Effect of high hydrostatic pressure and residual strain on the superconductivity of Nb-Al-Ge alloys with an A15-type structure

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The dependence of T_c on p (up to 38 kbar) is investigated in Nb-Al-Ge alloys annealed at 1650°C and possessing compositions lying in the stability region of the A15 phase. In all alloys, excluding Nb_3Al, T_c varies linearly with the pressure. A first-order phase transition with $\Delta V/V_0 \backsim 1\%$ is observed in the Nb_3Al alloy in the vicinity of 17 kbar; T_c of the new phase is somewhat higher. It is shown that when Ge replaces Al in $Nb_{3+y}(Al_{1-x}Ge_x)_{1-y}$ alloys, the function $dT_c/dp = f$ (at.% Ge) changes sign twice. This pattern is ascribed to the presence of singularities in the dependence of the state density at the Fermi surface on the composition. The alloys are found to be very sensitive to compression under nonhydrostatic conditions (p up to 20 kbar). Such action produces a strong "smearing out" of the transition to the superconducting state and a considerable decrease of the volume of alloys with a high T_c. The alloys which are most sensitive to inhomogeneous stresses are those which lie on the Nb–AL–Ge phase diagram near the phase equilibrium point or at the edges of the single-phase region.

From the instant of discovery [1] of the high critical parameters of the transition to the superconducting state, the alloys of the system Nb-Al-Ge have continued to attract constant attention from many investigators. Interest in these alloys increased particularly after a record-high superconducting transition temperature, $T_c > 20$°K, was attained with one of the alloys [2], namely $Nb_3(Al_{0.8}Ge_{0.2})$. In spite of the considerable number of investigations, questions concerning the nature of the superconductivity in these alloys, and especially the connection between the superconductivity in the crystal structure and other physical properties, cannot be regarded as completely solved. Therefore the results of an investigation of the behavior of these alloys at high pressure can yield definite additional information on their electronic structure. Attempts at such investigations were already made earlier [3,4]. Unfortunately, the samples used by Nebauer [3] were niobium wires coated with a thin layer of the alloy. Smith [4] determined the values of dT_c/dp only for the three alloys with greatly differing compositions. In addition, almost all the alloys investigated by both workers had a multiphase structure.

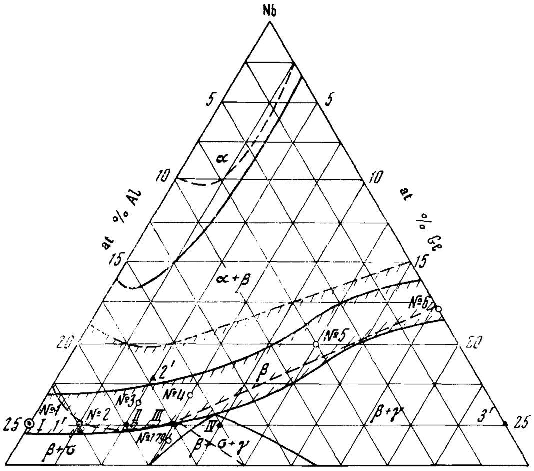

FIG. 1. Section of the phase diagram of the alloys Nb-Al-Ge [5] at 1700°C (solid curves) and 1000°C (dashed). The symbols ○, ●, and ▲ refer to alloy compositions investigated in the present study, in [3], and in [4], respectively (see also the table).

It is well known that the highest T_c in the system Nb-Al-Ge are possessed by alloys whose structure consists mainly of the phase A15. On the phase diagram [5] (Fig. 1), the narrow region of existence of the phase A15 extends from the compound Nb_3Al to the alloy $Nb_{3.28}Ge_{0.72}$. Replacement of aluminum by germanium is accompanied by a change in the number of valence electrons per atom of alloy and leads first to a small increase of T_c, and then, at appreciable Ge contents, to a strong decrease of this temperature. The region A15 then deviates from the $Nb_3(Al_{1-x}Ge_x)_1$ line towards alloys with larger Nb content.

We deemed it of interest to study the changes of T_c under pressure for a number of single-phase alloys, the compositions of which lie along this entire region. The maximal T_c of these alloys is somewhat lower than the record attained in this system. Since they have an identical crystal structure, it becomes possible to carry out at least a qualitative analysis of the changes of T_c due to changes in the electron concentration of the alloys, both in the case of alloying (by replacing Al with Ge) and under hydrostatic compression. This is the subject of the first part of the paper. We must stipulate immediately that we have not touched upon problems connected with the possibility of an ordering process taking place in the alloys during the course of low-temperature annealing, a process that leads to a certain growth of T_c. As is well known, owing to the great methodological difficulties, the superstructure in the alloys Nb-Al-Ge has not yet been reliably recorded. We have therefore investigated alloys whose initial states were obtained by high-temperature annealing. The only exception was a single alloy, used for comparison, with T_c equal to 20°K.

Recently, Matthias and co-workers [6] have demonstrated that a strong smearing of the superconducting transition, in the lower-temperature direction, takes place under the influence of inhomogeneous residual stresses in powdered samples of the alloys V_3Si, Nb_3Sn, and others, and that a second low-temperature step is produced on the transition curve. Such effects were attributed in [6] to the greater development of the low-temperature martensitic transformation in these alloys under the influence of the stresses than in the initial undeformed state.

