down. This approach had a negative impact on global research in the field of superconducting materials science.

However, not all scientists abandoned the search for high-temperature superconductors. One of them was Karl Alex Müller, whose group's work is well described in the article by A. Bussmann-Holder and H. Keller, "*1986 a landmark in the research of superconductivity: from elemental and simple crystalline systems to complex oxide ceramics*". Ultimately, high-temperature superconductivity with a T_c onset of 35 K was discovered in 1986 by J. Georg Bednorz and K. Alex Müller during their study of the multicomponent cuprate oxide $La_{2-x}Ba_xCuO_4$ — a discovery described in the article by Andrey Varlamov, "*Long-awaited discovery on the shores of Lake Zurich*". It is interesting to note that Müller was inspired by ideas concerning the ferroelectricity inherent in the normal state of perovskite oxides, bipolaron superfluidity, granular superconductivity in inhomogeneous systems, and percolation within them. All of these concepts were subsequently discovered — or at least appeared to be discovered — amidst the vast array of superconducting oxides spawned by that remarkable breakthrough. Yet the key factor, as always, was the extraordinary intuition of a true scientist, the same kind of intuition that had previously yielded a series of great discoveries for the finest experimentalists of the past, such as Michael Faraday and Lord Rutherford.

The discovery of high-temperature superconductors sparked a real boom in the field of superconductivity research, and, naturally, all departments of the B. Verkin Institute for Low Temperature Physics and Engineering (ILTPE) with even the slightest connection to the subject began intensively studying these new materials. Every morning, the institute's leading scientists met with the director, and from these meetings, fresh information about new achievements and discoveries reached us. Research was conducted extremely intensively at various Ukrainian research institutes, including the A. A. Galkin Donetsk Institute for Physics and Engineering (V. M. Svistunov, V. Yu. Tarenkov, V. N. Krivoruchko), the G. V. Kurdyumov Institute for Metal Physics in Kyiv (V. M. Pan, A. A. Kordyuk *et al.*), and the N. N. Bogolyubov Institute for Theoretical Physics in Kyiv, where a large group of theorists worked under the leadership of Academician V. M. Loktev. Important research was also carried out by the groups of E. A. Pashitskii, A. M. Gabovich, and D. P. Moiseev at the Institute of Physics in Kyiv with the support of Academician A. F. Prikhotko, and, naturally, at hundreds of other scientific centers worldwide. New information was arriving literally every day.

A. L. Solovjov recalls that the discovery of the now-classic compound $YBa_2Cu_3O_{7-\delta}$ (YBCO), with a critical temperature $T_c \approx 92$ K, sparked particular enthusiasm. However, the discovery of superconductivity in $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi2223), with a T_c of approximately 110 K, caused a real sensation. Initially, there was Bi2201, with a single CuO_2 conducting plane and a T_c of approximately 32 K. Then, Bi2212 was obtained, featuring two CuO_2 conducting planes and a T_c of approximately 90 K. Finally, Bi2223 was discovered, with three CuO_2 conducting planes and a T_c of approximately 110 K. There was eager anticipation that BiSrCaCuO with four — and subsequently five — conducting planes would soon be synthesized, thereby achieving room-temperature superconductivity. But this did not happen — nature could not be outsmarted.

The first international conference on high-temperature superconductivity, or, more precisely, a special session of the American Physical Society (APS), known as the Woodstock of Physics, was held in New York in March 1987, with a representative from ILTPE. The main topic of the hours-long meeting, which lasted until the early hours, was new discoveries in the field of high-temperature superconductivity. Around 2,000 participants gathered, and each presentation was given only 3–5 minutes.

The first conference in the USSR (the All-Union Meeting on High-T_c Superconductivity) took place in December 1987, and the scientists from ILTPE already had a lot to share. Although the high-temperature superconductor samples, primarily manufactured at the Kharkiv Institute of Single Crystals, were obtained as highly granulated ceramics, some new and interesting results were nevertheless obtained. Experimental evidence was obtained for Cooper pairing of electrons and the existence of long-range order in HTSC ceramics (B. I. Verkin, S. I. Bondarenko, A. A. Shablo, A. V. Lukashenko, 1987).

