

NEW SUPERCONDUCTORS\*

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THE phenomenon of superconductivity is presently attracting more and more attention on the part of a large group of physicists. This is connected principally with the fact that its practical utilization has become possible. One of the trends in the study of superconductivity is the development of new superconductors and the investigation of their properties. Many superconductors with different critical temperatures have been observed in recent years. Detailed information on many of them is contained in the extensive review of Roberts<sup>[1]</sup> and in the article by Matthias et al.<sup>[2]</sup> We shall dwell briefly only on certain new types of superconductors observed during the last 3-4 years.

If we start with pure elements, notice should be taken of the discovery of superconductivity in germanium and silicon. As is well known, under ordinary conditions both elements are semiconductors, and superconductivity appears in them only at a pressure of 120 kbar, just as in the case of Se and Te<sup>[3-5]</sup>. At such a pressure, these elements experience a polymorphic transformation. Figures 1 and 2 show curves of the transition of Ge and Si samples into the superconducting state. Owing to the brittleness of Ge and Si in the initial state, to perform measurements under pressure these substances were first ground into powder and the resistance of the pressed powder was measured as a function of temperature at constant pressure. Both elements revealed a metallic conductivity behavior. The value of  $\rho_{300^\circ\text{K}}/\rho_{4.2^\circ\text{K}}$  of Ge ranged from 18 to 27, and that of Si from 2 to 5.1. Unfortunately, polymorphic transformations of Ge and Si are reversible, and these elements, like Te and Se, cease to be superconducting after the pressure is removed, becoming again semiconductors, which, as a rule, do not turn into superconductors under ordinary conditions. An exception is Ge alloyed with Te. For example, an alloy of Ge with Te with composition  $\text{Ge}_{0.834}\text{Te}$ , as is well known<sup>[6]</sup>, goes over into a superconducting state and reveals at the

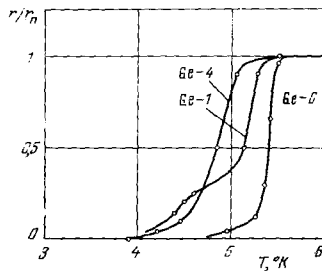


FIG. 1. Transition curves of germanium samples at a pressure 120 kbar (from [5]).

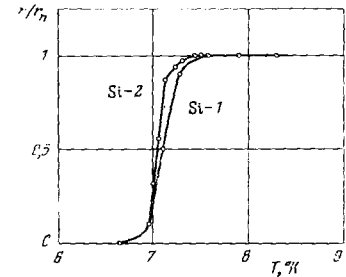


FIG. 2. Transition curves of silicon samples at pressures 120-130 kbar (from [5]).

same time a dependence of the critical temperature on the carrier density<sup>[6,7]</sup>.

The superconductivity of protactinium is most interesting. Protactinium<sup>[8]</sup> goes over into the superconducting state at  $T = 1.4^\circ\text{K}$ . It can be regarded as the

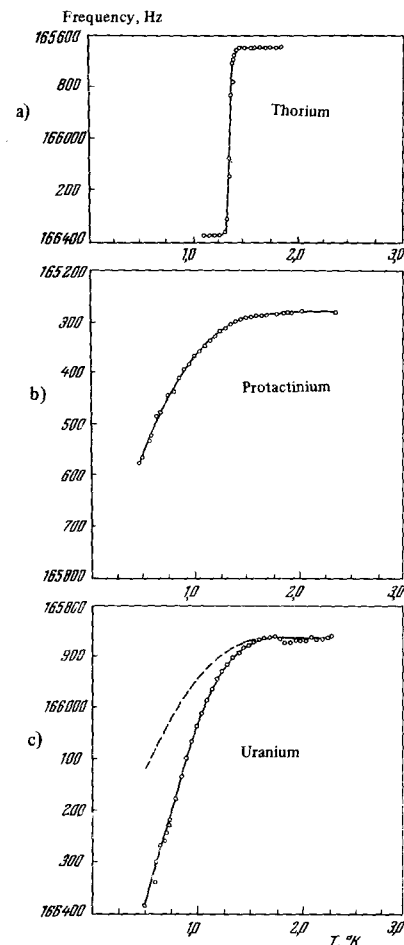


FIG. 3. Transition curves obtained in [8,9] for samples of thorium (a), protactinium (b), and uranium (c).

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first element of the 5f-series. The protactinium investigated in<sup>[8]</sup> was obtained by reducing  $\text{PaF}_4$  with Li vapor at  $1300^\circ\text{C}$ . Figure 3 shows the transition curves of thorium, protactinium, and uranium, taken from<sup>[8,9]</sup>. Unfortunately, the uniformity of the superconducting properties of the actinides, which follows from the presented curves, is violated somewhat by the fact that  $\alpha$ -uranium has apparently no superconductivity, and only the  $\beta$  and  $\gamma$  phases become superconducting; the presence of traces of the latter phases in samples leads to the appearance of superconductivity at  $T = 0.7\text{--}0.8^\circ\text{K}$ . It must be noted, however, that  $\alpha$ -uranium goes over into the superconducting state under a pressure of  $8\text{--}10$  kbar<sup>[10]</sup>.