In our preceding study [7] we investigated the behavior of the alloys of the system $V_3(Si_{1-x}Ge_x)$, where

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there is a regular decrease of T_c with increasing Ge content. It was established that a distinct correlation is observed, namely, the higher T_c the more appreciable the smearing effect, and, principally, there is a definite connection between these effects and the probability of the martensitic transformation. Inasmuch as the alloys Nb-Al-Ge have the same A15 structure, but the changes of T_c when elements are substituted in the sublattice X have a different character (the dependence of T_c on the atomic percentage of germanium has a maximum), it is of interest to investigate the behavior of the alloys in this system for the purpose of establishing possible correlations between the properties. In the second part of the paper we present the results of this investigation.

Composition and certain properties of the alloys Nb-Al-Ge

Melt no.	Composition formula	Lattice parameter, Å	T_c, °K	Micro-hardness H_μ, kg/mm²	$(dT_c/dp)\cdot 10^5$ deb/bar*	Reference
1	Nb_3Al	5.186	17.5	790	−0.9	
2	$Nb_3(Al_{0,9}Ge_{0,1})_1$	5.180	18.4	713	−0.2	
3	$Nb_{3,05}(Al_{0,75}Ge_{0,20})_{0,95}$	5.177	17.9	669	+1.2	
4	$Nb_{3,07}(Al_{0,63}Ge_{0,30})_{0,93}$	5.175	17.4	891	+0.9	
5	$Nb_{3,2}(Al_{0,3}Ge_{0.50})_{0,8}$	5.171	10.2	910	−1.0	
6	$Nb_{3,28}Ge_{0,72}$	5.170	6.2	1000	−1.7	
179	$Nb_{2,96}(Al_{0,73}Ge_{0,31})_{1,04}$	—	19.8	—	−1.8	
IV	Nb_3Al	—	17.11	—	−0.7	
I	$Nb/Nb_3(Al_{0,8}Ge_{0,2})$	—	18.25	—	−1.2	
II	$Nb/Nb_3(Al_{0,7}Ge_{0,3})$	—	18.60	—	−1.6	[3] **
III	$Nb/Nb_3(Al_{0,6}Ge_{0,4})$	—	17.80	—	−3.2	
3′	Nb_3Ge	—	6.28	—	−1.14	
2′	$Nb_{0,78}(Al_{0,75}Ge_{0,25})_{0,22}$	—	20.29	—	−0.2	[4]
1′	Nb_3Al	—	17.11	—	−0.7	

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*The error in dT_c/dp does not exceed ±20%.

**Samples I-III in [3] were niobium wires coated with a layer of alloy, the corresponding composition of which is given here.

EXPERIMENTAL PART

We investigated alloys fused from niobium (>99.9%), aluminum (>99.98%), and germanium (>99.999%) in an induction oven. The initial components were remelted twice in an atmosphere of argon in alundum crucibles. After melting, the alloys were annealed for 20–25 hours at 1650°C. Sample No. 179 was tempered additionally for 375 hours at 720°C. The phase composition and the parameters of the lattice were determined by x-ray diffraction using powdered samples. All the alloys had, after heat treatment, a single-phase structure of type A15. A microstructure analysis has also shown that the samples contained no inclusions of a second phase. The microhardness of samples No. 1–6, the compositions of which lie in the single-phase region, was measured with the PMT-3 instrument at a load of 50 g. The lattice parameters of alloys No. 1 (Nb_3Al) and No. 6 ($Nb_{3.28}Ge_{0.72}$) coincided with the published data on the alloys of the same composition [8]. The formulas for the alloy compositions are listed in the table, and the positions of the compositions on the Nb-Al-Ge phase diagram are shown in Fig. 1. The superconducting transition temperature T_c was determined for all the alloys after tempering. The measurements of T_c were performed by an induction method in an alternating magnetic field with $H_{max} < 1$ Oe and frequency 37 Hz [7]. Let us stop to discuss in somewhat greater detail the particulars of the method. The gist of this method consists of determining the temperature dependence of the inductance of measurement coils within which the sample is placed. Usually, the T_c of the sample is taken to be the temperature at which the change of the inductance reaches 50% of its total change in the transition. In our installation, the coils were wound in accordance with a differential-transformer scheme. The primary coil received a signal from a generator, and the two secondary measuring coils, which were placed inside the primary one, were connected to buck each other. The sample was placed in one of the secondary coils. The coils, together with the sample, were placed in a thick-walled copper cylinder. The temperature inside the cylinder could be regulated. The signal from the secondary coils was fed to a selective amplifier and from it to a phase detector. In all the measurements, the detector was tuned in synchronism with the generator. The superconducting transition of the sample, when the sample is either heated or cooled, leads to a change in its susceptibility and consequently to a change in the detector signal V. The latter is proportional to the real part of the susceptibility of the sample, i.e., to its diamagnetic moment. If the field of the primary coil is weak in comparison with the value of H_{c1} of the sample, then the detector signal V_T corresponding to each fixed temperature is proportional to the volume of the superconducting phase in the sample. Transition curves plotted in coordinates $(V_T - V_{20°K})/V_{20°K} = f(T)$ are in essence plots of the dependence of the diamagnetic moment on the temperature.