The microcontact spectroscopy (MCS) method was widely used for the research, which made it possible to study the first (dV/dI) and second (d^2V/dI^2) derivatives of the current-voltage characteristics of contacts between a normal metal (silver, niobium) and an HTSC in a wide range of temperatures above the T_c of niobium. A structure of narrow peaks, most likely associated with electron-phonon interactions, was discovered on the first derivative of the current-voltage characteristic of the Ag–YBCO single-crystal contact in the range of 4.2–30 K (I. K. Yanson, L. F. Rybalchenko, V. V. Fisun *et al.*). It was assumed that these peaks could be caused by nonequilibrium phonons with zero group velocity, accumulating near the N–S boundary and leading to an abrupt decrease in the energy gap of the superconductor in the nonequilibrium state. However, strictly speaking, there was no clear interpretation of these peaks. A convincing picture of the evolution of the MCS spectra with temperature was obtained in a study of the contact of Nb with a YBCO polycrystal (A. L. Solovjov, V. M. Dmitriev). At low temperatures, in the range of 4.2–45 K, a pronounced structure of periodic "phonon" peaks in the differential resistance $R_d(V) = dV/dI(V)$ was also observed at voltages $V > \Delta/e$, where Δ is the superconducting gap. However, in this case, the gap features were also clearly observed as two symmetrical minima in $dV/dI(V)$ at $V = \Delta/e$. Using the results of these measurements at $T = 4.2$ K, the ratio $2\Delta(0)/kT_c$ was estimated for the first time, which turned out to be 5–5.5 for YBCO. This value significantly exceeds the classical BCS theory ratio of $2\Delta(0)/kT_c = 3.52$, confirming that HTSCs are indeed strong-coupling superconductors. This result was presented at the first All-Union Meeting — where, incidentally, speakers were also allotted only five minutes — but it went virtually unnoticed, partly because it diverged sharply from conventional views on superconductivity. It was not until 2004 that a theoretical paper by K. W. Wang and W. Y. Ching, "*A structural-based microscopic theory on high-temperature cuprate superconductors*" (*Physica C* **416**, 47), reported for YBCO a value of $2\Delta(0)/kT_c = 5 \pm 0.2$. This confirms the forecast made in 1987 and mentioned earlier.

A similar episode took place at the Second All-Union Meeting on High-Temperature Superconductivity, held in Kharkiv in 1988. Memorable was the presentation by the renowned theorist Igor Orestovich Kulik, one of the principal authors of the MCS theory. Igor Orestovich took the floor and explained that, according to his calculations, the behavior of the superconducting gap Δ in HTSCs differs qualitatively from the predictions of BCS theory. Specifically, Δ does not drop to zero at T_c but transforms into a different gap that, conversely, increases as the temperature rises. He then drew a corresponding diagram on the board. However, the superconductivity community gathered from across the entire country at the time did not accept this idea, to put it mildly. Moreover, it was dismissed as absolute nonsense and nothing more. We now know that in cuprate HTSCs, specifically in the underdoped regime, the resistivity dependence $\rho(T)$ is linear at high temperatures but deviates downward from linearity at a characteristic temperature $T^* >> T_c$. Moreover, a number of studies have convincingly demonstrated that, at $T \leq T^*$, not only does $\rho(T)$ decrease, but so does the density of states at the Fermi level — a phenomenon known, by N. Mott's definition, as the pseudogap. However, at that time, we did not have the slightest idea about the pseudogap. In other words, I. O. Kulik was decades ahead of his time.

