Superconductors with unusual properties and possibilities of increasing the critical temperature

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Usp. Fiz. Nauk **148**, 363–380 (February 1986)

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1. NEW CLASSES OF SUPERCONDUCTORS

At present a renewed surge in interest in superconductors is being observed. It concerns not only the expansion of use of known superconductors and their penetration into microelectronics and cryogenic UHF technology, in addition to traditional fields of strong currents, magnet technology, and electrotechnology. One is dealing, so to speak, with the fundamental levels—discovery and study of new superconductors, and preparation of new superconducting materials based on them.

A recently published article[1] by the American physicists M. Beasley and T. Geballe (translation in this issue; see also Ref. 2) has briefly reviewed the current status of research on new superconductors. Currently one customarily speaks no longer of individual new superconductors, but of entire classes of them. Although the phenomenon of superconductivity has already been known for more than 70 years, even now not only are new classes of superconductors being discovered, but the number of such discoveries is even increasing. Here, despite the outstanding advances of the theory, many properties of real superconductors, especially the new and exotic ones, remain not fully understood. Up to now there have been no clear answers to such fundamental questions as: is there a bound on the critical temperatures T_c and what is it; in seeking among these materials superconductors with higher T_c, why, e.g., does an entire series of superconductors with uniquely high values of T_c exist in the compounds with an A15 structure? Many such questions have been posed in Ref. 1.

In the past decade such new classes of superconductors have been discovered as the superconductive $(SN)_x$ polymers,[3] which do not contain metal atoms; the relatively high-temperature superconductive oxides (ceramics) $Ba(Bi_{1-x}Pb_x)O_3$,[4] which transform into a semiconductive phase on changing the composition; superconductive metallic glasses,[5] which have rather high critical temperatures T_c and very high resistivities; superconductors with heavy fermions[6]; magnetic superconductors[7] (ferromagnetic ordering in these materials restores their resistance at low temperatures. Hence they are called "reversible"; the authors of Ref. 1 call the superconductivity of these materials "reentrant"); organic superconductors[8]; and other, less exotic systems. Definite overlaps can be observed among these classes of superconductors. Thus the effect has been observed in a superconductive spin glass of return to the normal state upon lowering the temperature.[9] Practically every one of these classes is unique and has attracted considerable attention to itself. Even the term "exotic superconductors" has appeared, and recently an entire series of conferences has been devoted to these systems (see, e.g., Ref. 10).

An interesting object of study continues to be the high-temperature superconductors. Primarily they are intermetallic compounds with an A15-type structure. For Nb_3Ge—a representative of this class of superconductors—complete superconductivity at 23 K has been attained, with the onset of the transition to the superconductive state at a temperature T exceeding 24 K.[11] They include the nitrides and carbonitrides of transition metals like NbN and NbCN (compounds with the B1 structure), whose maximum value of T_c reaches 18 K. They include palladium alloys with noble metals that become superconductive with T_c up to 17 K upon incorporating hydrogen and deuterium. An important discovery was the instability of high-temperature superconductors, which restricts the limiting T_c values. A number of observations (see Ref. 12) indicates their instability. Apparently the general reason for the instability of the high-temperature superconductive compounds of the transition metals is the existence of an energy fine structure in the electronic density of states near the Fermi energy.

Considerable attention is being paid to studying high-field superconductors–molybdenum chalcogenides (Chevrel phases). A record value of the upper critical magnetic field[13] has been reached in $PbMo_6S_8$ (and $PbGd_{0.2}Mo_6S_8$) of more than 600 kG. Increasing interest is being aroused in amorphous superconductors, whose properties are changed weakly by irradiation with high-energy particles. An entire field has appeared—localized superconductivity. The con-

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nection between the phenomena of localization and superconductivity has been discussed at conferences.[14,15] Multicomponent compounds (in addition to the ternary compounds already mentioned) having nonequivalent atomic positions in the unit cell of the crystal lattice open up rich potentialities for superconductivity.[16] Although important results have recently been obtained for all the classes noted above, nevertheless, an understanding on the quantitative level starting from the microtheory has not been attained.

In addition to the new classes of superconductive materials, other interesting superconductive systems have also been discovered in recent years. An example is the superconductivity of twin boundaries that arise in the low-temperature deformation of metal crystals[17] (it is also sometimes called localized superconductivity). An increase in T_c upon appearance of twin boundaries has been observed in crystals of Sn, In, and Tl,[17,18] and up to 7 K in Sn. The authors of Ref. 19 associate the increase in T_c to above 12 K in monocrystals of Nb with the appearance of these boundaries (as is known, plastic deformation lowers the critical temperature of niobium). Perhaps the values of T_c sometimes observed (in particular for niobium) that exceed the critical temperature of the homogeneous material involve specifically the appearance of these intercrystalline boundaries. Interestingly, in artificially prepared layered Nb-V systems the magnitude of T_c reached 15 K (in Nb-V alloys $T_c \lesssim 9$ K).[20] Such a considerable increase in T_c can also involve the appearance of layers having special properties near the boundaries of the different metals. The formation and study of such layers, especially from high-temperature semiconductors, can lead to a further increase in T_c. Extra possibilities of such an increase arise from suppressing the proximity effect (specimens of small dimensions, thin films).

In addition to superconductive twin boundaries and other intercrystalline boundaries, the superconductivity of systems of reduced dimensionality has been actively studied in recent years—granulated specimens and specimens of small dimensions, needle-shaped crystals (whiskers), quasi-one-dimensional and two-dimensional compounds, very thin films, layered materials (including artificial ones), and also inhomogeneous systems. Superconductors whose electron and phonon systems are excited by external radiations (e.g., laser radiation) or electron injection are still of interest. Interest is not lacking in studies of superconductivity of new phases of materials that arise under special conditions (e.g., under pressure). Very interesting surprises can occur here. For example, the behavior of sulfur at high pressures has been observed,[21] and was characterized by the authors as superconductivity at temperatures about 30 K. To draw final conclusions on the mechanism of the phenomenon observed here, requires a whole complex of studies that are difficult in the methodology that was employed. In this regard, considerable interest is aroused in the problem of appearance of superconductivity in the metallic phase in a dielectric-metal transition in amorphous materials under pressure.