McCarthy and Viswanathan [9] made some critical remarks concerning the procedure of determining the transition curves of powdered samples of the alloys V_3Si, Nb_3Sn and Nb-Al-Ge, which acquired, after pressing, an extended temperature interval of the superconducting transition and a second low-temperature step on the curve. Thus, they regarded the low-temperature step as a manifestation of screening of part of the sample volume by surface currents produced on flat defects such as slip bands in an alternating magnetic field. To ascertain whether the existence of two steps on the transition curve of the sample (when this curve is determined by the induction method) does indeed indicate the presence in the sample of two phases with different T_c, and whether the ratio of the height of the steps determines the ratio of the volumes of the phases, the following experiments were performed. We measured the temperature dependence of the diagmagnetic moment of the powdered sample No. 4, which showed clearly pronounced steps on the transition curve, in fields of 8.6 Oe (with the aid of a ballistic galvanometer) and 200 Oe (with a magnetic balance [10]). The 8.6 Oe field was smaller than $H_{c1} = 20$ Oe at 4.2°K for this sample. Thus, the transition to the superconducting state was registered in one and the same sample by three methods. Within the limits of the accuracy of the method, the transition curves coincided. Since the diamagnetic moment in $H < H_{c1}$ is proportional to the volume of the material in the superconducting state, the agreement of the transition curves indicates that the induction method also yields the distribution of the superconducting volumes of the material with respect to the temperature. The second step on the curve is due to the presence in the sample of a large amount of material (50–40%) with low T_c.

Measurements of T_c under pressure and of the compressibility at 300 and 4.2°K were carried out in a special press [11]. The high-pressure chamber had a construction of the "piston-cylinder" type. Samples in the form of cylinders of 2.25 mm diameter and 3–5 mm length were cut from ingots by the electric-spark method. The pressure-transmitting medium was a thin (<100 μ) layer of structureless graphite pressed into cigarette paper [12]. The transition to the superconducting state under pressure was also registered by an induction method. The samples were loaded in the press to pressures 35–38 kbar at 300°K, and then the press was cooled together with the chamber to helium temperatures and the values of T_c were measured at different pressures. The pressure was removed from the sample in steps directly at the helium temperatures. The sample temperature was measured with a (gold + iron) – copper thermocouple [13], which was inserted in a hole in the chamber and was secured to it with vacuum grease. The absolute value of the temperature was determined with an error less than ±0.1°K, and changes in the temperature were registered with accuracy no worse than ±0.02°K. The pressure calibration in the chamber at 300°K was based on the Bi I-II-III transitions, and the pressure calibration used in the determination of the $T_c(p)$ dependence was based on data on the value of T_c of pure tin, samples of which were placed in the chamber together with the investigated samples. The compressibility measurements were carried out by recording the piston displacement.

To determine the influence of the composition and of the value of the stress on the temperature interval in which the transition to the superconducting state takes place, the alloy samples were subjected to a treatment close to that used by Matthias et al. [6]. Pieces of the ingots were broken up and ground into powder in an agate mortar, and then the powder was wrapped in lavsan film and placed in a chamber of the "piston-cylinder" type, after which the powders were compressed to 20 kbar. After removal of the load, the resulting pellet was taken outside the chamber and the transition to the superconducting state was determined by the induction method.

RESULTS AND DISCUSSION

A. Superconductivity at High Pressure

The described procedure was used to measure T_c as a function of the pressure p on six samples, Nos. 1–6, the compositions of which lay in the single-phase region, and on one sample from the three-phase region (No. 179), which had the maximum T_c from among all our samples. Figure 2 shows, by way of example, the transition curves at different p for the sample $Nb_{3.28}Ge_{0.72}$ (No. 6). The same figure shows the transition curves of the "tin manometer." We see that the temperature intervals of the transitions under pressure are no larger than at p = 0, thus indicating a satisfactory degree of homogeneity of the pressure in the chamber channel.

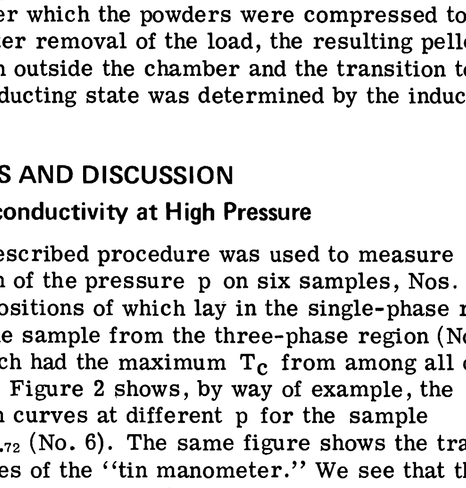

FIG. 2. Superconducting transition curves of the sample $Nb_{3.78}Ge_{0.72}$ (alloy No. 6) (a) and a tin "manometer" (b) at pressures 24, 22.5, 11.5, 9, 4, and <1 kbr (curves 1, 2, 3, 4, 5, and 6, respectively).

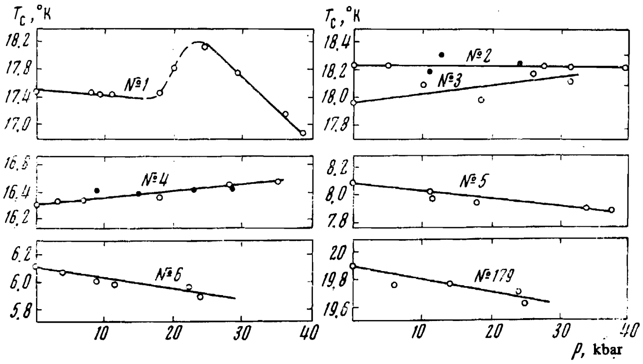

FIG. 3. Plots of $T_c(p)$ of all the investigated alloys (see the table for the compositions).

