Physical properties and electronic structure of superconducting compounds with the β-tungsten structure

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A review is given of the physical properties and of the theoretical models for transition metal compounds of the $A15$ (or β-tungsten) structure. Not only binary compounds of stoichiometeric composition are considered, but also their multiple alloys with one another. The behavior of the electronic specific heat, magnetic susceptibility, Knight shift, and other electronic properties as functions of the composition and temperature is discussed, and a comparison is made of these results with the optical and x-ray spectra. The anomalies of the elastic constants in V_3Si and Nb_3Sn are investigated in detail, and the nature of the martensitic transformation in them is analyzed. The superconducting transition temperature as a function of the composition, stoichiometry, electron concentration, and pressure is analyzed in considerable detail for both pure compounds and for their alloys. An account is given of the existing theoretical models for the electronic structure of these compounds, and the predictions of these models with regard to electronic and lattice properties are compared with the experimental data. It appears that none of the existing models is able to explain the entire set of observed phenomena. The direction of future experimental investigations is indicated.

CONTENTS

I. INTRODUCTION

The superconductors known at the present time with record properties, i.e., the highest transition temperatures T_C and the highest critical fields, belong to the class of compounds with β-W structure. In particular, the celebrated superconductors Nb_3Sn, Nb_3Al ($T_C = 18°K$), and V_3Si ($T_C = 17°K$) belong to this class. The superconductor with the highest known (up to the present time) transition temperature of approximately $23°K$—the compound Nb_3Ge—is a representative of this same class. Now approximately seventy pure compounds of β-W structure have already been synthesized; the majority of them sre superconductors, and in twelve of them T_C exceeds $10°K$. Many of these compounds form solid solutions with each other, crystallize into the same type of structure, and are also good superconductors.

There is no doubt that the β-W structure is extremely favorable for good superconducting parameters of the intermetallic compounds. The heightened interest in such compounds, which has been displayed in the last few years by both physicists (experimentalists and theorists) and technologists, is obviously due to this fact. It is just in these years that extensive experimental data pertaining to their different physical properties—electronic and lattice properties—has been accumulated, and moreover in some of these compounds, which are superconductors with high T_C, a martensitic structural transformation of the lattice from a cubic into a tetragonal phase is observed at temperatures slightly exceeding T_C. This unexpected discovery has attracted special attention to all compounds of β-W structure.

Apparently the high values of T_C and the presence of a martensitic transformation in a number of compounds of the type under consideration have a common physical origin, which is hidden in the properties of their crystal-chemical structure; many theoretical articles appearing in the last few years have been devoted to the search for this common origin. The basic goal of the physical investigations which have been carried out consists in an attempt to answer the following questions: Why are the superconducting transition temperatures so high in compounds with the β-W structure (but, on the other hand, why not in all such compounds), what kind of connection exists between the superconducting transition and the martensitic transformation, and is it possible to obtain higher values of T_C in solid solutions of these compounds than in the pure compounds?

To answer these questions, it is necessary to investigate and compare the physical properties of not only the high-temperature superconductors but of all representatives of this class of compounds. In the present review the authors set themselves the goal to collect and systematize the experimental data on all compounds with β-W structure, including solid solutions of these compounds with each other, using all of the scientific literature available to them up to and including 1973.[1] Theoretical models of the electronic band structure of these compounds and the attempts to explain the observed phenomena which follow from these models are discussed on the basis of this data.

Let us consider the basic features of the crystal structure of β-W type compounds having the chemical formula A_3B. In such compounds the B atoms form a body-centered cubic lattice, and the A atoms are distributed in pairs on the faces of the cube and parallel to the coordinate axes (Fig. 1). The unit cell of the compounds under consideration contains 8 atoms; the space group is O_h^3-Pm3n.