Finally, studies continue of unusual systems in which a sharp decrease in resistance or an appreciable increase in diamagnetism has been found (under conditions not controlled sharply enough). The cases are of interest in which these phenomena are observed (as a rule, irreproducibly) at very high temperatures (100–200 K). The authors of Ref. 1 call such systems "irreproducible superconductors." At present no concrete ways are known of obtaining superconductors with such values of T_c, and it is not even known whether such T_c values can be attained in principle. Yet the prospects that will be opened up in technology, even with a considerably more modest increase in T_c, require the careful verification of all such cases. One of these systems is the solutions of the alkali metals in ammonia.[22] Recently[23] in studying solutions of Na and K in ammonia quenched to 77 K, a transition was found to a state having a high conductivity induced by an electric field. Apparently precisely this state was observed in the early experiments of Ogg.[22] Another interesting system is CuCl, which was discussed by authors of Ref. 1. Recently a diamagnetic signal in a perpendicular magnetic field has been steadily observed[24] in CuCl films grown epitaxially on Si (111) substrates. The maximum value of the diamagnetic susceptibility (at $T \sim 100$ K) exceeded by two orders of magnitude the susceptibility of the normal compound (and amounted to 0.25% of the susceptibility of an ideal diamagnetic according to the estimate of the authors). Other interesting effects were also observed in Ref. 24 in CuCl films, e.g., a considerable paramagnetism in a parallel field. The observed phenomenon is reproducible and is associated with the presence of the boundary between the CuCl and the Si. Perhaps studying it will enable understanding the causes of the diamagnetic anomalies observed earlier[25] in CuCl. Finally, an anomalous decline (by a factor of 10^3) in the resistance at $T \approx 180$ K has been observed in thin Nb-Si films (less than 400 Å).[26] The temperature of the jump in resistance decreased with increasing measuring current and increasing external magnetic field. The properties of the films (and the character of the manifestation of the anomaly) were extremely sensitive to the conditions of preparation and measurement. The phenomenon greatly recalls the behavior of sulfur under pressure.[21] The interest in the stated systems from the standpoint of superconductivity also involves their instability, possible layering, decomposition, separation of small metal clusters, appearance of unstable phases, etc. That is, conditions appear that are favorable in principle for high-temperature superconductivity. However, it is hardly possible to rely on increasing the critical temperature, even in an unstable material, directly by an order of magnitude. Hence one must study (and create) systems unstable at lower temperatures.

The discovery of each new class of superconductors is always a microsensation. As a rule, something unusual is introduced here—a "new physics" not previously conjectured. Hence it proves impossible in most cases to predict it. This enhances the role of general qualitative regularities and correlations.[27] The observation of unexpected properties of new superconductors not only expands our knowledge of superconductivity, gives an impetus to the development of theory, points out new possible pathways for increasing the critical parameters and obtaining new planned characteristics, but it also favors the development of solid state physics as a whole. For example, the mentioned[1] problem of the competition of superconductivity and other types of ordering—magnetism, localization, waves of spin and charge density—and the effect of this competition on the limiting values of T_c are fundamental problems of solid state physics.

One of the main thrusts in the field of creating new superconductors is the preparation of materials with maximum high values of T_c (as a rule, the other critical parameters also increase here). Starting in 1964, the problem of increasing T_c of superconductors has attracted the attention of theoretical physicists. Apart from a number of reviews and monographs treating individual high-temperature classes of superconductors, the reviews of Refs. 28, 29 have been specially devoted to the problem of high-temperature superconductivity. The problem has been analyzed in greatest detail in the collective monograph of Ref. 30. Numerous attempts have been made to go outside the framework of the phonon mechanism of superconductivity. Here, instead of phonons, the role of carriers of the interaction of electrons has been considered to be played by the polarization of molecules,[31] excitons,[32] and other excitations, including plasmons and magnons (see Refs. 30, 33, and 81). Unfortunately, not one of these mechanisms has yet been reliably discovered experimentally, so that the problem has actually arisen of understanding why they do not operate (see Ref. 34).

2. METHODOLOGY

The creation of new superconductors requires new methodologies. The authors of Ref. 1 mention deposition from the gas phase as a powerful method of preparing films of superconductors. At present different variants of this method exist. Both thermal evaporation for easily volatile materials and evaporation by an electron beam have been highly recommended, as well as laser sputtering (including pulsed sputtering). Here alloys and compounds are obtained by simultaneous evaporation of the components in a vacuum. Cathodic (ion) sputtering in noble gases enables one to obtain very homogeneous pure films under conditions of good thermalization of the atoms ejected from the target. Specimens of Nb_3Ge with record-setting high values of T_c have been prepared precisely by this method. The requirements on the starting of the discharge are lowered in radiofrequency sputtering. Magnetron sputtering increases the rate of deposition of films. The method of molecular-beam epitaxy offers extra possibilities in the deposition of thin films. The method of chemical deposition from the gas phase has served well for high-temperature superconductors. Already long ribbons for practical use are being prepared by this method. The deposition of films in some of the methodologies cited above can be performed in the presence of active vapors and gases in the chamber in order to carry out some particular reaction. Films of NbN with high T_c have been obtained by reactive cathode sputtering of niobium in a nitrogen atmosphere. Recently films of NbC with a maximal approximation to stoichiometric composition and maximum T_c have been obtained by the method of laser reactive sputtering of niobium in the presence of vapors of carbon-containing substances.[35] The ion-implantation method is employed for producing metastable high-temperature superconductors.[36] This method can be a delicate instrument for compensating small deviations from stoichiometry, for elevating the solubility limit to give rise to new metastable alloys and to elevate T_c. High pressures are applied to obtain new superconductive phases. A number of more exotic methodologies has also been successfully applied, e.g., wires or films that explode under the action of a current pulse. The method of explosive compression has been successfully applied to synthesizing an unstable high-temperature superconductive compound such as Nb_3Si,[37,38] etc. A number of promising metallurgical methods of preparing superconductors is not mentioned here. Such of them as the "bronze technology" (a method of selective solid-state diffusion)[39] or the "*in situ* method" (formation of an A15 compound in the reaction of finely crystalline precipitates of Nb or V with Sn or Ga in a copper matrix)[40] have become genuinely industrial methods and allow one to obtain high-temperature superconductive leads and cables hundreds of meters and kilometers long. Several monographs and collected volumes have appeared recently that describe in detail the methods of preparing superconductive materials.[41–43] The developed methods offer rich potentialities of preparing specimens. When combined with modern analytical methods, they enable one to synthesize new superconductors successfully.