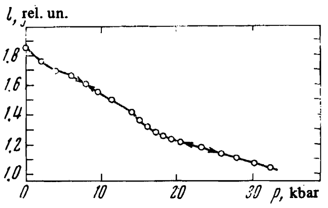

FIG. 4

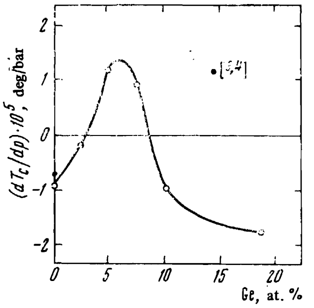

FIG. 5

FIG. 4. Dilatation diagram of the alloy Nb_3Al. The ordinates represent the sample length. The initial curvilinear section is due to the compaction of the entire high-pressure cell.

FIG. 5. Dependence of dT_c/dp on the Ge content in single-phase alloys of the Nb-Al-Ge system with A15 sturcture.

The plots of $T_c(p)$ for all the investigated alloys are shown in Fig. 3. For alloys No. 2 and No. 4, the experiments were performed twice (the points are indicated by the light and dark circles). As seen from Fig. 3, perfectly satisfactory reproducibility of the results is observed. The table lists the numerical values of dT_c/dp. It includes data obtained in [3,4]. Unfortunately, in these references only one alloy (Nb_3Al) lies in the single-phase region, and, in addition, this alloy is closest in composition to our alloy No. 179 with composition $Nb_3(Al_{0.7}Ge_{0.3})$. In those cases when the compositions coincided or are closest to each other, a satisfactory agreement between the results is observed. This indicates once more satisfactory homogeneity of the pressure in our experiments, since the authors of [3,4] obtained their pressures in bombs with frozen liquid.

The temperature T_c of all alloys, with the exception of Nb_3Al, has a nearly linear dependence on p. In the case of Nb_3Al (alloy No. 1), we observed that in five different experiments, in the region of 17 kbar, there was always a jump of $T_c(p)$ (Fig. 4), and the readings of the "tin manometer" in the case when the pressure was reduced near 17 kbar, indicated that the pressure increased instead of indicating a decrease of the pressure. This made it possible to assume that a transition from a high-pressure to a low-pressure phase, accompanied by a jump in volume, occurs in Nb_3Al when the pressure is lowered. Indeed, direct experiments aimed at measuring the volume compressibility at 300 and 4.2°K have revealed the presence of a first-order phase transition in the same region of pressures. Figure 4 shows a dilatation diagram of the alloy, taken at 300°K. From the results of Figs. 3 and 4 it is clear that the Nb_3Al is subject to a first-order phase transition with a volume effect ~1% in the pressure region 17–20 kbar [2]. An essential feature of the transition is the absence of hysteresis between the pressures in the direct and inverse transitions.

Since Nb_3Al has a close-packed structure, it can be assumed that this phase transition is not connected with a change in the crystal structure, but is due to a change in the interatomic distances.

We now examine the behavior of dT_c/dp of the alloys. Figure 5 shows a plot of dT_c/dp against the Ge content for single-phase alloys Nos. 1–6.[3] (It should be borne in mind (see Fig. 1) that the Nb content also changes when the percentage of Ge is changed.) As seen from the figure, with increasing Ge content in the alloys the plot of dT_c/dp against the composition passes through zero twice, and the sample with the highest T_c (among the alloys with compositions lying within the A15 region) has the minimum absolute value of dT_c/dp. Attention is called to the fact that the first change in the sign of dT_c/dp occurs at an alloy composition such that further alloying with germanium leads not only to a considerable lowering of T_c, but also to a strong deviation of the position of the single-phase region on the phase diagram from the stoichiometric section $Nb_3(Al_{1-x}Ge_x)_1$ towards larger niobium contents.

It is interesting that the alloys lying on the edge of the single-phase region and even outside this region (our sample No. 179, $Nb_3(Al_{0.7}Ge_{0.3})$, $Nb_3(Al_{0.6}Ge_{0.4})$ [3]) and having the highest values of T_c have larger values of dT_c/dp. Unfortunately, the results pertaining to these alloys are difficult to interpret even qualitatively, since it is difficult to determine how dT_c/dp is affected by the presence of several phases with different T_c in the structure of these alloys. We shall therefore attempt to consider only the behavior of single-phase alloys having the same crystal structure of the type A15, for which it is possible to assume, by way of simplification, that their band structures are approximately the same.

Following Brandt and N. Ginzburg [14], we shall assume that the dependence of the state density on the Fermi surface N(O) on the pressure in our alloys, as in many other alloys of transition elements, is determined by curves that are analogous to the plots of N(O) against the electron density n_B per cm³. It is then obvious that the sign of the derivative dT_c/dp of each alloy should be determined by the position of its composition, and consequently n_B, on the $N(O) = f(n_B)$ curve. The temperature T_c should increase upon compression for superconductors with $dN(O)/n_B > 0$, and decrease for superconductors with $dN(O)/n_B < 0$.