An investigation of films of pure metals has shown that in many cases the films go over into the superconducting state at much higher temperatures than the corresponding bulk metals. Thus, for example, films of tungsten, whose critical temperature reached  $4.1^\circ$ , were investigated in<sup>[11]</sup> (the thickness of these films was  $2 \times 10^{-5}$  cm).

The authors were inclined to regard this sharp increase of the critical temperature as traces of the manifestation of "surface" superconductivity, considered by V. L. Ginzburg<sup>[12]</sup> and arising as a result of formation of an oxide layer on the surface of the film. It was shown in<sup>[13]</sup>, however, that a layer of suboxide  $\text{M}_3\text{O}$  (in the case of W) or subnitride (in the case of Mo and Re) can be produced on the surfaces of tungsten, rhenium, and molybdenum films. It is therefore quite probable, as noted by the authors of<sup>[13]</sup>, that the critical temperature of the film is determined by the superconductivity of these compounds. The critical temperatures obtained in that investigation were  $3.35^\circ\text{K}$ ,  $5^\circ\text{K}$ , and  $7^\circ\text{K}$  for films of tungsten, molybdenum, and rhenium, respectively, and all films having these values of the critical temperature revealed on the x-ray patterns lines characteristic of the  $\beta$ -W structure (Fig. 4) or of the face-centered subnitride. Our investigations of the superconductivity of rhenium films<sup>[14]</sup> have shown that in the case when the films are obtained by evaporation in a closed evacuated vessel, and their superconductivity is investigated in such a way that the vessel with the film is not opened and the film does not come in contact with the atmosphere, the critical temperature of the film barely differs from the critical temperature of the bulk rhenium. On the other hand, if the film is made of rhenium evaporated by means of an electron beam and

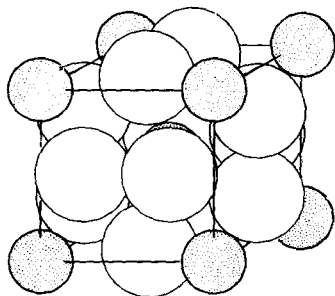


FIG. 4. Crystal structure of  $\beta$ -W ( $A = 15$ ). The large light circles denote the atoms of the transition metal.

then exposed to air prior to placing in the cryostat, its critical temperature is much higher and usually amounts to  $3.5^\circ\text{K}$ . These data confirm the influence of the contact of the film with the air atmosphere on the increase of its critical temperature.

Attempts were made in several investigations to attribute the increase of the critical temperature of aluminum films and its dependence on the thickness to the formation of an oxide layer and the associated surface conductivity (see, e.g.,<sup>[15]</sup>). The data of<sup>[16]</sup>, however, indicate that the formation of the oxide layer is, at any rate, not the only cause of the increase of  $T_C$  of the film. It is not excluded that in the case of aluminum the increase of the critical temperature of the film may be connected with the quantization effect considered in<sup>[17]</sup>. It should be noted that the quantization effect does not exclude the possibility of an influence of the oxide layer on  $T_C$ .

The number of recently discovered superconductors among compounds is much greater than that among pure elements. Among the metallic compounds with  $\beta$ -W structure\*, as is well known, are the superconductors with the highest temperatures, for example,  $\text{Nb}_3\text{Sn}$  ( $T_C = 18.05^\circ\text{K}$ ) and  $\text{V}_3\text{Si}$  ( $T_C = 17.1^\circ\text{K}$ ). However, many compounds with such a lattice do not have superconductivity at all, for example  $\text{V}_3\text{Ir}$  ( $T_C < 0.3^\circ\text{K}$ ), or have a low critical temperature— $\text{V}_3\text{Sb}$  ( $T_C = 0.8^\circ\text{K}$ ). A brief summary of the data on these compounds is given in Table I (the parentheses indicate the critical temperature<sup>[18]</sup> in  $^\circ\text{K}$ ).

$\text{V}_3\text{Si}$  has a polymorphic transformation in the temperature region  $20\text{--}30^\circ\text{K}$ , going over into a tetragonal phase<sup>[19]</sup>. The degree of tetragonality increases to its limiting value, at which  $c/a = 1.0025$ , in a range of several degrees below the transition point. A polymorphic transformation similar to that occurring in  $\text{V}_3\text{Si}$  occurs apparently also in other compounds with  $\beta$ -W structure, for example,  $\text{Nb}_3\text{Sn}$ <sup>[20,21]</sup>. The high critical temperatures of the compounds with  $\beta$ -W structure stimulate the search for new superconductors among the compounds with such a structure. However, such searches can also lead to erroneous results.