The instability of high-temperature superconductors (and a number of others) has required the study of the different aspects of this phenomenon, primarily the possibilities of synthesizing and stabilizing them. A good model system for this is the metastable compound Nb_3Ge. A number of studies has been devoted to stabilizing the high-temperature superconductive A15 phase of the Nb-Ge system. A number of methods of stabilizing it has been developed. We can point out the epitaxial growth of the A15 phase on substrates of Nb_3Ir and Nb_3Rh,[44] the introduction of catalytic impurities, e.g., oxygen or chlorine, stabilizing admixtures of silicon,[45] etc. The methods of autoepitaxy and of gradual enrichment of compounds with germanium have been employed. The important role of the temperature of the substrate in the process of formation of Nb_3Ge films has been shown—it enables a sufficiently high mobility of the impurity with a relatively low mobility of the atoms of the compound. Finally, it has proved extremely essential to reduce the energy of the particles bombarding the growing film (use of high argon pressures and low voltages in cathode sputtering).

The process of formation of superconductive films of Nb_3Ge with record high values of T_c in cathode sputtering with admixtures of oxygen has been studied in detail in Ref. 46. It was found that the growth of Nb_3Ge films with high T_c occurs according to the vapor-liquid-crystal pattern (VLC mechanism). Oxygen admixture considerably lowers the melting temperature of the alloy in the thin near-surface layer and enables functioning of the VLC mechanism. The liquid phase on the surface of the film (and of the crystallites) is a type of solution of Nb and Ge in oxygen, which enables producing perfect enough crystals of Nb_3Ge at relatively low temperatures. The separation of the oxygen (and also other impurities) at the boundary of the crystallites and the film is

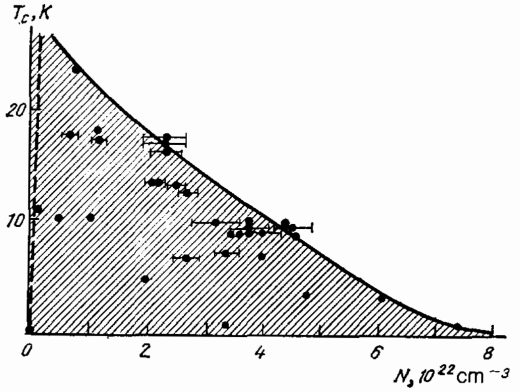

FIG. 1. Correlation of the T_c's of metals and alloys with the concentration N of conduction electrons. The bars indicate the errors of measurement in N.

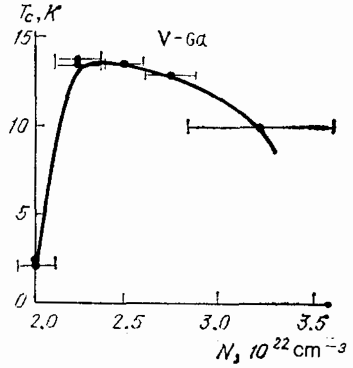

FIG. 2. Dependence of T_c on N for the V-Ga system. The bars indicate the errors in N.

associated with a decrease in the Gibbs thermodynamic potential in this process. One attains supersaturation of the A15 phase with germanium and approach of its composition to stoichiometric by this method. The metastable A15 phase cannot decompose after loss of the oxygen, owing to the rather low temperature. The growth of the competing σ-phase (Nb_5Ge_3) by the VLC mechanism involving oxygen is impeded, since decomposition (and the corresponding rearrangement) of the hexagonal phase $Nb_5Ge_3O_x$ formed in the presence of oxygen is necessary for its formation. Thus oxygen plays a catalytic role in the formation of the compound Nb_3Ge. The difficulty of obtaining specimens of Nb_3Ge with the maximum T_c results from the need for optimizing the amount of oxygen, since an oxygen deficiency sharply hinders the possibility of formation of the high-temperature superconductive phase, while an excess of it in the film appreciably diminishes T_c. The problem is aggravated by the fact that the optimal amount of oxygen is a function of the conditions of preparation. The creation of higher temperature superconductors (and more unstable ones) requires further studies of the mechanism of their formation and the problem of stabilization.

3. POSSIBILITIES OF INCREASING T_c

What can we expect with regard to increasing T_c beyond the already known classes of superconductors, and where should we seek possible new high-temperature superconductors? As is known, the equations of superconductivity themselves contain no internal restrictions on the limiting value of T_c. However, this restriction can be introduced by the characteristics of the normal state.[30,47] Therefore it is important to understand what values of the characteristics of the normal state are admissible for high-temperature superconductors. The correlations found between T_c and the characteristics of the material in the normal state cast a certain light on this problem. Reference 1 has noted an interesting dependence of T_c on N for materials with a low enough concentration N of carriers: a continuous increase in T_c is observed with increasing N. Unfortunately, at high concentrations N of conduction electrons this correlation is inverted in metals and alloys. Figure 1, which was taken from Ref. 27 (with points for Nb_3Ge and Ba(Pb, Bi)O_3 added), shows the values of T_c as a function of N, both for pure metals and alloys with a known concentration of electrons. We see that high-temperature superconductors are absent among the materials with large N. That is, the upper bound of T_c declines with increasing N. The dotted line on the diagram indicates the decline in T_c on the low-concentration side (semiconductive region).

An analogous result—decline in T_c with increasing N—is also observed for a number of concrete alloys. Figure 2 shows the T_c (N) relationship for the V-Ga system. The electron concentration N in the alloy was varied by varying the composition. The sharp decline in T_c at low concentrations is associated with a change in the structure of the alloy. Similar curves have been obtained for the Nb-Sn, Nb-Ti, and Nb-Ge systems.

The observable correlation of T_c with N is manifested especially graphically if we plot the dependence of T_c on the optimal electron concentrations (the maximum T_c is at-

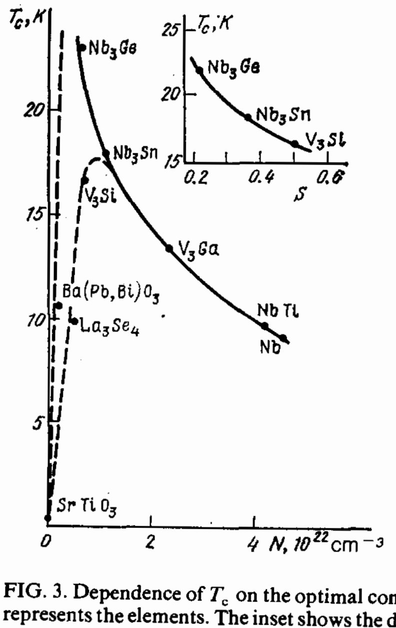

FIG. 3. Dependence of T_c on the optimal concentrations of electrons. Nb represents the elements. The inset shows the dependence of T_c on the ratio of areas of the real Fermi surface and the Fermi sphere S of free electrons for superconductors having the A15 lattice.

