

## SUPERCONDUCTIVITY OF SOME BINARY AND TERNARY ALLOYS

N. E. ALEKSEEVSKIĬ and N. N. MIKHAĬLOV

Institute for Physics Problems, Academy of Sciences, U.S.S.R.

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A number of alloys are investigated at temperatures between 1.3 and 20°K. Superconductivity in  $\text{Be}_{13}\text{W}$  is observed at  $T = 4.1^\circ\text{K}$  and also in a number of other Al, Zr, and Nb compounds. Possible causes of the superconductivity are discussed.

**S**UPERCONDUCTING alloys have been the subject of many investigations. However, in spite of much progress in this field in recent times (for example, the production of alloys and compounds with high values of  $T_c$ ), much is still unclear in the superconductivity of alloys. Attempts to establish empirical laws on the basis of the experimental data can likewise not be regarded as satisfactory. In this connection, further detailed investigation of the superconductivity of binary and ternary alloys is of interest.

We have recently investigated many alloys and observed in some of them superconductivity at a temperature higher than in pure components. The alloy specimens were obtained either by sintering small bars from pressed powders of the pure components, or by melting in a high-frequency furnace. Superconductivity was detected by the variation of the magnetic moment of the specimen disclosed in turn by the change in the mutual inductance of the measuring coils measured with an ac bridge or a ballistic galvanometer.

Measurements in the temperature range between liquid helium and liquid hydrogen were made with an instrument consisting of two Dewars. The specimen was placed in the internal Dewar, which was filled with helium gas, and liquid helium was poured

in the outer Dewar. The space between the walls of the internal Dewar was filled with helium gas or pumped out with a carbon sorption pump placed in the outer Dewar. By varying the pressure of the heat-exchange helium, and also by varying the amount of heat produced by a heater placed in the internal Dewar, it was possible to establish the required temperature, which was measured with a constantan thermometer. The magnetic field was produced by solenoids situated outside the nitrogen Dewar.

Table I lists the critical temperatures of the investigated alloys. To eliminate errors due to impurities that are impossible to control, all measurements were made with several specimens of the same composition.

It is known<sup>[1]</sup> that there are two W-Be compounds:  $\text{WBe}_2$  with a hexagonal structure of the  $\text{MgZn}_2$  type, and  $\text{WBe}_{13}$  with a tetragonal lattice. Whereas the first compound does not go into a superconducting state down to 0.1°K, the  $\text{WBe}_{13}$  compound is superconducting near 4°K. It must be noted that although neither W nor Be are superconducting<sup>[2]</sup>, Be films obtained by condensation of vapor on a cold surface go into a superconducting state at  $T = 8.0^\circ\text{K}$ <sup>[4]</sup>.

In the Zr-Re system there is a compound  $\text{ZrRe}_2$ ,

Table I

System	Composition	$T_c, ^\circ\text{K}$	Structure*
W - Be	$\text{WBe}_{13}$	4.1	t, $a = 10.14$ , $c/a = 0.416$
Zr - Re	$\text{ZrRe}_2$	5.9	h, type $\text{MgZn}_2$ (C 14), $a = 5.262$ , $c/a = 1.633$
	$\text{Zr}_5\text{Re}_{24}$	3.0	[3]
Ga - Pt	$\text{Ga}_7\text{Pt}_3$	2.9	c, type $\text{CaF}_2$
	$\text{GaPt}$	1.74	c, type $\text{FeS}$ , $a = 4.91$
Al - Ge	$\text{AlGe}_2$	1.75	} No compounds according to the literature
Al - Ca - Si	$\text{Al}_2\text{CaSi}$	5.8	
Al - Pd - Mo	$\text{AlPdMo}_6$	2.1	

\* t - tetragonal structure, h - hexagonal, c - cubic.