A recent communication<sup>[22]</sup> reports observation of superconductivity in the compound  $\text{V}_3\text{In}$  with  $T_C = 13.9^\circ\text{K}$ . In the same paper, the authors report that they obtained many other compounds based on V, with  $\beta$ -W structure. The samples were prepared by diffusion annealing of a vanadium wire in a quartz ampoule at  $T = 1000\text{--}1200^\circ\text{C}$  for 20 hrs. N. N. Mikhailov and the author attempted to obtain  $\text{V}_3\text{In}$  and  $\text{V}_3\text{Al}$  by sintering in a high-frequency furnace samples suspended on vanadium foil in a quartz ampoule<sup>[23]</sup>, and observed superconductivity of  $\text{V}_6\text{In}$  at  $T_C = 10^\circ\text{K}$ , and of  $\text{V}_3\text{Al}$  at  $T_C = 15^\circ\text{K}$ . It turned out later, however, that if the walls of the quartz ampoule are covered with vanadium foil (in the case of  $\text{V}_3\text{In}$ ), or if the sintering is performed in an aluminum crucible (in the case of  $\text{V}_3\text{Al}$ ), then  $T_C$  drops abruptly (to  $1.9^\circ\text{K}$ ). A spectral analysis has shown that all samples that are superconducting at

\*As is well known, the  $\beta$ -W structure is actually the structure of  $\text{W}_3\text{O}$ .

Table I

						<sup>13</sup> Al	<sup>14</sup> Si	<sup>15</sup> P
						Nb <sub>3</sub> Al (17.5) Mo <sub>3</sub> Al (0.58)	V <sub>3</sub> Si (17.4) Cr <sub>3</sub> Si Mo <sub>3</sub> Si (1.30)	
<sup>26</sup> Fe	<sup>27</sup> Co	<sup>28</sup> Ni	<sup>29</sup> Cu	<sup>30</sup> Zn	<sup>31</sup> Ga	<sup>32</sup> Ge	<sup>33</sup> As	
	V <sub>3</sub> Co				V <sub>3</sub> Ga (16.5) Cr <sub>3</sub> Ga Nb <sub>3</sub> Ga (14.5) Mo <sub>3</sub> Ga (0.76)	V <sub>3</sub> Ge (6.01) Cr <sub>3</sub> Ge Nb <sub>3</sub> Ge (6.90) Mo <sub>3</sub> Ge (1.43)	V <sub>3</sub> As	
<sup>44</sup> Ru	<sup>45</sup> Rh	<sup>46</sup> Pd	<sup>47</sup> Ag	<sup>48</sup> Cd	<sup>49</sup> In	<sup>50</sup> Sn	<sup>51</sup> Sb	
Cr <sub>3</sub> Ru (3.3)	V <sub>3</sub> Rh (0.38) Cr <sub>3</sub> Rh Nb <sub>3</sub> Rh (2.50)				Nb <sub>3</sub> In (9.2)	V <sub>3</sub> Sn (7.0) Nb <sub>3</sub> Sn (18.05) Ta <sub>3</sub> Sn (6.4)	Ti <sub>3</sub> Sb (5.8) V <sub>3</sub> Sb (0.80) Nb <sub>3</sub> Sb	
<sup>76</sup> Os	<sup>77</sup> Ir	<sup>78</sup> Pt	<sup>79</sup> Au	<sup>80</sup> Hg	<sup>81</sup> Tl	<sup>82</sup> Pb	<sup>83</sup> Bi	
Nb <sub>3</sub> Os (1.05) Mo <sub>3</sub> Os (7.2)	Ti <sub>3</sub> Ir (5.4) V <sub>3</sub> Ir Cr <sub>3</sub> Ir (0.45) Nb <sub>3</sub> Ir (1.7) Mo <sub>3</sub> Ir (8.8)	Ti <sub>3</sub> Pt (0.58) V <sub>3</sub> Pt (2.83) Cr <sub>3</sub> Pt Nb <sub>3</sub> Pt (9.2)	Ti <sub>3</sub> Au V <sub>3</sub> Au (0.74) Zr <sub>3</sub> Au (0.92) Nb <sub>3</sub> Au (11.5)			Zr <sub>3</sub> Pb (0.76)		

$T \geq 10^\circ \text{K}$  revealed an intense Si line, whereas samples having low  $T_C$  revealed no Si lines. This suggests that deoxidation of the quartz surface by the metal vapor took place in<sup>[22]</sup>, and the ternary systems  $V_3\text{In}_x\text{Si}_{1-x}$ , having a lattice of the  $\beta$ -W type, were produced in<sup>[23]</sup>. It is quite probable that the compounds  $V_3\text{In}$  and  $V_3\text{Al}$  either do not exist at all, or are produced only under definite and special conditions<sup>[24]</sup>.