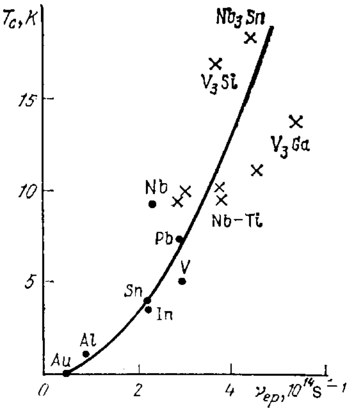

FIG. 4. Correlation of T_c with the frequency ν_{ep} of electron-phonon collisions.[48] The dots indicate the data for metals, the crosses for alloys. The magnitudes of ν_{ep} were measured at room temperature.

tained at the optimal concentration in the system). This dependence is shown in Fig. 3 (niobium represents the pure elements). The dotted line again indicates the sharp declines in T_c in the low-concentration region.

We see from Figs. 1 and 3 that one must have materials with a concentration of conduction electrons $1\times10^{21} \lesssim N \lesssim 2\times10^{22}$ cm^{-3} to attain critical temperatures exceeding 20 K. These results indicate the relative narrowness of the region of electron concentrations favorable for high-temperature superconductivity.

The correlation of T_c with the frequency ν_{ep} of electron-phonon collisions for a series of metals and alloys[48] is shown in Fig. 4. This correlation reflects the increase in T_c with increase in the electron-phonon interaction constant λ. High frequencies of electron-phonon collisions $\nu_{ep} \gtrsim 5\times10^{14}$ s^{-1} (strong electron-phonon interaction) are required for high-temperature superconductors. The noted correlation indicates a possible bound on critical temperatures in superconductors having a phonon mechanism of superconductivity, since the frequency ν_{ep} is bounded owing to the limitation on the minimum value of the mean free path of electrons.

A number of other correlations of the critical temperature with the characteristics of materials in the normal state—atomic, electronic, phonon, structural, and other—has been studied in Ref. 27. Analysis of these correlations shows that a possibility exists of increasing the observed upper bound on T_c of superconductors up to 27–30 K. However, the solution of this problem in each concrete case faces the fact that the maximum T_c's are attained at the limits of stability of systems, at phase boundaries, in narrow intervals of parameters, etc. The properties begin to depend strongly on the quality of the specimen. Certain models associate high T_c, the existence of anomalies, and the lattice instability of high-temperature superconductors with a single cause—strong electron-phonon interaction, which leads to narrow peaks of electron density of states, which give rise to a temperature "softening" of the phonon spectrum (see Refs. 30 and 49). The discovery of new high-temperature superconductors requires the development of new methodologies of stabilizing metastable, nonequilibrium systems.

Along with the problem of surpassing the record value of T_c, and important scientific and practical problem is to increase the critical temperature of each promising class of superconductors. This will allow us to understand better the mechanisms of superconductivity and to employ effectively the potentialities of each such class. The most interesting ones from this standpoint are the superconductors with the A15 lattice. Their potentialities seem not to have been exhausted. First of all, they obey general correlations of T_c with the electronic characteristics, as is implied by Figs. 1–3. The need for reducing the concentration of conduction electrons in them to elevate T_c can also be seen from the dependence of the critical temperature on the reduced area S of the Fermi surface (inset in Fig. 3). Here S is the ratio of the area of the Fermi surface to the area of the Fermi sphere of free valence electrons.[46] High-temperature superconductors of A15 type also exhibit a correlation of T_c with the quantity $\int \alpha^2F(\omega)d\omega$, which is a measure of the intensity of the electron-phonon interaction.[27,50] Here, in order to attain $T_c = 27$–30 K, the area of the effective phonon spectrum $\alpha^2F(\omega)$ must amount to 15–17 meV.

High-temperature superconductors of the A15 type are characterized by an appreciable "softening" of the phonon spectra with decreasing temperature.[12] Figure 5 shows the correlation of T_c with the temperature variation of the root-mean-square frequency $\langle\omega^2\rangle^{1/2}$ of the phonon spectrum of A15 compounds.[27] The magnitude of $\langle\omega^2\rangle^{1/2}$ of superconductors having $T_c = 27$–30 K must vary by 20–25% upon changing the temperature from room temperature to liquid-helium temperature. The details of the structure of the phonon spectrum can vary even more strongly. Figure 6 shows the dependence on T_c in A15 compounds of the temperature-variation of the position of the low-frequency peak of the phonon density of states.[51] (Here ω_r and ω_0 are the frequencies of the low-temperature maximum of the density of phonon states, respectively at room and low temperatures). The strong variation of the phonon spectrum in high-temperature superconductors indicates their closeness to lattice instability.

For individual systems of alloys having an A15-type lattice, one observes an increase in T_c with decrease in the lattice constant a_0. A correlation of T_c with a_0 is also ob-

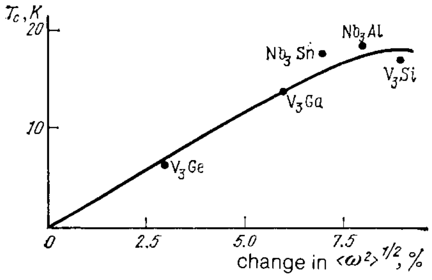

FIG. 5. Correlation of T_c with the temperature variation of the root-mean-square frequency of the phonon spectrum for A15 compounds. The change in $\langle\omega^2\rangle^{1/2}$ is taken for a variation of temperature from 297 to 4 K, but to 77 K for V_3Ga.

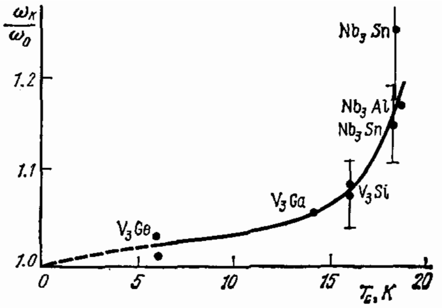

FIG. 6. Correlation of T_c with the temperature variation of the position of the low-frequency peak of phonon density of states in A15 compounds.