This is undoubtedly a very crude model, applicable only to alloys with identical structure; it is valid in first-order approximation, and does not take into account the changes of the phonon spectrum under pressure. For a number of alloys, however, good agreement was observed between this model and the experimental results [15]. If it is assumed that the change of T_c under hydrostatic compression is due mainly to N(O) and to a lesser degree to changes of other parameters, then the situation observed in Nb-Al-Ge alloys is not accidental. Indeed, the complicated character of the dT_c/dp dependence of the composition is evidence of the onset of two singularities in the dependence of the state density on the concentration when the aluminum is replaced in $Nb_{3-y}(Al_{1-x}Ge_x)_{1+y}$ by germanium. At low germanium contents (alloys No. 1 and No. 2), the state density should decrease, since these alloys have a negative sign of dT_c/dp. The small absolute value of dT_c/dp of the alloy $Nb_3(Al_{0.9}Ge_{0.1})$ indicates that $N(O) = f(n_B)$ has a minimum near this composition.

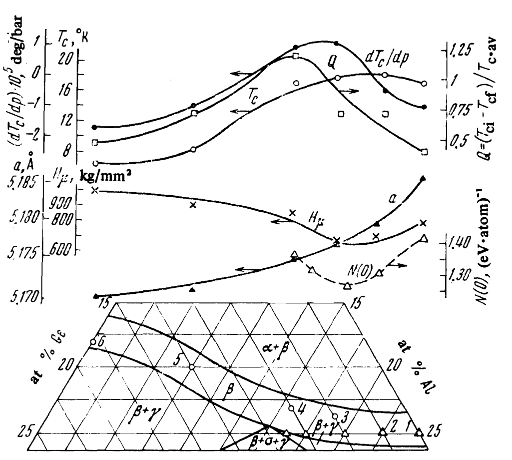

FIG. 6. Values of T_c, dT_c/dp, a, and H_μ of the investigated alloys and of N(O) [16] in appropriate scale, compared with the positions of the alloys on the section through the phase diagram of Nb-Al-Ge at 1700°C. This temperature is close to the 1650°C annealing temperature of the samples. △-alloys with composition $Nb_3(Al_{1-x}Ge_x)$ for which N(O) were measured in [16].

Recently, Dekhtyar and co-workers [16] measured by an independent method, using an investigation of the electron-positron annihilation, the state density on the Fermi surface for a number of Nb-Al-Ge, with composition $Nb_3(Al_{1-x}Ge_x)$. Some of the compositions of these alloys coincide with ours or are close to them. Figure 6 compares the results of the measurements of T_c, dT_c/dp, N(O), and the microhardness H_μ as functions of the concentration. As seen from the diagram, according to measurements by the direct method, N(O) decreases with increasing germanium content. A minimum is observed on the plot of $N(O) = f(n_B)$ near the composition $Nb_3(Al_{0.8}Ge_{0.2})$. (We recall that replacement of aluminum by germanium at a constant niobium constant causes n_B to increase in the alloys, since germanium has a higher valence.) Unfortunately, the measurements in [16] were made on single-phase alloys with only a small Ge content, and it is still impossible to compare the measured values of dT_c/dp with the data on the values of N(O) for alloys from the entire A15 region. However, if it is assumed that the dependence of T_c on p is determined by the same parameters for all single-phase alloys, then we can predict on the basis of our data on dT_c/dp that there exists one other singularity in the dependence of N(O) on the composition in the case of alloys close to $Nb_{3.2}(Al_{0.3}Ge_{0.5})_{0.8}$. A simple calculation shows that in our samples n_B first increases when the composition changes from Nb_3Al to $Nb_{3.28}Ge_{0.72}$, goes through a maximum near the composition $Nb_{3.2}(Al_{0.3}Ge_{0.5})_{0.8}$ (alloy No. 5), and then decreases. And it is precisely near this composition that the dependence of dT_c/dp on the Ge content reverses sign again. It is of interest to perform direct measurements of N(O) in this region of composition.

The presence of a minimum in the dependence of the state density on the concentration near the composition $Nb_3(Al_{0.8}Ge_{0.2})$ is evidently of great significance for the stability of the A15 structure relative to the concentration of the components in the Nb-Al-Ge alloys. This is reflected in the location of the A15 region on the phase diagram. Indeed, in the alloys $Nb_3(Al_{1-x}Ge_x)$, when the ratio of the Al content to the Ge content reaches 8:2, the single-phase structure is not preserved with further increase of the atomic percentage of germanium, and the A15 region is deflected towards larger Nb contents. This means that replacement of Al by Ge in the sublattice X, without a change in the ratio Nb:X = 3:1, becomes energywise unprofitable in our alloys, namely, the Nb begins to occupy the places of the aluminum and germanium in the sublattice X. What is most remarkable is that it is precisely in this concentration region that the alloys with maximum T_c are located. This circumstance was already pointed out earlier [5]. As seen from the obtained data, the behavior of alloys under pressure is also evidence of the presence of singularities in the electronic structure of Nb-Al-Ge alloys that are close in composition to $Nb_3(Al_{0.8}Ge_{0.2})$, which has the highest T_c among all the single-phase alloys.