The characteristic feature of this structure is the fact that the A atoms form a series of interpenetrating linear chains, where the distance between the atoms in
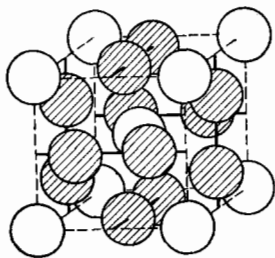
FIG. 1. The β-W structure of intermetallic compounds of the type A_3B (atoms: ●—A, ○—B).

TABLE I. T_c in compounds with β-W structure (°K)

B \ A3	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
Al				11.65	18.80			0.58	
Ga				14.80	20.3		<0.35	1.20	
In				13.9	9.2				
Tl	<0.35	<0.35		<4.20					
Si				17.1	19.0 (from [123])		<0.015	1.70	<1.20
Ge				6.01	17.0 [114] (23,2 from)		<1.20	1.75	
Sn	5.80	0.93		3.80	18.0	8.35			
Pb		0.76		<4.2	<1.20				
P				<1.00					
As				0.20					
Sb	5.7	<1.20		0.80	2.00	0,72			
Bi		2.85		<4.20	2.25				
Fe									
Ru								3.42	
Os				5.15	0.94			4,68	12.С5
Co				<0.015					
Rh				<0.015	2.64		0.07		
Ir	5.40			1.71	2.85		0.75		9.6
Ni				0.30					
Pd				0.082					
Pt	0.58			3.20	10.9	0.40	<0.015	8.11	
Cu									
Ag									
Au	<0.015	0.92		2.40	10.8	16.0			
Zn									
Cd									
Hg	<0.35	<0.35		<4.20					

one chain is the shortest distance between the atoms in the β-W structure and is 22% less than the distance between A atoms belonging to different chains.

Transition elements of group IV, V, or VI (Ti, V, Cr, Zr, Nb, Mo, Ta, W) invariably appear as the A atoms, while the B atoms may be either nontransition elements (Al, Si, P, Ga, Ge, As, In, Sn, Sb, Pb, Bi) or transition elements (mainly elements from group VIII: Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Au). Vanadium forms the largest number of A_3B compounds with the β-W structure.

The majority of these compounds have narrow regions of homogeneity.[2] However, in a number of vanadium compounds with components of similar atomic radii, the formation of the β-W structure does not occur in peritectic reactions but in the process of ordering a solid solution with a body-centered cubic lattice, and these compounds possess rather extended regions of homogeneity[3]

A mechanism involving the substitution of atoms materializes, as a rule, in the compounds under consideration upon deviations from stoichiometry in either direction. This means that the linear chains remain undisturbed in the compound $A_{3+x}B_{1-x}$, and the excess A atoms occupy B-sites. However, a partial destruction of the chains of A atoms is possible in the compound $A_{3-x}B_{1+x}$.

One of the interesting structural features of the A_3B-phase with a β-W type lattice is their tendency towards a high degree of ordering. However, the degree of ordering turns out to depend on the type of B atom involved, i.e., whether the B atom is a transition element or a nontransition element. If the A_3B compounds containing nontransition B elements are, as a rule, highly ordered, then for the second group of these compounds the degree of ordering depends on the mutual location of elements A and B in the periodic table.[4]

Now let us proceed to an investigation of the physical properties of the A_3B compounds.

II. EXPERIMENT

1. The superconducting transition temperature of pure compounds and their alloys. The data known in the scientific literature (ending in 1973) on superconducting transition temperatures in compounds of β-W structure are shown in Table I. As the techniques for synthesizing these compounds have improved, there has been a continuous improvement in the accuracy of the determinations of T_c; therefore, the results of the most recent measurements are compiled in Table I from [2, 5-13, 114, 123].

Even a brief acquaintance with the results cited in Table I indicates that, for A_3B compounds of vanadium and niobium with β-W structure, the highest superconducting transition temperatures are obtained when the B atom is a nontransition element: Al, Si, Ga, Ge, Sn. It is precisely among these compounds that the highest temperature superconductors Nb_3Ga with $T_c = 20.3°K$[13] and Nb_3Ge with $T_c = 23.2°K$[114] are found. A number of unusual phenomena can be noted for this group of compounds. Let us take, for example, the compounds of V with Si, Ge, and Sn. The three metalloids form a single group, the valence electron concentrations are identical in all three compounds, but the values of T_c differ markedly. One might think that the decrease of T_c from V_3Si to V_3Sn is related to the increasing mass of the B element. But if we take compounds of niobium with Si, Ge, and Sn, the values of T_c hardly change at all.