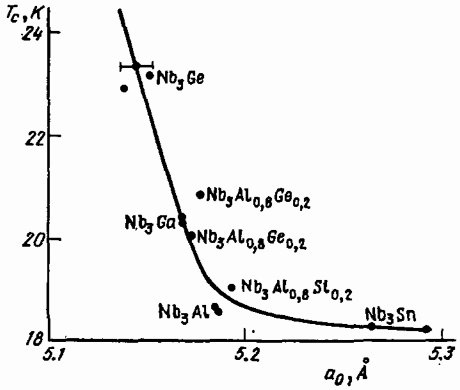

FIG. 7. Correlation of T_c with the lattice constant a_0 for Nb_3X compounds.

served for the entire set of high-temperature compounds Nb_3X, where X is a non-transition element (Fig. 7).[27] This dependence reflects the increase of T_c with decreasing atomic volume in these superconductors. The T_c (a_0) relationship indicates compounds with X atoms of small radius (Si, C, B) as promising. However, the difficulty of preparing these compounds sharply increases with smaller atoms X.

The high-temperature superconductivity of a number of niobium and vanadium compounds with the A15 structure involves the fact that this structure makes possible a more effective electron-lattice interaction while maintaining just as high a density of states $N(E_F)$ as in the corresponding pure transition metals. Generally, as a rule, the favorable structures for high-temperature superconductivity are structures of the A15 type—with an anisotropic arrangement of atoms, with the presence of both metallic and covalent bonding, with a small distance between nearest neighbors, and with a low coordination number. The analysis of the data for A15 compounds,[46] in particular the analysis of the obtained correlations, shows that the maximum value of T_c can be elevated by several degrees, although this involves considerable difficulties.

One of the promising high-temperature superconductors having an A15 lattice is the *compound* Nb_3Si. Apparently the maximum value of the product $N(E_F)\langle I^2\rangle$, which determines the magnitude of λ in A15 compounds, is realized in it (here $\langle I^2\rangle$ is the mean square of the matrix element for electron-ion scattering). For Nb_3Si one predicts values $T_c \approx 25$–30 K. Actually the value $T_c \approx 19$ K is attained. Here it has already been obtained for specimens prepared by different methods (explosive compression, cathode sputtering). The strong instability of this compound requires using simultaneously a number of stabilizing factors. Thus, in the preparation of Nb_3Si with $T_c \approx 19$ K by cathode sputtering,[46] along with optimizing the general conditions of preparation, one requires in addition: introduction of nucleus-forming microadmixtures of germanium; autoepitaxy; gradual enrichment of the A15 phase with silicon; and shortening of the deposition time of the film in order to prevent decomposition of the high-temperature superconductive phase. We note that, even in the highest-temperature specimens of Nb_3Si the lattice parameter a_0 exceeds by 0.015–0.02 Å the constant calculated from the Geller radii of Nb and Si. But the dependence T_c (a_0) for such values of a_0 is rather sharp (see Ref. 7). Undoubtedly the prepared specimens of Nb_3Si are still far from perfect. For example, explosive compression appreciably lowers T_c of materials having the A15 lattice[52] (owing to increased inhomogeneity of the specimen and decreased electronic density of states at the Fermi surface). All this definitely indicates the possibility of appreciably increasing T_c upon approaching ideal Nb_3Si. However, despite the great "limiting" possibilities of this compound, its instability is so great that it proves much more difficult to realize them than in Nb_3Ge.

A large number of other alloys with the A15 lattice is of interest from the standpoint of possibly increasing T_c. In certain systems the A15 phase is formed at compositions very far from stoichiometric. An example is the system V-Re, in which the A15 phase (having $T_c \approx 8.5$ K) is formed in a narrow concentration range around 70 atom % Re (stoichiometric composition is V_3Re).[53] The temperature variations of the resistance, the magnetic susceptibility, and the heat capacity for this phase show anomalies in the region 45–70 K. It is of interest to study the possibilities of increasing T_c as such phases approach stoichiometry.

A very promising class of superconductors with high T_c is the *carbides and nitrides of the transition metals* (B1 struc-

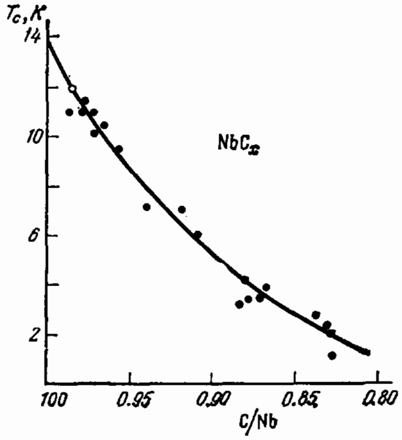

FIG. 8. Dependence of T_c on the relative content of carbon in the alloy NbC_x.

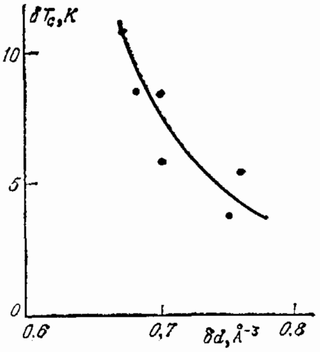

FIG. 9. Dependence of the variation of T_c in going from the carbide to the corresponding nitride having the B1 lattice on the difference of concentration of valence electrons per unit cell.

ture). Figure 8 shows the dependence of T_c on the composition for the compounds NbC_x. The compound with stoichiometric composition is unstable. Specimens close to stoichiometric show a softening of the longitudinal acoustic and optical modes with decreasing temperature. The maximum value of T_c is attained with the closest approach to stoichiometry, and is obtained in films prepared by the method of laser reactive sputtering.[35] One can prepare specimens with a minimum of carbon vacancies by this method. We have $T_c \approx 14$ K for the stoichiometric composition. The carbides are attracting attention with their relatively low density of electronic states at the Fermi level $N(E_F)$ with rather high T_c's. To understand how to increase $N(E_F)$ without appreciably weakening the electron-phonon interaction means to solve the problem of increasing T_c in these systems.