It was not until 2003 that a high-quality study by Japanese researchers (Y. Yamada *et al., PRB* **68**, 054533) appeared, in which the intrinsic tunneling effect in Bi2223 (with $T_c \approx 110$ K) was investigated by passing current perpendicular to the conducting CuO_2 planes. The result obtained agreed with what I. O. Kulik had predicted: the superconducting gap $\Delta(T)$ did not vanish at $T = T_c$ but smoothly transitioned into the pseudogap $\Delta^*(T)$. This effect was observed up to 150 K, which, within the framework of the local-pair theory, corresponds to the pairing temperature T_{pair} of Bi2223. Thus, T_{pair} is the temperature of the Bose–Einstein-condensation (BEC)–BCS crossover in HTSCs. A theoretical analysis of various aspects of the Berezinskii–Kosterlitz–Thouless phase transition and the BEC–BCS crossover is presented in another paper in this issue: V. M. Loktev and V. Turkowski, "*On the theory of 2D superconductivity: The peculiarities of Berezinskii–Kosterlitz–Thouless transition and crossover from local to Cooper pairs* (*Review Article*)".

Theoretical approaches to the problem of high-temperature superconductivity are based either on a description of the superconducting wave function involving overlapping Cooper-pair wave functions or on a description of small-sized bosons approximating a bound electron pair. In either case, the constituent electrons are treated as wave functions, even though most illustrative diagrams depict them as "particles" in the classical sense. Alexander Gabovich's Analytical Review, "*What about wave-particle duality? No equity*", addresses precisely this quantum-mechanical issue, namely the frequently used yet outdated concept of wave-particle duality, as it applies to individual electrons and Cooper pairs. This Analytical Review opens the present issue.

In the decades immediately following the discovery by Bednorz and Müller, interest in high-temperature superconductivity research was immense. This is evidenced by the staggering number of papers — estimated at over 300,000 — devoted to the subject. It is worth noting that the highest critical temperature T_c of approximately 134 K (rising to 165 K under a pressure of about 30 GPa) was achieved in the mercury-based cuprate $HgBa_2Ca_2Cu_3O_8$ seven years after the discovery of high-temperature superconductivity. To date, no higher T_c has been attained in cuprate HTSCs. To search for other, higher-temperature superconductors, it would be useful to determine the mechanism of superconducting pairing in cuprates, which remains a mystery to this day. Studying the pseudogap, the physical nature of which is also not fully understood, could shed light on various properties of high-temperature superconductors and, in particular, on the mechanism of superconducting pairing. In this context, based on the study of HTSCs in the form of well-structured YBCO films, a method for analyzing the pseudogap from excess-conductivity measurements was developed at B. Verkin ILTPE (A. L. Solovjov, V. M. Dmitriev, 2006). These studies led to the experimental observation of the BEC–BCS crossover in HTSCs and the subsequent investigation of the influence of various external factors on the magnitude and temperature dependence of the pseudogap in different HTSC materials. These studies are extended by the paper "*Hydrostatic pressure effect on the pseudogap in* $Y_{0.66}Pr_{0.34}Ba_2Cu_3O_{7-\delta}$ *single crystals*" by A. L. Solovjov *et al.*, presented in this issue. This work investigates the effect of pressure on the pseudogap in a YBCO single crystal containing 34% magnetic Pr impurities. It is anticipated that studies of the influence of various external factors — such as hydrostatic pressure, magnetic fields, magnetic impurities, high-energy electron irradiation, and long-term storage — will help elucidate the mechanism of superconducting pairing and other unusual properties of high-temperature superconductors.

In this issue, dedicated to the 40th anniversary of the discovery of high-temperature superconductivity, in addition to the papers cited above, we have collected a significant number of research and review articles covering a wide range of topics in the physics of superconductivity and related phenomena. In particular, high-temperature superconductors are investigated in the paper by S. Dzhumanov *et al.*, "*Distinctive doping- and temperature-dependent metallic conductivity in moderately doped* Y*-based cuprate superconductors*". The evolution of the pseudogap and metallic conductivity in yttrium-based cuprate superconductors as a function of doping level x and temperature T was calculated, compared with experimental data, and interpreted based on the concepts of polaron fermions and bipolaron bosons as Cooper pairs.