Thus, the chemical kinship of the elements in a single group of compounds does not, in the general case, lead to the proximity of their values of T_c, and this difference between them is not governed by the mass of the atoms.

The superconducting transition temperatures are lower as a whole for the second group of superconducting A_3B compounds with transition B-elements: T_c reaches a value between 13 and 16°K[2] for the highest temperature superconductor in this group, Ta_3Au. If roughly identical values of T_c are encountered just about as frequently for vanadium as for niobium in the first group of A_3B compounds, one can note a different picture for the second group of compounds—namely, the superconducting transition temperatures for the niobium compounds as a rule exceed the values for the corresponding vanadium compounds by a factor of two or three.

Investigation of the superconducting properties of A_3B compounds in the region of homogeneity has shown that the highest values of the superconducting transition temperature are generally attained as the stoichiometric composition is approached. Deviation from stoichiometry is usually characterized by a decrease in the value of T_C.[12,14,15] For example, T_C = 16.85 to 17.1°K for stoichiometric V_3Si whereas T_C = 9.40°K when the same compound contains 20.1 at.% Si.[14] The compound V_3Ir, which is not superconducting when its composition is stoichiometric (T_C < 0.015°K), is an exception; superconductivity appears in this phase at 31 at.% Ir, and the maximum transition temperature is reached at 38 at.% Ir.[12]

In connection with this point, it is interesting to note that transition temperatures of 6.9°K and 14.9 to 16.0°K, respectively, were first obtained for the compounds Nb_3Ge and Nb_3Ga. In this connection it was noted that both compounds crystallized with a deviation from stoichiometry. By using a special technique of synthesis with the application of rapid quenching, it was possible to obtain a closer approach to stoichiometry and, as a consequence, a substantial increase of the superconducting transition temperature, up to 23.2°K for Nb_3Ge and up to 20.3°K for Nb_3Ga.[13,16,114]

Now let us proceed to an investigation of the superconducting properties of the alloys of compounds with β-W structure. Two cases are possible in connection with the formation of solid solutions as a result of doping A_3B compounds: The isomorphic replacement of A atoms by A′ atoms, and the isomorphic replacement of B atoms by B′ atoms.

For the first group of solid solutions, the superconducting transition temperature of the alloys has been investigated in greatest detail in the following systems: $V_3Si - Mo_3Si$, $Nb_3Au - V_3Au$, $V_3Sn - Nb_3Sn$, $V_3Sn - Ta_3Sn$, and $Nb_3Sn - Ta_3Sn$.[2] In all of the enumerated cases and in many other cases which are described in[2], there is a smooth and continuous variation of T_C as the composition of the alloys changes. However, not a single case is known in which the replacement of an A atom by another transition element A′ has led to an appreciable increase of T_C, such that its value would exceed the superconducting transition temperature of the highest-temperature component from the alloyed compounds. A similar situation is observed in connection with alloys of A_3B compounds in which the B atom is a transition element and its replacement by B′, another transition element, takes place. Here the alloy systems which have been studied in most detail are: $Nb_3Rh - Nb_3X$ (X = Co, Ru, Pd, Os, Ir, Pt, Au),[17] $Mo_3Ir - Mo_3Ru$, and $Mo_3Os - Mo_3Ru$.[115]