In the opinion of a number of authors, an important feature for compounds having the  $\beta$ -W structure is that the atoms of the transition metal form a three-dimensional grid consisting of three mutually perpendicular linear chains of atoms (e.g., of niobium). Such a grid allows us to consider the motion of an electron along a linear chain as quasi-one-dimensional<sup>[25]</sup>; the violation of the order in this chain, i.e., replacement of the transition-metal atom by another component, lowers  $T_C$ <sup>[26]</sup>. This apparently is the cause of the increase of  $T_C$  of  $\text{Nb}_3\text{Ge}$  when the composition comes close to stoichiometric<sup>[27]</sup>. The idea that an important role is played in the appearance of superconductivity by low-lying optical branches of the vibrations of lattices of the type  $\beta$ -W has been recently advanced<sup>[28]</sup>. The polymorphism of  $V_3\text{Si}$  is also associated with this role<sup>[19]</sup>. Measurements of the speed of sound in the 4.2–300°K region have shown that the  $V_3\text{Si}$  crystal loses its stiffness against shear vibrations propagating in the [110] direction<sup>[29,30]</sup>. The elastic modulus corresponding to such a deformation decreases greatly with decreasing temperature. At 30°K this modulus is so small that the crystal becomes opaque to the sound. The lattice vibrations propagating near the binary axis have an anomalously low velocity. The displacement of  $T_C$  under unilateral compression turns out to be strongly anisotropic. Thus,  $(\partial T_C / \partial P)_{(100)} = -5 \times 10^{-4} \text{ deg/atm}^{[31]}$ , and under hydrostatic compression  $(\partial T_C / \partial P) = +2 \times 10^{-4} \text{ deg/atm}^{[32]}$ .

All the foregoing points to a major role for the photon spectrum; however, it must nevertheless be noted that high values of  $T_C$  are possessed only by compounds with a large electronic specific heat, i.e., with a higher density of electron states on the Fermi surface. Table II lists data on the coefficient  $\gamma$  of the linear term of the specific heat for five compounds having  $\beta$ -W structure<sup>[33]</sup>.

From a comparison of the presented data on  $\gamma$  for the first three compounds with the values of  $\gamma$  obtained for other superconductors, it is clearly seen that  $\gamma$  is much higher in compounds having high  $T_C$ . The high values of the densities of states of such compounds are perfectly sufficient to ensure their high values of  $T_C$ , and it is therefore not excluded that the specific features of the elastic properties of the lattice noted above does not play the major role. It is quite probable, however, that both the high value of the density of states and the features of the elastic properties of such compounds are the consequence of the fact that their Fermi level is located very close to the narrow maximum of the density of state<sup>[32]</sup>.

The most timely problem in the investigation of superconductivity is, naturally, the possibility of increasing the upper limit of the critical temperature.

Table II

	$T_C$ °K	$\gamma \cdot 10^4$ , cal mole-deg	$\Theta_D$ , °K
Nb <sub>3</sub> Sn	18.05	450	290
V <sub>3</sub> Ga	16.6	244	310
V <sub>3</sub> Si	17.1	186	330
V <sub>3</sub> Ge	6.1	73	405
Mo <sub>3</sub> Ir	8.5	30	325

i.e., to rise above the value of  $T_C$  of  $Nb_3Sn$  (18.05°K). It is shown in recent papers that such a rise is possible. In the investigation of the four-component system Nb-Sn-Al-Ge<sup>[34]</sup> it was observed that whereas in the quasibinary systems  $Nb_3Sn-Nb_3Al$  and  $Nb_3Sn-Nb_3Ge$  the critical temperature decreases smoothly from  $(T_C)Nb_3Sn$  to  $T_C$  of the second component, in the  $Nb_3Al-Nb_3Ge$  system the dependence of  $T_C$  on the content of the components C has a maximum in the region of concentrations approximately corresponding to  $(Nb_3Al)_4Nb_3Ge$ . Further investigations of such alloys have shown that by special heat treatment the critical temperature of the alloy, corresponding to the maximum of the dependence of  $T_C$  on C, can be raised to 19°K<sup>[35]</sup>, and according to the data of<sup>[36]</sup> even to 20°K. A recent measurement by the authors of<sup>[35]</sup> of the critical fields of this system has shown that  $\partial H_{C_2}/\partial T$  has sufficiently high value and amounts to  $\approx 20$  kOe/deg for a sample with  $T_C = 19.45^\circ K$ , if  $H_{C_2}$  is chosen to be the value of the magnetic field at which the resistance begins to differ from zero. Figure 5 shows the change of the resistance of one of the samples of the Nb-Al-Ge alloy on going to the superconducting state at  $H = 0$ .

By increasing the homogeneity of the sample it is apparently possible to raise  $\partial H_{C_2}/\partial T$ . An estimate of the sign of  $\partial T/\partial p$  at a pressure  $\approx 2000$  atm has shown that, just as in  $Nb_3Al$ <sup>[34]</sup>, the derivative  $\partial T_C/\partial p$  of the Nb-Al-Ge alloy is also possible.

It is quite probable that the use of multicomponent systems will increase the limiting critical temperature (see, e.g.,<sup>[37]</sup>), but it should be noted that high-temperature superconductors with lattice of the  $\beta$ -W type have a rather large constant  $\rho$  in the expression  $T_C = 1.140 \Theta_D \cdot e^{-1/\rho}$ . It is not excluded that an attempt to increase  $\rho$  will lead to instability of the lattice<sup>[64,65]</sup>.