A very interesting system is the *compound* MoN having the B1 structure. A value $T_c = 29.3$ K for a stoichiometric composition of it has been predicted[54] from calculations of its band structure. An interesting observation was made on the basis of empirical correlations by the authors of Ref. 55: in going from the carbide to the corresponding nitride having the B1 lattice, T_c increases (by the amount δT_c). The dependence of the change in the critical temperature δT_c on the difference of concentrations of valence electrons δd of these compounds is shown in Fig. 9 (here $d = n/a_0^3$, where n is the number of valence electrons per unit cell, and a_0 is the lattice constant). The maximum increase in T_c is observed for the minimum change in the concentration of electrons. One can estimate from the curve that one should observe $T_c \approx 19$–20 K for MoN having the B1 structure ($\delta d = 0.075$ Å^{-3}). The curve also indicates a possibility of increasing T_c in NbN ($\delta d = 0.070$ Å^{-3}).

Since the MoN phase having the B1 structure is unstable, a number of methods has been used to prepare it that have been developed for metastable compounds (see the references in Ref. 56). However, the values of T_c found in these studies did not exceed 5 K. The studies of Ref. 56 show that the T_c's obtained up to now for MoN specimens of B1 type are diminished, likely, by the presence of vacancies and interstitial atoms (the T_c of the B1 compounds of transition metals with nitrogen is very sensitive to the nitrogen/metal ratio). Actually it was found[56] that the x-ray photoemission spectra of MoN specimens with excess nitrogen ($x \geqslant 1.3$) are very close to the theoretical energy-dependence of the density of electron states. At the same time, the observed electronic structure of a specimen of stoichiometric composition differed from the B1-type structure. It was also shown[56] that the density of states $N(E_F)$ in B1-type MoN_x with $x = 1.5$ is higher than in the hexagonal phase of MoN, whose critical temperature reaches 14.8 K. This also indicates that T_c in a perfect B1-type MoN crystal can be rather high. Moreover, it was found[56] that the onset of the transition to the superconductive state for a single-phase specimen of B1-type $MoN_{1.1}$ was as high as 12.5 K.

The following T_c's have been attained in the *sesquicarbides* (formula Me_2C_3): in the binary compound Y_2C_3—12.6 K, and in the ternary compound $(Y_{0.7}Th_{0.3})_2C_3$—17.1 K (see Ref. 57). We must note that these values were obtained at not exactly stoichiometric compositions. Since the superconductive properties of the sesquicarbides are also very sensitive to deviation from stoichiometry, while the maximum T_c's are observed, as a rule, near the stoichiometric composition, we can hope for a further increase in T_c upon stabilizing the high-temperature phases. In many cases doping with various elements elevates the T_c's of sesquicarbides, and the same is observed in mutual alloying. We should expect an effective influence of the pressure on T_c. An interesting feature of these carbides is their capability of crystallizing in different structures depending on the method of preparation and the conditions. Here the *bcc* structure (Pu_2C_3-type), which is favorable for superconductivity, is formed only by combining high pressures and temperatures.[58]

The *metal hydrides* continue to offer interest from the standpoint of elevating T_c, especially palladium and its alloys with the noble metals (PdH of stoichiometric composition has a B1-type structure). Values $T_c = 16$–17 K have been attained[59] in Pd-Ag and Pd-Cu alloys upon implanting hydrogen (and also deuterium). Interestingly, the value of T_c depends on the method of introducing hydrogen into the alloy.[60] That is, the anomalously high T_c's obtained upon implanting hydrogen involve the features of the metastable state that arises here. A phase transition was observed in the alloy-hydrogen system, accompanied by tetragonal distortion of the fcc sublattice of the metal.[60] The theoretical calculations indicate soft optical modes arising upon introduction of hydrogen as the major cause of superconductivity in this system. An increase in T_c upon introducing hydrogen has been observed also in other palladium alloys—with Nb, Mo, and W.[61] The series of hydrides of other metals can prove promising for attaining high T_c, e.g., the hydrides of platinum[62] or its alloys. A considerable increase in T_c has been observed experimentally only in the hydrides of Ti, Zr, and Hf (see Ref. 63). An interesting system is the cubic thorium hydride Th_4H_{15}, in which (as in Th_4D_{15}) the value of T_c has been raised to 9 K.

Unfortunately, hydrogen (and other interstitial impurities) mainly lower T_c of the high-temperature compounds with the A15 lattice, although there are occurrences of slight elevation of T_c at a low hydrogen concentration (e.g., in

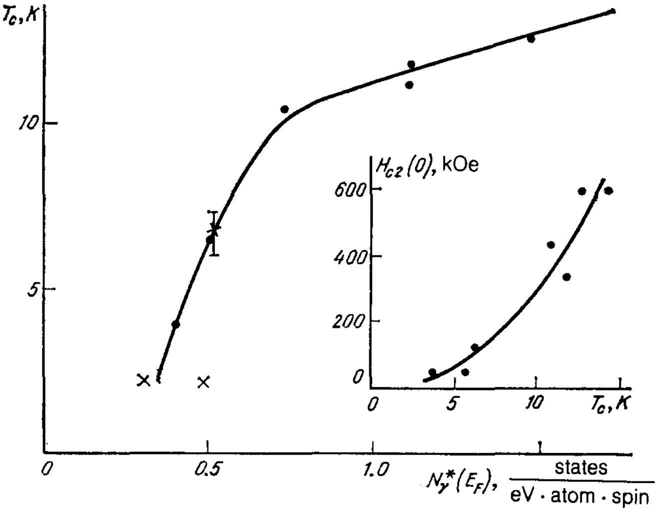

FIG. 10. Dependence of T_c on the density of electronic states at the Fermi surface for ternary chalcogenides of molybdenum. Dots—sulfides; crosses—selenides. The values of the density of states $N_\gamma^*(E_F)$ renormalized owing to the electron-phonon interaction were determined from measurements of the electronic heat capacity $N_\gamma^*(E_F) = (1+\lambda)N(E_F)$, where $N(E_F)$ is the band density of states). The inset shows the dependence of the upper critical field at $T=0$ on the T_c's of these compounds.

Nb_3Sn).[64,65] The lowering of T_c in these compounds is associated, first, with the blurring of the peak of the density of electron states near the Fermi energy and the decrease of $N(E_F)$ (owing to the decrease of the relaxation time of electrons when defects appear in the structure), and second, with the increased concentration of conduction electrons and the shift of the Fermi level. The second effect proves to be rather strong. We can estimate its influence on T_c by comparing the dependence of T_c on the residual resistance for hydrogen-containing specimens and specimens subjected to irradiation with ions or high-energy particles.[64] In this regard it is interesting to study carefully the effect on T_c of impurities that lower the concentration of electrons in compounds having the A15 lattice (as is known, a number of impurities at low concentrations somewhat elevate T_c, e.g., Nb_3Sn and other alloys. This is usually associated with their stabilizing influence and the approach of the composition of the alloy to stoichiometric).