In systems of the type $A_3B - A_3B'$, where atoms B and B′ are both transition elements, the formation of the following solid solutions has been established: $V_3Si - V_3Ga$, $V_3Si - V_3Ge$, $V_3Si - V_3Sn$, $Nb_3Sn - Nb_3Al$, $Nb_3Sn - Nb_3Ge$, $Nb_3Sn - Nb_3Sb$, $Nb_3Al - Nb_3Ge$, $Nb_3Al - Nb_3Sb$,[2,116] etc. Here the situation is somewhat different from the first group of solid solutions. For example, an increase of the superconducting transition temperature up to 20.05°K was first observed[18] in the $Nb_3Al - Nb_3Ge$ system in 1967. In recent years this result has been repeated by many investigators, and their combined efforts have been able to bring the superconducting transition temperature in this system

first to 20.7°K ($Nb_3(Al_{0.75}Ge_{0.25})$)[19] and finally to 21.05°K ($Nb_3(Al_{0.763}Ge_{0.237})$).[20]

The preparation of the highest values of T_C in this compound was found to be possible after long periods of annealing at relatively moderate temperatures, in connection with which the authors of[19] conjectured that this is related to ordering processes. Here it was assumed that, side by side with the ordering of the Nb atoms in the β-W structure (which is indicated by the fact that the highest value of T_C is reached in the $Nb_{3+x}Al_yGe_{1-y}$ system when x = 0), there is also an ordering of the Al and Ge atoms. However, the x-ray structural analysis performed on a polycrystalline sample of $Nb_3(Al_{0.75}Ge_{0.25})$ in the work[4] did not establish the presence of new superstructure lines in the x-ray diffraction pattern.

The study of the superconducting properties in the solid solutions $Nb_3(Al_{1-x}Me_x)$, $Nb_3(Sn_{1-x}Me_x)$, and $Nb_3(Ga_{1-x}Me_x)$[21,117] showed that it is also possible to obtain some increase in the value of T_C by the isomorphic replacement of the atoms of the nontransition element B by B′ atoms not only in the system Nb_3(Al − Ge) but also in other systems, for example, in Nb_3(Al − Ga), Nb_3(Sn − Ga), Nb_3(Al − B), and Nb_3(Al − Be).

However, in spite of the definite optimism which undoubtedly appeared for the experimentalists after the publication of article[18], it is necessary to state that during the last five years the numerous doping attempts with the utilization of various model criteria as guides have essentially not led to any encouraging results (see, for example,[22]). And what is more, the latest successes in the synthesis of the compounds Nb_3Ga (T_C = 20.3°K) and Nb_3Ge (T_C = 23.2°K) give grounds for the following reflections: either to continue the experimental doping attempts in more complicated systems or else to concentrate efforts on the development of new methods of synthesis, which might enable us to obtain compounds which are closer to stoichiometry.

It is convenient to systematize the extensive experimental data on the effect of impurities on the superconducting transition temperature T_C in A_3B compounds of β-W structure by using the following principles. In the first place, in order to compare the effect of the impurities on different initial compounds with transition temperature T_C^0 (the value associated with strict stoichiometric composition) it is convenient to plot the concentration dependence of the relative transition temperature $T_C/T_C^0 = t$. In the second place, it is necessary to distinguish the points in the lattice where the impurity enters, i.e., whether it replaces one of the type A atoms (transition elements) which form the chains or one of the type B atoms (nontransition or transition elements) which are located at the vertices or at the center of the cube. Figures 2 and 3 have been constructed according to this principle, where the data pertaining to ternary systems of the type $(A_{0.75-x}A'_x)B_{0.25}$ with $0 < x < 0.75$[2,15,23-26] is shown in Fig. 2, and the data pertaining to systems of the type $A_{0.75}(B_{0.25-x}B'_x)$ with $0 < x < 0.25$[2,17,21,27] are shown in Fig. 3. For each separate curve shown in the figures, the initial compound was chosen to be the one with the largest value of the transition temperature T_C. That is why the quantity T_C/T_C^0 is smaller than 1 everywhere for the limiting concentration of the third component.
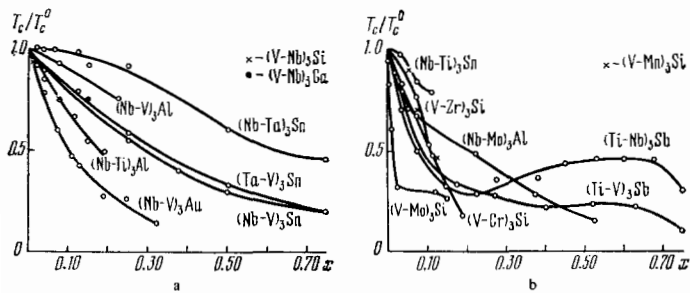
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FIG. 2. The dependence of T_C on the composition of the alloy $(A - A')_3B$. In Fig. 2 (a) the elements A' belong to the same group of the periodic table as the elements A. In Fig. 2 (b) A and A' are elements belonging to different groups of the periodic table.