In recent years, a widely used approach in the theory of superconductivity of alloys with A15 structure is one according to which the quantity T_c and its dependence on the composition in these alloys are determined primarily by the characteristics of the phonon spectrum. This concept was developed, for example, by Hopfield [17]. He started out with the fact that the values of N(O) of Nb_3Al and Nb_3Sn differ by more than two times, as follows from data on the specific heat, even though these alloys have close values of T_c. In accordance with this approach, the change of the value of Tc in Nb-Al-Ge alloys when Al is replaced by Ge is most probably due not so much to N(O) (to the growth of n_B), but principally to the change in the phonon spectrum due to the change in the mass of the atoms in the sublattice X. Indeed, when the quantities characterizing the rigidity of the lattice, such as the microhardness H_μ (see Fig. 6) and the longitudinal speed of sound v_l [16] are compared with the values of T_c, a clear-cut correlation is observed, namely, the maximum T_c is possessed by those alloys of the Nb-Al-Ge system in which H_μ and v_l are minimal$^{4)}$, i.e., in which the effective vibration frequencies ω_{eff} are minimal. From this point of view, it is no longer surprising that alloys with minimal T(O) have maximal T_c.

We see that investigation of the behavior of T_c under hydrostatic compression helps reveal singularities of the electronic structure of such complicated and at the same time exceedingly interesting materials as the Nb-Al-Ge alloys. For better understanding of their nature, however, it is undoubtedly necessary to measure directly the characteristics of the electronic and phonon spectra both of alloys with different composition and directly under pressure.

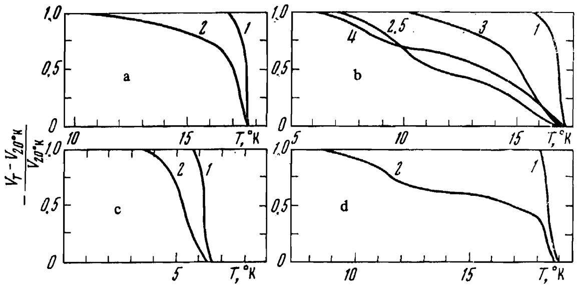

FIG. 7. Superconducting transition curves of certain Nb-Al-Ge alloys in the initial state (curves 1) and after compression to 20 kbar (curves 2): a—Nb_3Al (No. 1); b—$Nb_{3.07}(Al_{0.63}Ge_{0.30})_{0.93}$ (No. 4); c—$Nb_{3.28}Ge_{0.72}$ (No. 6); d—$Nb_{2.96}(Al_{0.73}Ge_{0.31})_{1.04}$ (No. 179). In Fig. b, curve 3 was obtained for a powder after crushing; curves 4 and 5 were obtained after pressing this powder to 2 kbar, and then to 10 kbar; curves 1 and 2 are the same as for the other samples.

B. Influence of Residual Stresses on the Superconducting Transition of Nb-Al-Ge Alloys

To investigate the influence of the composition on the probability of formation of a second low-temperature step on the superconducting-transition curve of samples subjected to nonuniform compression, and also on the temperature interval in which the transition takes place, all the alloys were placed under pressures up to 20 kbar. As a result of such treatment, residual stresses were produced in the powdered sample. X-ray photography has shown that the residual deformation of the lattice was approximately the same in all alloys. The relative distortions of the lattice parameter were $(a-a_0)/a_0 \approx 1\times10^{-3}$, where a_0 is the lattice parameter in the initial state. If it is assumed that the bulk moduli of all the alloys are of the same order as in Nb_3Al, i.e., ~1700 kbar, then the maximum residual stresses that were produced in the samples did not exceed 2 kbar. Figure 7 shows the most typical transition curves of certain alloys after such treatment and in the initial state. As follows from the data obtained, considerable smearing of the transitions is observed after pressing the powders of all the alloys under nonhydrostatic conditions, and distinct second steps are seen on most curves, with the exception of alloy No. 6. The observed picture depends essentially on the composition of the alloy. The degree of smearing of the transition can be estimated quantitatively by introducing the arbitrary quantity $Q = (T_{ci} - T_{cf})/T_{c0.5}$, where T_{ci} and T_{cf} correspond to the temperatures of the start and end of the transition, and $T_{c0.5}$ is the temperature at which the signal changes by 50%.

A comparison of the values of Q of the samples in the initial state and after the compression makes it possible to estimate the extent to which the temperature distribution of the superconducting volume of the sample is affected. Figure 6 shows the plot of Q against the composition for samples compressed to 20 kbar. Sample No. 179 had Q = 0.71. In the initial state, the values of Q of most samples were approximately the same (≈0.12), and only sample No. 5 had Q = 0.25. We see that the largest effect is observed in alloys located near the critical point of the phase equilibrium on the phase diagram, i.e., in the region of compositions that are least stable from the point of view of phase equilibrium.

Preliminary experiments have shown that if one takes a number of alloys whose compositions run across the single-phase region A15, for example the composition $Al_{3+x}(Al_aGe_b)_{1-x}$ with a:b = 2.33:1, and compress them to 20 kbar, then the smearing of the transition and the value of Q turn out to be the largest for alloys lying at the edges of the region and just outside the region. For single-phase alloys located inside the region, Q is noticeably smaller. The smearing of the transition and the second step on the curve for sample No. 179, after passing through a prolonged low-temperature tempering, are approximately the same as for untempered samples.