Interestingly, the "hydrogenation" of the high-temperature ternary sulfides of molybdenum, while insignificantly affecting T_c, can appreciably elevate the critical current.[66] Study of the metastable hydrides of palladium and other metals and alloys shows that impurities can be a delicate instrument of action, both on the electronic structure (blurring of sharp singularities in the density of states, shift of the Fermi level, etc.) and on the phonon spectrum, and that the possibilities of elevating T_c and other critical parameters along this pathway have not been exhausted (optimization of their influence).[63]

In the superconducting *ternary chalcogenides of molybdenum* (Chevrel phases), in addition to a record value of H_{c2}, rather high T_c have also been attained ($LaMo_6Se_8$, $T_c = 11.4$ K; $PbMo_6S_8$, $T_c = 15.2$ K). The properties of these materials have been reviewed.[13,43] The critical temperature of these compounds increases with increasing density of electron states $N(E_F)$ (Fig. 10). We should note the rather high density of states $N(E_F)$ in the molybdenum chalcogenides having the highest critical temperatures. This may involve the existence of a peak in the density of states near E_F. Apparently it is hard to expect an appreciable increase in $N(E_F)$ in these compounds without "impairing" the phonon properties. However, an increase of T_c by 1 K in them potentially increases $H_{c2}(0)$ by 100 kOe (inset in Fig. 10). This makes them a highly attractive object for further studies. In addition to high values of H_{c2} and T_c, the ternary chalcogenides of molybdenum have a number of other unusual properties. In a number of chalcogenides one observes low-temperature structural transitions and magnetic ordering along with superconductivity (in the compounds with rare earths). A strong temperature-dependence of the Debye frequency has been found. Their phonon spectrum has strong low-temperature peaks, and other anomalies in the acoustic properties have been observed. However, in practice it is extremely complicated to prepare a compound of strictly stoichiometric composition. At the same time, the deviations from stoichiometry depress T_c (and attenuate the anomalies). Certain potentialities of increasing T_c in the chalcogenides are also realized upon doping. Addition to the ternary compounds $MeMo_6S_8$ of a fourth component often increases the critical temperature (if substitutions are made specifically at the positions of the metallic element Me). We should note that the binary compound Mo_6S_8 is unstable, in contrast to Mo_6Se_8, and is not a superconductor. Partial substitution of sulfur in it by bromine or iodine leads to superconductivity at $T \approx 14$ K ($Mo_6S_6I_2$).[13] We note also that the chalcogenides of molybdenum are not yet technical materials. Their elevated brittleness, which involves the presence of covalent bonds, and low critical current density (especially at high magnetic fields) hinder their widespread introduction. However, prospects clearly exist here.[43]

New potentialities are open up by the superconductive chalcogenide $In_3Mo_{15}Se_{19}$ ($T_c = 4.3$ K, $H_{c2}(0) = 203$ kOe),[67] in which blocks of Mo_6Se_8 and Mo_9Se_{11} are arranged in ordered fashion in a hexagonal structure. This compound has an enormous value of dH_{c2}/dT at T_c of up to 78 kOe/K.

Among the other chalcogenides we should note the unstable sulfides $Li_xTi_{1.1}S_2$ ($x = 0.1$–0.3) having T_c's up to 13 K and having a hexagonal structure.[68]

The possibilities are not exhausted of elevating T_c in superconductive *oxygen compounds*. In the superconductive ceramic $BaPb_{1-x}Bi_xO_3$, the maximum value $T_c = 13.4$ K is attained at the stability boundary of the metallic phase. In addition to instability involving transition to a semiconductive phase with increasing x, an additional instability has been found in this system. A jump in the heat capacity at $T = T_c$, which was observed in the first days after preparing the specimens ($x = 0.25$), disappeared in the course of time if the specimens were kept at room temperature.[69] The state of the specimens and the jump in heat capacity were restored by annealing at 400 °C. The existence of this compound shows the possibility in principle of obtaining high T_c's without transition metals.

A value $T_c = 13.7$ K has been reached in the oxygen compounds of transition metals of the type $Li_xTi_{3-x}O_4$ (at $x = 1$) having the spinel structure and with a very low density of electron states.[70] The maximum T_c was also fixed at a composition lying near the boundary of the metal-dielectric transition. The development of methods of stabilizing unstable phases allows us to hope for elevating T_c in these systems.

There exists a number of classes of superconductors that are promising from the standpoint of elevating T_c. Among them we should note the *Laves phases* (chemical formula AB_2, crystallizing in different structures, of which the C15 structure is of especial interest from the standpoint of superconductivity). Among them the maximum attained T_c is 10.4 K, while $H_{c2}(0)$ exceeds 300 kOe—for $(V, Nb)_2Hf$. An interesting feature of these compounds is the high density of electron states, the existence of a structural transition at rather high temperatures, and a number of other anomalies in lattice and electronic properties, high radiation stability, and low sensitivity to deformations.[43] Certain compounds have exhibited a correlation between lattice instability and features of the electronic characteristics. For a number of the compounds, just as in the case of the A15-type superconductors, one observes an increase in T_c as the temperature T_m of the structural transition decreases (in $Hf_xZr_{1-x}V_2$ we have $\delta T_c \approx 1$–2 K with $\delta T_m \approx 30$ K). The high initial value of T_m (100–150 K) allows us in this case to hope reaching $T_c \gtrsim 15$ K. The pressure appreciably raises the T_c of these compounds (in HfV_2 we have $\delta T_c \approx 1$ K at a pressure of 10 kbar).