Table II

System	Composition	T <sub>c</sub> , °K	System	Composition	T <sub>c</sub> , °K
Nb—Sn—Ge	Nb <sub>3</sub> Sn <sub>0,5</sub> Ge <sub>0,5</sub>	11.3	Nb—Zr—Be	Nb <sub>5</sub> Zr <sub>2</sub> Be <sub>8</sub>	5.2
Nb—Zr—Sn	Nb <sub>3</sub> Sn <sub>0,5</sub> Zr <sub>0,5</sub>	16.7	Nb—Re	Nb <sub>4,4</sub> Re	4.8
Nb—Zr—In	Nb <sub>3</sub> Zr <sub>0,5</sub> In <sub>0,5</sub>	6.4	Nb—Mg	NbMg <sub>2</sub>	5.6

Table III

Composition	Measurement methods	Temperature to which measurements were made	Structure
AgTe	R, M	1.34	
Al <sub>5</sub> Y <sub>2</sub>	M	1.55	
Al <sub>4</sub> Ca	M	1.7	tb c, $a = 4.36$ , $c = 11.09$ , $c/a = 2.54$
Al <sub>2</sub> Ca	M	1.7	c, type MgCu <sub>2</sub> (C 15), $a = 8.038$
As <sub>2</sub> Pd <sub>3</sub>	M	1.4	
AsW	R	1.4	
AsZn	M	1.3	
AuSb <sub>2</sub>	R	1.4	c, type S <sub>2</sub> , $a = 6.657$
AuTe <sub>2</sub>	M	1.34	
BeCr <sub>2</sub>	M	1.75	h, type MgZn <sub>2</sub> (C 14), $a = 4.27$ , $c = 6.92$ , $c/a = 1.62$
Be <sub>2</sub> Mo	M	1.68	h, type MgZn <sub>2</sub> (C 14)
Be <sub>2</sub> Re	M	1.68	h, type MgZn <sub>2</sub> (C 14), $a = 4.354$ , $c = 7.101$ , $c/a = 1.631$
Be <sub>2</sub> W	M	1.68	h, type MgZn <sub>2</sub> (C 14), $a = 4.446$ , $c = 7.289$ , $c/a = 1.639$
Be <sub>2</sub> Zr	M	1.68	h, type AlB <sub>2</sub> (C 32), $a = 3.82$ , $c = 3.24$ , $c/a = 0.848$
Be <sub>13</sub> Mo	M	1.68	tb c, $a = 7.271$ , $c = 4.234$
Be <sub>13</sub> Zr	M	1.68	c, type NaZn <sub>13</sub> , $a = 10.047$
Ca <sub>3</sub> Ge	R, M	0.15	
Ca <sub>2</sub> Si	M	1.68	c f c, $a = 4.743$
CaSi	M	1.3	r, $a = 3.91$ , $b = 4.59$ , $c = 10.795$
CaSi <sub>2</sub>	M	1.68	r, (C 12), $a = 10.4$ , $x = 21^{\circ}30'$
FeSb <sub>2</sub>	R	1.45	$a = 3.195$ , $b = 5.831$ , $c = 6.53$
Ge <sub>2</sub> Pd	R	1.47	
K <sub>2</sub> Te <sub>3</sub>	M	1.46	
NaTe	M	1.3	
Na <sub>3</sub> Sb	M	1.45	r, $a = 5.366$ , $c = 9.515$ , $c/a = 1.773$
NiSb <sub>3</sub>	R	1.45	
NiP	M	1.57	
Ga <sub>3</sub> Zr	M	1.38	

Remarks: 1) The following notation is used in the table: M—measurement of magnetic moment, R—measurement of resistance, 2) The following abbreviations are used: tb c—tetragonal body centered lattice, c f c—cubic face centered, h—hexagonal, r—rhombohedral.

also with a structure of the MgZn<sub>2</sub> type. As can be seen from the table, this compound goes into a superconducting state at  $T = 5.9^{\circ}\text{K}$ . In addition, according to Kripyakevich et al.<sup>[3]</sup>, there exist also the compounds Zr<sub>5</sub>Re<sub>24</sub> and Zr<sub>2</sub>Re<sup>1)</sup>. We measured a specimen with composition Zr<sub>5</sub>Re<sub>24</sub> and obtained for T<sub>c</sub> a value  $\sim 3.0^{\circ}\text{K}$ .

The ternary system Al—Ca—Si, as far as we know, has not yet been investigated. Binary systems Al—Ca, Al—Si, and Ca—Si have been investigated with sufficient detail<sup>[1]</sup>. In the Al—Ca system there are two compounds, Al<sub>4</sub>Ca and Al<sub>2</sub>Ca, none of which becomes superconducting above  $1.7^{\circ}\text{K}$ . In the Al—Si system there are no compounds.