An analysis of the results shown in Figs. 2 and 3 indicates that the general rule which holds in all of the situations under consideration is the following: if two compounds A_3B and A'_3B' are alloyed with a third, the superconducting transition temperature T_C of the resulting alloy becomes lower than the maximum T_C for the pure, initial compounds. This "unfortunate" rule has only a few exceptions, which were considered above.

If the region of small concentrations x of the third component (the impurity situation) is considered, one can easily see an appreciable reduction of T_C with increasing impurity concentration in the majority of alloys pertaining to all five cited cases. As a rule this drop is very strong in the case when atoms in the chains are replaced (Fig. 2). Physical mechanisms for the lowering of T_C due to the presence of impurities will be discussed below.

We have already mentioned that T_C is sensitive to deviations from stoichiometric composition. Investigation of the region of homogeneity of the alloys V_3Si and Ti_3Sb[14,15] has shown that in both cases the maximum transition temperature is reached near the stoichiometric composition. T_C is weakly modified by the presence of an excess of type B atoms, whereas a sharp drop in the value of T_C is observed when there is a shortage of B atoms (i.e., when transition element atoms replace the nonmetal atoms in the B positions). The latter fact apprently indicates that, in the alloys under consideration the strong decrease of T_C is connected with an increase of the interaction between the chains through the transition element atoms occupying B positions.

Thus, the superconducting transition temperature is very sensitive to substitutions of the atoms in the linear chains, independently of whether this occurs upon doping or associated with deviations from stoichiometric composition.

2. The dependence of the superconducting transition temperature, the electronic specific heat, and the magnetic susceptibility on the electron concentration. An analysis of various empirical criteria for superconductivity indicates that the clearest correlation is observed between T_C and N_e—the average number of valence electrons per atom (the electron concentration).[2] In fact, it follows from a consideration of Fig. 4 that the superconductors with the highest values of T_C are grouped around two intervals of the electron concentration: 4.50 to 4.75 and 6.25 to 6.60 e/a (electrons per atom). The first region includes compounds in which element B is either a nonmetal or a simple metal, and the second region—compounds in which the B atom is a transition element or a noble metal.

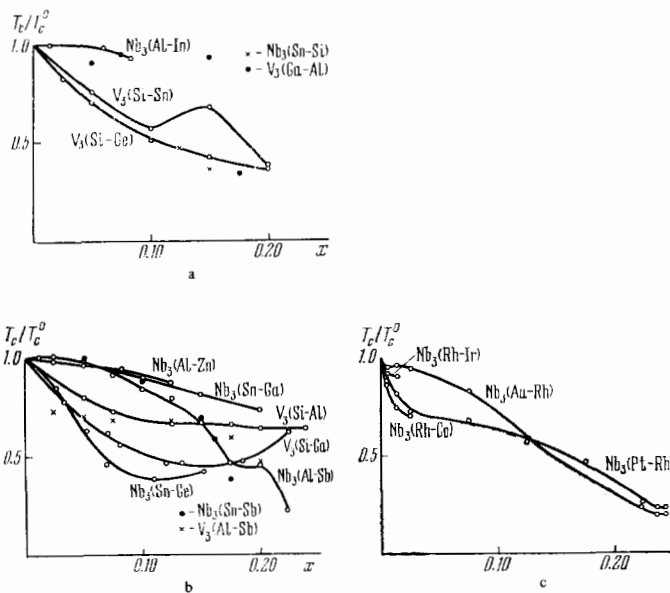However, a careful analysis of Fig. 4 leads to the