As is well known<sup>[1]</sup>, bismuth forms a large number of superconducting compounds with a whole series of nonsuperconducting metals. Recently<sup>[38]</sup>, attempts were made to synthesize under pressure bismuth compounds that are not formed under ordinary conditions. The results confirmed the existence of the CuBi compound, which was obtained earlier electrolytically at a large cathode overvoltage. This compound, as shown earlier<sup>[39]</sup>, becomes superconducting at  $T_C = 2.2^\circ K$  and disintegrates when heated to 120°C. Besides CuBi, compounds of bismuth with silver, magnesium, cobalt, and several other metals were obtained in<sup>[38]</sup>\* and also turned out to be superconducting. Like CuBi, these compounds are metastable. Synthesis under pressure made it possible to discover new compounds of bismuth with nonsuperconducting metals. They have the following composition:  $AgBi_2$  with  $T_C = 2.78^\circ K$ ,  $MgBi_4$  with  $T_C \approx 1^\circ K$ , and  $CoBi$  with  $T_C \approx 0.50^\circ K$ . It is noted in<sup>[38]</sup> that apparently the nearest neighbors of Bi-Bi produce superconductivity in any nonmagnetic metallic matrix, regardless of the structure, symmetry, and composition; it is proposed that this is a common property of atoms with five valence electrons, including niobium. Without discussing the degree to which such a point of view is likely, it should be noted that bismuth has  $\beta$

\*It should be noted that, unlike in<sup>[39]</sup>, the CuBi obtained in the cited investigation becomes superconducting at 1.4 – 1.33°K.

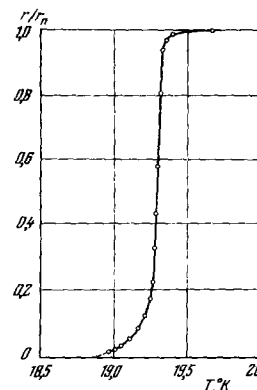


FIG. 5. Transition curve of sample of Nb-Al-Ge alloy. The ordinates represent the ratio of the electric resistance of the sample to its electric resistance in the normal state.

and  $\gamma$  modifications which are unstable under ordinary conditions and which become superconducting at 8 and 5°K<sup>[40]</sup> and it is possible that this is the reason why bismuth forms many superconducting compounds. The analogs of bismuth in this sense are Ga and Be<sup>[1]</sup>. All these metals, when condensed on a surface having  $T = 4.2^\circ K$ , form, as is well known, layers that become superconducting at sufficiently high temperatures. These metals also form a large number of superconducting compounds. Thus, for example, the compound  $Ag_3Ga$  was recently investigated and found to be superconducting<sup>[41]</sup>. It is an electronic compound with  $n = 1.5$  electrons per atom. The superconductivity of electronic compounds having less than two electrons per atom demonstrates once more that the empirical rule<sup>[1]</sup>, according to which  $n$  must be larger than two for superconductors, is too primitive.

A large number of beryllium compounds also become superconducting. The first superconducting compounds of beryllium\* were AuBe, with  $T_C = 2.64^\circ K$ <sup>[1]</sup>, and  $Be_{13}W$ , with  $T_C = 4.1^\circ K$ <sup>[37]</sup>. New data have recently appeared concerning the superconductivity of beryllium compounds. The highest critical temperature among these compounds is possessed by  $Be_{22}Re$ , which has  $T_C = 9.6^\circ K$ <sup>[42]</sup>. A characteristic feature of beryllium compounds is the fact that they apparently have a high Debye temperature; for example,  $Be_{22}Re$  has  $\Theta_D = 990^\circ K$ <sup>[42]</sup>, which is considerably higher than  $\Theta_D$  of other superconductors. The electronic specific heat of  $Be_{22}Re$  is only three times larger than the value obtained for pure beryllium, and has a much lower value than all other known superconductors. Additional information on the superconductivity of beryllium alloys were recently reported<sup>[43-45]</sup>. It was shown, for example, that in the Be-Ga system superconductivity is observed at  $T_C = 6.5^\circ K$ <sup>[45]</sup>. Compounds having a large beryllium content are of special interest. In these compounds the density of states (determined from the value of the electronic specific heat) is much lower than in other known superconductors. One can therefore hope that an increase of the density of states can lead to an appreciable increase of  $T_C$  of such alloys.\*

\*Superconductivity of beryllium films condensed on a substrate having  $T = 4.2^\circ K$  was observed by B. G. Lazarev and co-workers [1].

\*The possible influence of virtual Friedel bound states on the appearance of superconductivity in beryllium alloys is discussed in [44]. It is also noted there that the electron-photon interaction can be influenced by local modes of oscillation due to the presence of the heavy atoms.