The Ca—Si system has three compounds: Ca<sub>2</sub>Si, CaSi, and CaSi<sub>2</sub>, which apparently are likewise not superconducting. The superconducting transition at  $T = 5.8^{\circ}\text{K}$ , observed in the ternary system<sup>2)</sup>, is of interest apart from superconductivity, since there are grounds for assuming that a compound with possible composition Al<sub>2</sub>CaSi exists in this system.

In addition to the systems listed in Table I, we investigated some compounds and alloys based on Nb. The values obtained for the critical temperatures are listed in Table II. Table III gives some of the alloys and compounds which we investigated and which displayed superconductivity.

<sup>1)</sup>The first ZrRe<sub>2</sub> specimen was furnished by M. A. Tylkina, for which the authors are deeply grateful.

<sup>2)</sup>It must be noted that preliminary x-ray investigations of superconducting specimens point to the existence of a single-phase system.

## DISCUSSION OF RESULTS

The superconducting compound  $WBe_{13}$  is the second compound of Be which becomes superconducting. As is well known<sup>[1]</sup>, the compound AuBe becomes superconducting at  $T = 2.6^\circ K$  and has a structure of the FeSi type. The  $WBe_{13}$  compound probably has a tetragonal structure with parameters  $a = 10.14 \text{ \AA}$ ,  $c = 4.23 \text{ \AA}$ , and  $c/a = 0.416$ . An analogous structure is possessed by  $MoBe_{13}$ , which exhibits no superconductivity.

The nonsuperconducting compound  $WBe_2$  has a hexagonal structure of the  $MgZn_2$  type:  $a = 4.446 \text{ \AA}$ ,  $c = 7.289 \text{ \AA}$ ,  $c/a = 1.639$ . The nonsuperconducting compound  $ZrBe_{13}$  has a cubic structure of the  $NaZn_{13}$  type with  $a = 10.47 \text{ \AA}$ .

Thus, of the three Be compounds having a composition  $MBe_{13}$ , with complicated structure and a large number of atoms per cell, only  $WBe_{13}$  becomes superconducting, while not a single  $MBe_2$  superconducting compound has been observed so far. We see from the accompanying table that these compounds are  $ReBe_2$ ,  $MoBe_2$ ,  $WBe_2$ , and  $ZrBe_2$ . The  $ZrRe_2$  compound has a structure of the  $MgCu_2$  type (Laves phase). As is well known<sup>[5]</sup> among the compounds having such structure there are many superconductors.

The connection between  $T_C$  and the type of the crystal lattice (although discussed in the literature) not only remains unexplained to date, but has not even been clearly established. One can note, however, that complicated lattices are apparently more favorable for the occurrence of superconductivity. Indeed, among the compounds having a lattice of the  $\beta$ -W type there are many superconductors with high values of  $T_C$ . The same can apparently be said regarding the Laves phases. It must also be noted that the  $\beta$  and  $\gamma$  modifications have higher values of  $T_C$ , and in some cases they are the only superconducting ones<sup>[5,6]</sup>. It is possible that these facts can be

connected with the question of the stability of the lattice. As follows from the work of Tyablikov and Tolmachev<sup>[7]</sup>, the parameter  $\rho$  in the expression  $\Delta = \omega e^{-1/\rho}$  cannot exceed 0.5. The Coulomb repulsion,<sup>[7]</sup> and also intense thermal vibrations<sup>[7]</sup>, can apparently contribute to an increase in the lattice stability. Nor is it excluded that a similar influence can be exerted by lattice distortions due, for example, to plastic deformation. The fact that plastic deformation increases  $T_C$  as a rule, and also that superconductors with high  $T_C$  contain no metals or alloys with low melting points, is an argument in favor of the foregoing considerations (which, however, can be at present regarded only as a hypothesis that calls for theoretical and experimental proof).

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<sup>2</sup>N. Alekseevskii and L. Migunov, *J. of Physics*, USSR 11, 95 (1947).

<sup>3</sup>Kripyakevich, Tytkina, and Savitskii, *Izv. Vuzov—chern. metallurg. (News of the Universities, Ferrous Metallurgy)*, No. 1, 12 (1960).

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<sup>6</sup>Alekseevskii, Brandt, and Kostina, *Izv. AN SSSR* 26, 233 (1962), *Columbia Tech. Transl.* in press.

<sup>7</sup>S. V. Tyablikov and V. V. Tolmachev, *JETP* 34, 1254 (1958), *Soviet Phys. JETP* 7, 867 (1958).