Finally we should note several classes of new superconductors in which, perhaps, very high T_c's have not yet been reached, but which attract attention of investigators by their unusual properties. The *magnetic superconductors* have T_c's up to 9.8 K ($TmRh_4B_4$). They are found among five classes of ternary compounds. The greatest number of them is found in the molybdenum chalcogenides and in the ternary borides of the type $(RE)(T)_4B_4$, where RE is a rare earth and T is a transition metal (Rh, Ir). The magnetic superconductors are attractive as objects in which competing orderings occur—superconductive on the one hand, and magnetic (ferro- or antiferromagnetic) on the other hand. Here the ferromagnetic ordering restricts the increase in T_c. Interesting examples are observed for these superconductors in which magnetic ordering restores superconductivity in strong magnetic fields.[1] In the case of $EuMo_6S_8$ this phenomenon arises from compensation of the field due to polarization of the magnetic atoms (Jaccarino-Peter effect).[71] In one of the highest-temperature reversible superconductors $ErRh_4B_4$ ($T_{c1} = 8.7$ K), a decrease in the elastic moduli has been found at low temperatures, involving the development of lattice instability (analogous phenomena are observed in the A15-type superconductors).[72] The existence of competition and coexistence of the superconductive and magnetic orders leads to a mass of interesting phenomena in the magnetic superconductors.[73] We can note, for example, the change in the type of superconductivity from the second type in the region near T_{c1} to the first type near the magnetic-ordering temperature or the discovery of reversible superconductivity in the rare-earth rhodium and osmium stannides having no real long-range magnetic order. The problem is interesting of creating high-temperature magnetic superconductors; $T_c = 11.5$ K has already been attained in the ternary borides with the rare earths ($LuRh_4B_4$).[16]

In the superconductive *metallic glasses* (disordered materials prepared by fast quenching from the liquid state) $T_c = 8.7$ K has been reached (in $(Mo_{0.8}Re_{0.2})_{80}P_{10}B_{10}$). These materials possess high strength together with homogeneity and a certain degree of deformability. They have a large electric resistance $\rho \approx 100$–200 $\mu\Omega\cdot$cm and a weak temperature-dependence of $\rho(T)$. High values of the density of electron states are attained in certain metallic glasses (in $Zr_{70}Pd_{30}$ the band value found from the electronic heat capacity is $N(E_F) = 0.99$ states/Ev·at·spin). The magnitudes of dH_{c2}/dT as $T \to T_c$ for them are rather high (31 kOe/K in $Nb_{60}Rh_{40}$). The Ginzburg-Landau parameter reaches values of 50–100 in them (the maximum for any superconductors). The superconductive properties of metallic glasses are changed weakly with considerable doses of irradiation with high-energy particles.[74] Partly crystalline materials with very small grains (high density of grain boundaries, i.e., strong pinning of vortex filaments, can be obtained by thermal treatment of these glasses. The aggregate of these properties renders the metallic glasses (and other metastable amorphous materials with similar characteristics) a very promising object of study. Unfortunately the small mean free path of electrons and the high values of ρ make the properties of metallic glasses insensitive to the details of the electronic structure and the atomic structure. Hence we can hope for elevating T_c in these systems only by altering the integral characteristics (by using the found dependences of the type of the dependence of T_c on the valency for amorphous metals and alloys[74]).

Extremely great progress in elevating T_c has been made in *organic superconductors*. In the five years that have passed from the moment of their discovery, their maximum critical temperature has increased by a factor of eight. Recently a superconductive phase with $T_c \approx 7$–8 K has been found in the system $(BEDT\text{-}TTF)_2I_3$.[75] Here superconductivity is observed at ambient pressure. A magnetic field of 50 kOe lowers the transition temperature of this phase by only 2 K. As was noted in the review of Ref. 76, the creation of organic conductors with a high degree of one-dimensionality and a "soft" phonon spectrum makes them dielectrically unstable with decreasing temperature. A more rigid and less anisotropic stable lattice consequently has small constants of electron-phonon interaction. Further increase in T_c of organic superconductors is made possible by optimizing their structures. Unfortunately, as yet very little is known of the phonon spectra of organic superconductors and of the role of the Coulomb interaction in them.

Superconductors with heavy fermions,[77,78] though having as yet $T_c \lesssim 1$ K, are a very interesting class of superconductors, perhaps differing in principle from all those known in the type of electron pairing. The three such superconductors[1)] ($CeCu_2Si_2$, UBe_{13}, and UPt_3) are further adjoined by a number of uranium compounds with $T_c^{max} = (3.86$ K (U_6Fe) and cerium (among them several Laves phases) with $T_c^{\max} = 6$ K (CeRu$_2$). They are all distinguished primarily by the extremely high density of states $N(E_F)$, as determined from the low-temperature heat capacity or the Pauli spin susceptibility (in the superconductors with heavy fermions proper it is 450–1100 mJ/mole·K^2, i.e., it exceeds the density of states of ordinary metals by a factor of 10^2–10^3). They possess a number of unusual properties that have already been established experimentally. Their current carriers with heavy masses directly participate in superconductivity, as indicated by the large jump in heat capacity at T_c and by the high values of H_{c2}. The magnitude of dH_{c2}/dT near T_c reaches the gigantic value of 440 kOe/K in UBe$_{13}$.[77] The lack of clarity of the nature of the superconductivity, the presence of atoms having an unstable f shell, the unusualness of combining extremely high $N(E_F)$ and low T_c, the closeness to a localized state, and other features draw considerable attention to these superconductors. In any case the correlation of T_c with N proves true for them (high values of the effective electronic mass sharply diminish the value of N/m in them). We can hope for increasing their T_c's by decreasing the effective mass, as is observed in the above-stated compounds of U and Ce (although there is apparently no simple correlation $T_c \sim N(E_F)^{-1}$).[77]

In addition to the superconductors that we have treated, the literature has also discussed the possibilities of superconductivity and of obtaining high T_c in other systems, including such unusual ones as metallic hydrogen, domain walls, electron-hole droplets, and various artificial superconductive structures. Unfortunately the inadequacy of experimental data impedes making an estimate of the prospects of most of these systems.

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As we see, the current stage of study of superconductivity is that it is an extensive and interesting field of activity with rich potential and prospects. This is confirmed again by the review of Ref. 1 and also by the research programs in the USA[79] and Japan[80] that have been recently published. The research on and applications of superconductors will continuously expand, even if there is no appreciable increase in T_c. Undoubtedly, the upper bound of T_c will rise, and here even an advance of several degrees is important. "Hydrogen" superconductors, i.e., systems showing superconductivity at the temperature of liquid hydrogen, have already been found. Creation of "neon" superconductors (with $T_c \gtrsim 27$ K) and development of superconductive materials that operate in the hydrogen temperature region is next in line to be realized.

[1)] It was recently found[82] that the antiferromagnet CePb$_3$ having heavy fermions becomes a superconductor with $T_c \approx 0.6$ K, but only in high magnetic fields $\gtrsim 150$ kOe. This opens up new possibilities for seeking superconductors among magnetic materials nonsuperconductive under ordinary conditions.

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Translated by M. V. King