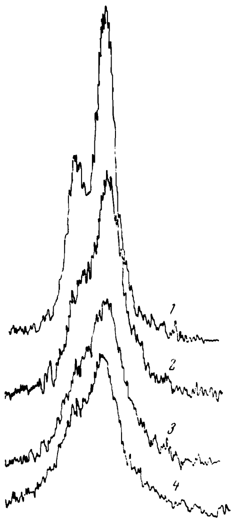

FIG. 8. Profile of the (421) line on diffraction patterns of powders of the alloy $Nb_{3.07}(Al_{0.63}Ge_{0.30})_{0.93}$ (No. 4) in the initial state (1) and after compression to 2 kbar, (2), 10 kbar (3), and 20 kbar (4).

To determine the influence of the pressure on the character of the transition, we performed the following experiment. A bulky sample of alloy No. 4, which revealed the largest value of Q, was ground into powder in an agate mortar and then compressed in the manner described above to 2, 10, and 20 kbar. The transition curves of these samples are shown in Fig. 7b. Figure 8 shows sections of diffraction patterns with plots of the angular dependence of the intensity of the (421) line, obtained to estimate the value of the maximum distortions of the lattice parameter as a result of the residual stresses. As seen from Fig. 8, the line broadening increases when the pressure is increased to 10 kbar. With further increase of pressure, the line shape remains practically unchanged. The quantities $\Delta a/a_0$ in samples subjected to pressures 2 and 10–20 kbar are respectively 7×10^{-4} and 10.5×10^{-4}. The superconducting transition curves of powders compressed to 10 and 20 kbar did not differ from one another. We note that the transition curves of samples of the alloy V_3Si were the same after application of nonuniform pressures from 8 to 30 kbar [6].

It is important in this case that an increase in the stresses in the material causes an increase not in the smearing of the transition, but in the size of the low-temperature step, i.e., all that occurs is an increase (up to a certain limit) of the volume of the superconducting phase with the lower T_c. The temperatures T_{ci} of the start of the transition remain practically unchanged for all alloys after grinding them to a powder and compressing them to maximum pressure, in comparison with T_{ci} in the initial state, while the $T_{c.av}$ of the low-temperature steps shifted by not more than 1-2°K. Thus, the T_c of part of the sample volume always remains close (within 1–2°K) to T_c in the undeformed state. The transition broadens only towards lower temperature.

When an attempt is made to explain the observed effect, it is necessary to forgo immediately, just as in the case of the $V_3(Si_{1-x}Ge_x)$ alloys [7], the opinion that the effect is due simply to the presence of static deformations and alloy lattice distortions in the sample. Indeed, the maximum lowering or raising of T_c caused by the residual deformation in at least part of the volume of the samples cannot exceed ±0.2°K, since the maximum residual stresses are ≤ 2 kbar, and dT_c/dp lies in the range $\pm2\times10^{-2}$ deg/kbar.

The smearing effect is likewise not due to the small dimensions of the powdered particles obtained as a result of the breakdown of the material under nonhydrostatic compression. Indeed, a control tempering of alloy No. 4, which has a smeared transition, for several hours at 650° led to a vanishing of the second step on the transition curve, and the curve assumed the same shape as for the sample in the initial state. Undoubtedly, tempering at such a low temperature could not lead to a sintering of the powder, and caused only a lifting of the residual stresses. In addition, in one of the experiments in which we measured dT_c/dp of bulky sample No. 4, owing to the poor homogeneity of the pressure in the chamber, we observed exactly the same two-step transition as in the pressed powder sample. When the pressure was removed from the sample, the entire transition curve shifted in temperature. This also proves that the sample dimensions did not play any role in the smearing effect.

When seeking for the possible causes of the effect, one must regard as most probable the explanation given by Matthias and coworkers [6]. They assumed that residual inhomogeneous stresses in the alloys V_3Si, Nb_3Sn, Nb-Al-Ge, and many others on cooling give rise to a stronger development of the martensitic low-temperature transition than in the initial state. In this case a larger amount of martensitic phase with low T_c, up to 50% of the sample volume and more, is produced. If we examine the behavior of the Nb-Al-Ge alloys from this point of view, we observe features quite similar to those observed in ordinary martensitic transitions. It is known, for example, that in many martensitic alloys, stresses or plastic deformation in the initial state raise the martensitic point T_M, by the same token increasing the amount of martensitic phase produced at one and the same measurement temperature. The martensitic process is practically never concluded, and some fraction of the initial phase remains in the samples. The martensitic point itself and the amount of the phase produced depend strongly on the composition.

If, in the analysis of the transition curve of the Nb-Al-Ge alloys, we ascribe the high-temperature step, as do Matthias et al. [6], to a superconducting transition of the initial cubic phase, and ascribe the low-temperature step to a tetragonal martensitic transition, then a fair analogy is observed with the ordinary martensitic transition. Thus, a certain amount of material with T_c close to the value of T_c in the initial state remains in all alloys after compression. The temperature intervals in which the first and second transitions take place do not change with increasing residual stresses, and only the volumes of the phases with different T_c change. Stronger smearing and larger values of the low-temperature step are observed for alloys whose compositions are located near the boundaries between the phase regions or near the triple point on the phase diagram. Owing to the appreciable temperature dependence of the positions of the boundaries in the Nb-Al-Ge system (see Fig. 1), such alloys turn out to be in a metastable structural state at temperatures 300°K and below after melting and cooling, and also after high-temperature annealing.