a

b

c

FIG. 3. Dependence of T_C on the composition of the alloy $A_3(B - B')$ $(A_{0.75}(B_{0.25-x}B'))$. In Figs. 3 (a) and 3 (b) the element B' is a nontransition element, where in Fig. 3 (a) B' is taken from the same group as B, but in Fig. 3 (b) B' and B are taken from different groups; in Fig. 3 (c) the elements B and B' are both transition elements.
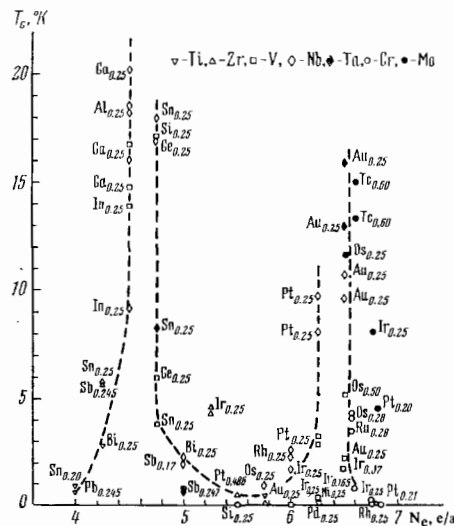
FIG. 4. The superconducting transition temperature in compounds of β-W structure as a function of the electron concentration N_e.

conclusion that, the ranges of valence electron concentrations, which are indicated above as being favorable for high T_C, are essentially the regions in which for one and the same electron concentration there exists a larger number of A_3B compounds than exist for other values of N_e.

For example, two groups of A_3B compounds with one and the same electron concentration stand out very predominantly in the region of the first "peak": either 4.50 e/a (Nb_3Ga, Nb_3Al, V_3Ga, V_3In, V_3Al, Nb_3In) or 4.75 e/a (Nb_3Ge, V_3Ge, V_3Si, Nb_3Sn, V_3Sn, Nb_3Pb). The same feature can also be noted in the second "peak." It is natural that different compounds, corresponding to identical concentrations of valence electrons per atom, have different superconducting transition temperatures which are distributed along a vertical line on the graph of T_C vs. N_e. Here the scatter in the values turns out to be greatest precisely in the ranges 4.50 to 4.75 e/a and 6.25 to 6.60 e/a; a value in these intervals is apparently a necessary but not a sufficient condition for obtaining high values of T_C. In connection with this we wish to note that, in describing the dependence of T_C on N_e one often talks about the existence of two maxima, forgetting about the fact that in the middle part of the "favorable" electron concentrations, where the depicted peaks are usually found, there is not a single A_3B compound of stoichiometric composition (see, for example, the dependence of T_C on N_e presented in[28]). If the data on ternary compounds, for which a continuous variation of the electron concentration can be obtained, were plotted on this figure, we would see that their T_C assume quite different values (depending on the composition within the limits of one and the same value of N_e), uniformly filling the space between the vertical lines, which bound the region of "favorable" electron concentrations. Therefore, we are not inclined to attach the importance of an "absolute" parameter to the dependence of T_C on N_e, such that only by being governed by this parameter can one knowingly seek alloys of A_3B compounds with high T_C. However, this parameter turns out to be convenient for the investigation of other physical properties of the compounds in question.

The values of the electronic specific heat[11] and the paramagnetic susceptibility[12] as functions of the same quantity N_e are plotted on Figs. 5 and 6 for A_3B compounds. It is not difficult to notice a certain similarity between the nature of the variation of these properties and the dependence of T_C on the electron concentration (see Fig. 4). The relative location of the points are the same (with rare exceptions) on all three diagrams (see Figs. 4—6).