An interesting class of superconductors are the compounds of alkali metals with carbon. These include, as is well known, compounds with composition  $C_8M$  and  $C_{16}M$ . Compounds in which the metal  $M$  was K, Rb, and Cs were investigated in<sup>[40]</sup>. The highest transition temperature was possessed by the C-K system; this temperature varied with the composition, and its maximum value reached  $0.55^\circ\text{K}$ . It should be noted that this temperature corresponded not to the exact stoichiometric composition, but to one shifted slightly towards K. In C-Rb samples,  $T_C$  varied from  $0.023$  to  $0.151^\circ\text{K}$ , and in the C-Cs system from  $0.020$  to  $0.135^\circ\text{K}$ .  $T_C$  increased with increasing excess of alkali metal, and depended also on the quality of the initial graphite. The width of the transition of the investigated superconductors usually was only several millidegrees.

The samples were prepared by heating the pure alkali metal with pyrolytic graphite in vacuum. By varying the ratio of the components, it was possible to obtain either a green modification, corresponding to  $C_8M$ , or a blue one corresponding to  $C_{16}M$ . No superconductivity was observed for  $C_{16}M$  compounds down to  $0.011^\circ\text{K}$ . The absence of superconductivity in the pure components was verified down to the same temperature. The structure of such compounds is very anisotropic and has a layered character (Fig. 6). The mean free path of the electrons in the hexagonal plane is much larger than in the direction perpendicular to it. The authors attempt to attribute to this circumstance the large anisotropy of the critical magnetic field in samples of the C-K system. Thus, for example, for a C-K sample having  $T_C = 0.55^\circ\text{K}$ , the value of  $H_C$  at  $T = 0.32^\circ\text{K}$ , is 160 Oe when  $H$  is perpendicular to the  $[0001]$  direction and 7300 Oe when  $H$  is parallel to  $[0001]$ . Even greater anisotropy of  $H_C$  is observed in C-K samples with  $T_C = 0.39^\circ\text{K}$ . In this case  $H_C = 25$  Oe when the field is perpendicular to the hexagonal axis and 250 Oe when it is parallel to it.

In the discussion of the results obtained in<sup>[38b]</sup>, the absence of superconductivity in compounds of the  $C_{16}M$  composition is regarded as an indication that two-

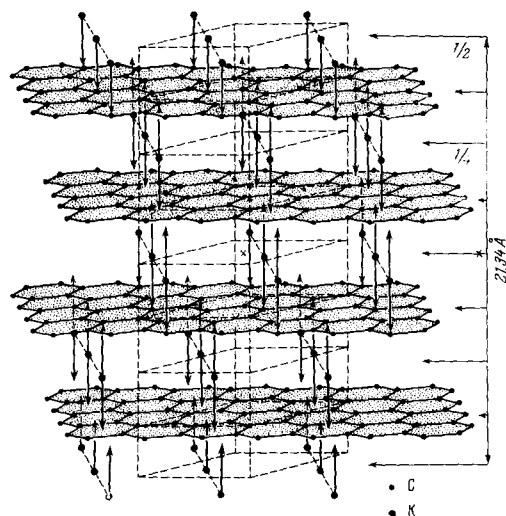


FIG. 6. Crystal structure of the  $C_8M$  compound (from<sup>[38]</sup>).

dimensional superconductivity is impossible. This conclusion is based on the fact that in  $C_{16}M$  and  $C_8M$  the layers of the metal are practically identical, but in the former case they are separated by two layers that do not contain any metal, and in the latter by one; in the former case exchange between the metal layers is impossible, whereas in the latter one such an exchange is quite probable. It should be noted, however, that superconducting  $C_8M$  compounds, in which both the electron and phonon spectra are strongly anisotropic (as is manifest by the strong anisotropy of the superconducting properties), can nevertheless be regarded as quasi-two-dimensional superconducting systems; the absence of superconductivity in  $C_{16}M$  can then be due to the fact that their phonon spectrum differs somewhat from the spectrum of  $C_8M$ .

Superconductivity was recently observed in  $Ag_2F$ <sup>[47]</sup>. This compound also has a layered structure, consisting of hexagonal close-packed layers of Ag and F, superimposed on one another in the sequence  $F - Ag - Ag - F - Ag - Ag$ . The  $Ag_2F$  has metallic conductivity along the hexagonal axis. This compound becomes superconducting at  $T_C = 0.066^\circ\text{K}$  and its crystal field is  $H_{C0} = 2.5$  Oe. The value of  $\gamma$  determined from  $H_{C0}$  and  $T_C$  turn out to be  $0.62 \times 10^{-3}$  J/mole-deg (in Ag  $\gamma = 0.67 \times 10^{-3}$  J/mole-deg).

Mention should also be made of a class of superconducting compounds containing alkali and alkali-earth metals—these are the tungsten bronzes with composition  $M_xWO_3$ , where  $M$  is an alkali or an alkali-earth metal (Na, K, Rb, Cs, Ca, Sr, Ba), and  $x$  ranges from 0.1 to 0.5<sup>[48,49]</sup>. The critical temperatures of such compounds lie in the interval from 0.1 to  $0.5^\circ\text{K}$ . Superconductivity is observed for compounds having a tetragonal or hexagonal lattice, whereas for bronze with  $WO_3$  structure or with structure of the perovskite type, no superconductivity was observed.