It has been established by now that in a number of alloys with A15 structure, such as V_3Si [19], Nb_3Sn [20], and others with different structures, a loss of lattice stability is observed, leading to a low-temperature martensitic transition. It is natural to assume that in those systems where lattice stability is observed, the greatest tendency to this instability and to the martensitic transition will be possessed by alloys whose compositions lie near the boundaries of the phase regions. Such alloys have a tendency to lattice restructuring accompanied by displacements of the atoms with a frequency tending to zero, and are characterized by the lowest [5] values of $\langle\omega_{\text{eff}}\rangle$. (In alloys of the In-Tl system, this was demonstrated experimentally in [21].) Unfortunately, no reliable structure data have been obtained as yet on the martensitic transition in Nb-Al-Ge alloys, although the question of this transition is under lively discussion. In the isostructural alloys $V_3(Si_{1-x}Ge_x)$, however, a two-step curve is possessed only by those alloys for which such a transition has been observed (or can be observed) by x-ray diffraction. In the V_3Ge alloy, for example, where no such transition takes place, the transition curve remains practically unchanged after compression [7]. A direct check of the existence of the martensitic transition in Nb-Al-Ge alloys by x-ray diffraction is therefore urgently needed. Until this is done, the explanation presented here for the details of the picture of the smearing effect, on the basis of the hypothesis of Matthias and co-workers, must be regarded as only one of the possible variants.

Just as in the $V_3(Si_{1-x}Ge_x)$ alloys [7], the largest smearing is observed in those Nb-Al-Ge alloys in which T_c is largest and the lattice rigidity is minimal. We arrive now at one of the most interesting and most timely aspects of the superconductivity of compounds with A15 structure, namely the connection between their superconducting properties, particularly the value of T_c, and the properties and stability of the alloy crystal lattice. It was already noted above that in accordance with Hopfield's model the T_c of alloys of the Nb_3X type depends principally on the phonon-spectrum parameters, in particular $T_c \sim 1/\omega_{\text{eff}}^2$. Therefore, if Hopfield's model is valid, then it is precisely the alloys that lie at the edges of the phase regions of the Nb-Al-Ge system and have minimal $\langle\omega_{\text{eff}}\rangle$ that should have the higher T_c and simultaneously, in our opinion, should be more prone to the martensitic transition. From this point of view, the record $T_c > 20$°K observed [2] for the alloy $Nb_3(Al_{0.8}Ge_{0.2})$, the composition of which lies near the edge of the region of the existence of the A15 phase, is quite normal. At the same time, as seen from the obtained data, the sensitivity of these alloys to the action of external and internal inhomogeneous stresses is higher, and this also confirms the point of view that the smearing of the transition is the result of a martensitic transition.

In conclusion, it should be stated that these properties should apparently be possessed by alloys of the solid-solution type not only with the A15 structure, but also with other crystal structures. When many phase diagrams are compared with the corresponding plots of T_c against the composition (see [22]), a remarkable picture is observed. In the overwhelming majority of systems where there are regions of solid solutions based on a lattice of pure components, or else regions of intermediate phases that exist in sufficiently wide concentration intervals, the extremal values of the dependences of T_c on the composition are encountered in alloys having compositions close to the boundaries of the regions. This occurs in Ti-based alloys with V, Nb, Mo, Zr, and Zr + Nb, in Cd-Hg and In-Sn alloys, in Re with Nb, Mo, and W, and in many others. In many of them, for example in martensitic alloys of titanium, one can expect to observe instability of the lattice, or else a decrease of its "rigidity," in the series of alloys with compositions approaching the limit of the phase-stability region. This has probably already been observed in alloys of Ti with Mo [23]. In other systems, the extremal T_c appear on the boundary probably because of singularities not only in the phonon spectrum, but also in the electron spectrum. Thus, it is in the "boundary" alloys that searches for materials with the largest T_c offer the greatest promise [6].

In conclusion, we wish to express deep gratitude to B. N. Kodess for supplying the alloys and to V. F. Degtyareva for the x-ray photography. We are grateful to L. P. Gor'kov, Ya. A. Iosilevskiĭ, and É. I Rashba for valuable remarks during the discussion of the work and for their interest in it.

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[1] We are grateful to Yu. S. Karimov and A. V. Zvarykina for these measurements.

[2] In spite of the fact that the behavior of Nb_3Al under pressure was investigated earlier by Nebauer [3], no jump of T_c could be observed in his work, since the pressures obtained did not exceed 16.5-17.0 kbar.

[3] For the alloy Nb_3Al, the plot shows the value of dT_c/dp pertaining to the low-pressure phase, the structure of which is the same as in other alloys.

[4] That the Nb-Al-Ge alloys with maximum T_c have a minimal microhardness was noted earlier by Matthias [18], although his samples had a multiphase structure.

[5] We are grateful to Ya. A. Iosilevskiĭ for pointing this circumstance out to us.

[6] After this paper was completed, we became acquainted with a preprint [24] in which it is reported that a sharp increase of T_c was observed in Mo-Re alloys in which the concentration had been varied towards the limit of σ-phase stability. This increase is attributed to temperature instability of the lattice.

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