Since both the electronic specific heat and the paramagnetic susceptibility in metals are proportional to the density of electron states at the Fermi level, the presence of the indicated correlation gives a basis for concluding that the high values of T_C in compounds of β-W structure are associated with a high density of the electron states at the Fermi level. (Typically the same correlation between T_C, γ, and χ is also observed in the region of homogeneity of the compounds under investigation.[12,14])

However, certain deviations from the described regularity are observed in stoichiometric compounds of niobium. For example, the high value of T_C for the compound Nb_3Al ($T_C = 18.8°K$) corresponds to relatively low values for γ and χ (Figs. 5 and 6). In connection with this point some authors have concluded (see, for example,[6]) that, in this compound the high-temperature properties are not related to the location of the Fermi level near a peak in the density-of-states curve $\rho(E)$, but perhaps are determined by other factors, for exam-
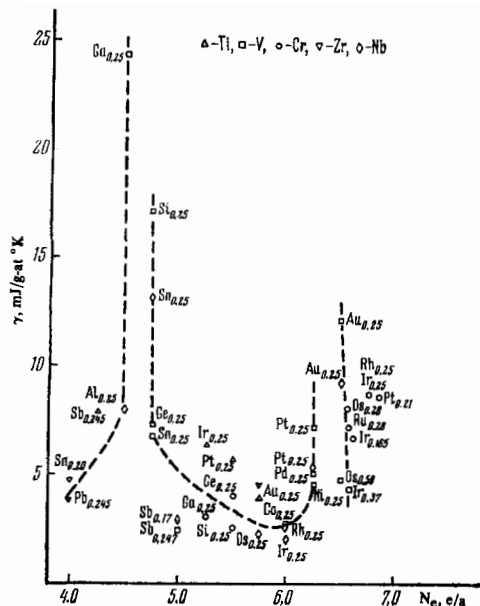
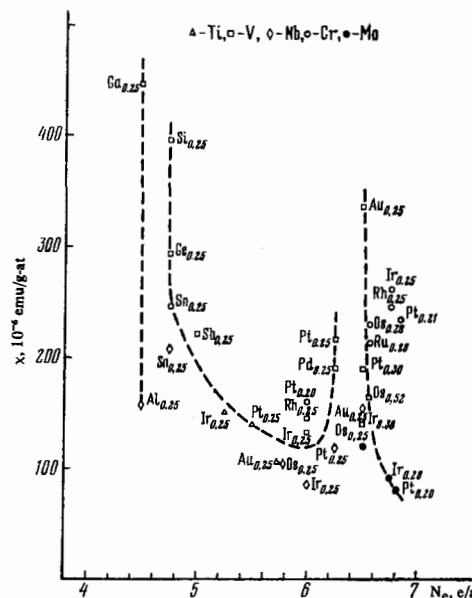FIG. 5. The electronic specific heat of compounds with β-W structure as a function of N_e.

FIG. 6. Paramagnetic susceptibility as a function of N_e for compounds with β-W structure.

ple, the structure of the vibrational spectrum. In turn we wish to call attention to the following fact: Although the values of γ in the A_3B compounds of niobium with high T_C are not as large as one might expect in analogy with the vanadium compounds, nevertheless there is a general correlation between T_C and γ in the series $Nb_3Os - Nb_3Ir - Nb_3Pt - Nb_3Au$ [29] (Figs. 4 and 5), that is, higher values of T_C correspond to higher values of γ.