A very interesting class of superconductors are the titanates of strontium<sup>[50]</sup>, which become superconducting, after heat treatment in hydrogen or in vacuum, at  $T \approx 0.4^\circ\text{K}$ ; their critical temperature depends on the carrier density. In the first experiments they used single crystals, but superconductivity was observed also in ceramic samples (and also in ceramic samples of mixed compounds<sup>[51]</sup>). Recently, experiments were

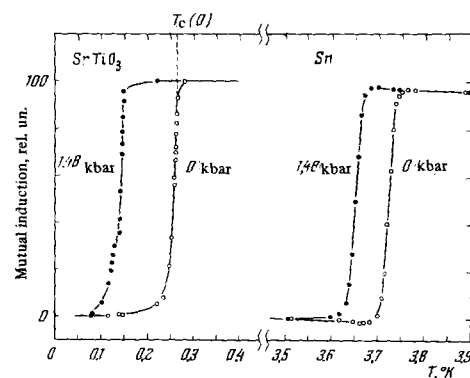


FIG. 7. Transition curves of  $SrTiO_3$  with and without pressure. Right - transition curves of tin, which serves as a manometer. Ordinates - mutual induction in relative units.

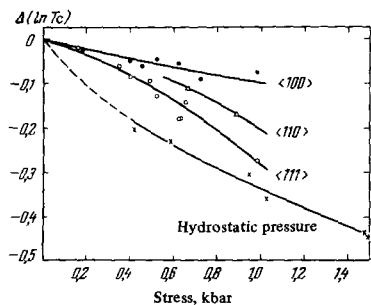


FIG. 8. Plot of  $\Delta(\ln T_c)$  vs. unilateral pressure applied to the  $\text{SrTiO}_3$  sample and vs. the hydrostatic pressure (lower curve).

made for the purpose of determining the influence of hydrostatic compression on the critical temperature of single-crystal  $\text{SrTiO}_3$ . The measurement data obtained at pressures up to 1.480 kbar point to an appreciable nonlinear and anisotropic variation of the quantity  $\Delta(\ln T_c)$  with pressure (Figs. 7 and 8).

Among the superconducting compounds of the semi-conducting type, notice should be taken also of sulphur compounds. One of them has been long known, namely  $\text{CuS}^{[1]}$ . Its critical temperature is  $1.62^\circ\text{K}$ . Recently, superconductivity was observed in the systems  $\text{La-S}^{[53]}$  and  $\text{La-Se}^{[54,55]}$ . However, the superconductivity is observed only in samples with metallic conductivity, and  $T_c$  depends strongly on the carrier density. Metallic conductivity is possessed by the compounds  $\text{La}_3\text{S}_4$  and  $\text{La}_3\text{Se}_4$ , whereas  $\text{La}_2\text{S}_3$  and  $\text{La}_2\text{Se}_3$  are semiconductors. The critical temperature for  $\text{La}_3\text{S}_4 \leq 6.5^\circ\text{K}$ , and for  $\text{La}_3\text{Se}_4 \leq 8.6^\circ\text{K}$  (according to the latest data<sup>[55]</sup>,  $\text{La}_3\text{Se}_4$  has  $T_c \approx 10^\circ\text{K}$ ). On going over from the metallic compound to the semiconducting one, the critical temperature decreases sharply, but the lattice constant does not change, since the  $\text{La}_2\text{Se}_3$  structure has vacancies that occupy one third of the places of the La atoms. On going from  $\text{La}_3\text{Se}_4$  to  $\text{La}_{2.8}\text{E}_{0.2}\text{Se}_4$ , where E are vacancies,  $T_c$  changes from 10 to  $1^\circ\text{K}$ . The dependence of  $T_c$  on the concentration, in accordance with the opinion of the authors of<sup>[55]</sup>, is sufficiently well described by the BCS formula, provided the electron-phonon interaction is regarded as constant and it is assumed that the change of  $T_c$  is due to the change of the number of electrons.

A highly unique superconductor is silver clathrate  $\text{Ag}_7\text{O}_8\text{NO}_3$ , which becomes superconducting near  $1^\circ\text{K}$  ( $1.04^\circ$ )<sup>[56]</sup>. The clathrates are produced by electric oxidation of aqueous solutions of silver salts. This com-

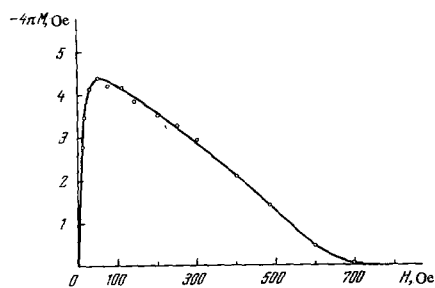


FIG. 9. Dependence of the magnetic moment on the field for a sample of silver clathrate at  $T = 0.1^\circ\text{K}$  [56].