In the article "*Collective excitations of two-phase* Bi2223 *and* Bi2212 *superconducting condensates in* Bi*-based high-temperature superconductors*" by V. N. Krivoruchko and V. Yu. Tarenkov, MCS and tunneling studies of Bi2223 and Bi2212 superconductors were conducted. The observed conductivity properties were attributed to the excitation of the collective Leggett mode. The challenge of sample preparation has always been — and remains — a key issue in materials science, particularly in the field of high-temperature superconductors. The article by B. Dabrowski and K. Rogacki, "*Search for the improved synthesis conditions and the enhanced properties of the* Mo*-substituted* $YBa_2Cu_3O_{7-d}$ *type superconductors*", investigates a promising avenue of research in this area. It was demonstrated that the formation of MoO_6 octahedra leads to a significant increase in the critical currents, a finding of great importance for the practical application of these materials. The differential electrical conductance in the superconductor α-M_xTiNCl was studied in the article by Akira Sugimoto *et al.,* "*Dependence on the interlayer spacing of nanoscale electronic states in layered nitride chloride superconductors* α-M_xTiNCl *investigated by scanning tunneling microscopy/spectroscopy*". A pseudogap similar to that observed in cuprate HTSCs was also found in this material.

This issue also features studies of other superconductors. The enigmatic Sr_2RuO_4 could be considered a close relative of high-temperature superconductors. However, that is not the case. In fact, for almost three decades, this compound was regarded as an example of an extremely rare triplet superconductor. Details can be found in the article by James F. Annett and Karol I. Wysokiński, "*Puzzling superconductivity in strontium ruthenate: Then and now*". Ising-type superconductivity, particularly in the context of $NbSe_2$ and related compounds, is investigated in the article by D. Sergeyev *et al.*, "*Universal transport signatures of Ising superconductivity in two-dimensional van der Waals heterostructures*". Although the superconducting transition temperatures of these materials remain significantly lower than those of cuprate HTSCs, the physical mechanisms underlying their exceptional magnetic stability represent an important avenue for the further development of high-temperature superconductivity research. The classical multiple-band superconductor MgB_2 with its high $T_c = 39$ K is presented by the Wrocław group that studied its transport properties in the article by Michał Babij *et al.*, "*The influence of microstructure on the transport critical current density in* MgB_2 *wires obtained by PIT methods*".

The quasiparticle density of states in the low-temperature superconductor V_2Ga_5 was investigated by measuring magneto-quantum oscillations of the heat capacity: Ye. V. Petrenko *et al.*, "*AC calorimetric study of magneto-quantum oscillations in anisotropic multiband* V_2Ga_5 *superconductor*". The DOS oscillations were revealed using the Fourier-transform technique. The article by Mikhail Belogolovskii *et al.,* "*Superconducting nitrides: Versatile thin-film platforms for cryogenic technologies*", included in this collection, is devoted to the application of superconductors in electronics. The authors study a number of nitrides and compare their properties with those of HTSCs. An overview of a different type of quantum technology — the creation of semiconductor-based qubits — is presented in the article by A. Chroneos and A. Daskalopulu, "*Perspectives of low temperature physics: From defect engineering strategies to quantum technologies*". The authors compare this technology with high-temperature superconductor-based technology.

A recent article by M. J. Winiarski, M. Powałowski, and T. Klimczuk, titled "*A note on the reliability of superconducting material databases and the report of the absence of superconductivity in the* Mn_5Si_3*-type* Zr_5Ga_3 *compound*", addresses the important issue of the reliability of reports regarding the discovery of new HTSCs and the accuracy of datasets covering all known superconductors. Although this work does not directly concern high-temperature superconductivity, it raises significant questions that are undoubtedly relevant to the field, given the increasingly widespread use of machine learning models (trained on data from these sets) to predict new superconducting materials with even higher T_c values.

In summary, this issue describes the rich history of high-temperature superconductivity and the current state of this field of condensed matter physics. It should be of interest to both experimentalists and theorists working on the topical problems in the physics of high-temperature superconductivity that have arisen since the discovery made by Bednorz and Müller.

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