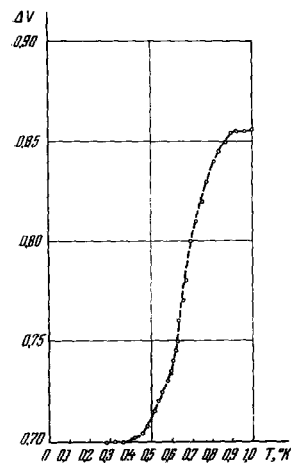


FIG. 10. Transition curve of silver clathrate, according to the data of N. N. Mikhailov and the author.

pound has at room temperature a cubic lattice which, according to the data of<sup>[56]</sup>, becomes tetragonal near  $200^\circ\text{K}$ . With this,  $(c/a)_{10^\circ\text{K}} = 0.9603$ . The transition to the tetragonal phase, in the opinion of the authors of<sup>[56]</sup>, is accompanied by the alignment of the planes of the  $\text{NO}_3$  groups perpendicular to the  $c$  axis (see<sup>[57]</sup> and Fig. 11). This compound has metallic conductivity, and its resistance drops by a factor of 200 when cooled from  $300^\circ\text{K}$  to  $4.2^\circ\text{K}$ . The value of  $H_{c0}$  is 57 Oe, and the calculated value of  $\gamma$  is  $0.050 \times 10^{-3} \text{ J/cm}^3 (\text{°K})^2$ . The value of  $\gamma$  obtained for silver clathrate is close to the value of  $\gamma$  of silver ( $0.065 \times 10^{-3} \text{ J/cm}^3 (\text{°K})^2$ ); since the number of carriers in this compound is much smaller than in pure silver, the width of the conduction levels, as noted by the authors of<sup>[56]</sup>, should be smaller and the effective masses should be much larger than in pure silver. In addition to clathrates made of nitrate salts of silver, clathrates made of fluoride and borofluoride compounds of silver were also investigated; these became superconducting at 0.3 and  $0.15^\circ\text{K}$ , respectively<sup>[56]</sup>. The measurements of  $T_c$  of  $\text{Ag}_7\text{O}_8\text{NO}_3$  were repeated by us; the results obtained essentially confirmed the data of<sup>[56]</sup>, although the value of the critical temperature was somewhat lower than  $0.9^\circ\text{K}$  (Fig. 10).

It is seen from all the foregoing that superconductors spread more and more over the periodic table. Pro-

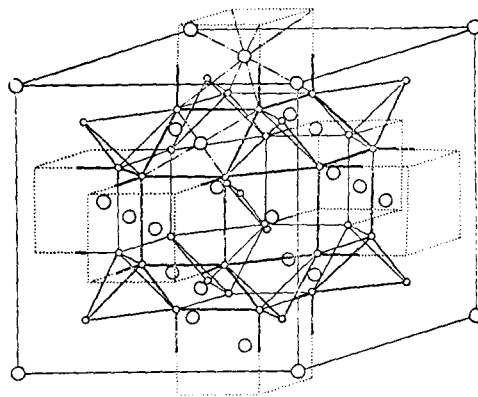


FIG. 11. Crystal structure of silver clathrate. Small circles - oxygen ions; large circles - silver ions; nitrogen - in the center of the cell.

tactinium, and also germanium and silicon, are a new confirmation of this fact. Among the recently developed superconductors with interesting properties we can point out alloys of Be with Re, the increase of  $T_C$  of  $Nb_3Ge$  on approaching stoichiometric composition, and, of course, the increase of  $T_C$  in Nb-Al-Ge to 19–20°K.

Apparently superconductivity is realized in many-valley semiconductors (Ge-Te alloy) and also in titanates, in which the principal role in the occurrence of superconductivity is probably played by the distinctive features of the phonon spectrum of the polar crystal, by the singularities in the behavior of the dielectric constant, and possibly by the effective screening of the Coulomb interaction<sup>[59]</sup>.

The anisotropy of the superconducting properties of  $C_6M$ , in spite of the different point of view advanced in<sup>[38b]</sup>, is more similar to two-dimensional superconductivity, and, being the limiting anisotropic case of superconductivity, deserves of a special study.

Great interest attaches also to an investigation of compounds having high values of the electronic specific heat. As noted above, the electronic specific heat of  $Nb_3Sn$ ,  $V_3Si$ ,  $Nb_3Ca$ , and other compounds exceeds by several times the highest values of the electronic specific heat of pure transition metals. An exhaustive study of the physical properties of such systems, a clarification of the connection between the electronic specific heat and the density of states of the electrons on the Fermi surface, and particularly of ways of increasing the density of states, besides a detailed study of the phonon spectrum, will probably help find ways of increasing  $T_C$ .

As is well known, a number of recent theoretical papers have discussed possible new mechanisms of superconductivity (see<sup>[60]</sup>). However, these investigations have not yet found experimental confirmation. There is no doubt that it is necessary to continue the search for such systems, where new superconductivity mechanisms become manifest. The surface superconductivity, predicted in<sup>[12]</sup>, deserves in this sense particular attention.

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