Thus, from the results presented above it follows that, although the electron concentration is not some kind of universal parameter which one can use to seek alloys of β-W compounds with higher values of T_C, the investigation of a number of physical properties as functions of the electron concentration turns out to be useful. It leads us to the important conclusion that the high values of T_C in the compounds under discussion
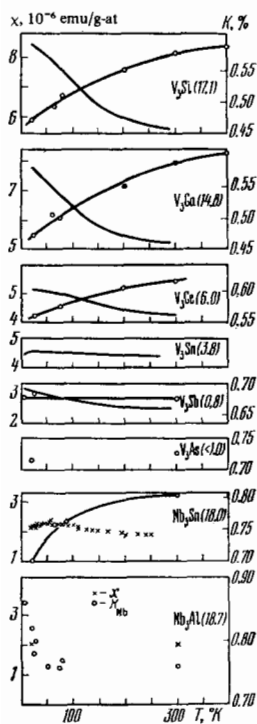
FIG. 7. The temperature dependence of the susceptibility χ and of the Knight shift K for A_3B compounds of vanadium and niobium (B is a nontransition element) according to the data given in [6,30-33].

Compound	T_c, °K	$2\Delta/kT_c$	Temperature of measurements, °K	Method measurement	Reference
Nb₃Sn	17.5	1.3	1.7	Tunneling	39
	—	3.6	1.2	Tunneling	40
	14.0	2.3—3.1	1.5	Tunneling	41
	17.8—18.3	0.2; 1.0; 1.4; 3.0	1.9	Tunneling	42
	18.3	1.0—2.8	2.0—4.2	Tunneling	43
	18.3	3.7	5.0; 78	Infrared reflectivity	44
	18.3	3.56	2.6—2.8	Thermal conductivity	45
	—	3.8	2.0—40	Photoluminescence	46
	18.0	4.8	1.0—42	Thermal conductivity	47
	18.3	4.4	—	Inelastic scattering	48
V₃Si	17.0	3.8	1.3	Tunneling	49
	—	1.8; 3.8	1.2	Tunneling	40
V₃Ge	—	3.2	1.2	Tunneling	40

are, as a rule, associated with a high density of electron states at the Fermi level.

3. Temperature dependence of the magnetic susceptibility and of the Knight shift. X-ray and optical spectra. Many compounds with high values of T_c turn out to have interesting dependences of such properties as the variation of the susceptibility and the Knight shift with temperature. It is well known that the ordinary Pauli susceptibility and the Knight shift (which is proportional to the susceptibility) should not depend on the temperature for a degenerate electron system, which is also observed for the majority of metals. However, a strong temperature dependence of these characteristics was observed in compounds of β-W structure and, what is of even greater interest, this phenomena was observed precisely in those compounds which have the highest transition temperatures. Does this indicate that one should necessarily anticipate high values of T_c where the temperature dependences of the susceptibility and of the Knight shift are stronger? The experimental investigations [30-32] indicate that such a correlation is in fact observed for the V_3X compounds (X = Si, Ga, Ge, Sn, As, Sb, Pt, Au) (Fig. 7). For example, the strong temperature dependence of $K_V(T)$ and $\chi(T)$ for V_3Si is accompanied by a high value of T_c (17°K), and, conversely, for V_3As ($T_c = 0.2$°K) and V_3Sb ($T_c = 0.8$°K) the indicated dependences are almost absent.

However, for niobium compounds the temperature dependence of the susceptibility was found to be weakly expressed, and the temperature variation of the Knight shift has a more complicated nature than in V_3X compounds. [6,12,33,34] It was found to be impossible to establish any correlation between the behavior of these characteristics and the superconducting properties of Nb_3X compounds. Thus, in regard to this group of properties one can remark that the niobium compounds stand as isolated objects and exhibit completely different behavior than the vanadium compounds.

Let us return to the investigation of the unusual de-

pendence of the susceptibility and of the Knight shift in V_3X compounds. The observed, strong temperature dependence of $K_V(T)$ and $\chi(T)$ in V_3X compounds with high values of T_c indicates that the Fermi level apparently lies near a narrow peak in the density of states, this peak being so narrow that its width is comparable with the energy kT. [32] What kind of electron states can form such a peak? A series of other experiments enables us to obtain such information and, to begin with, the x-ray spectra. Investigation of the x-ray spectra for different series of binary components of V_3X compounds gives the possibility to establish the nature of the distribution of the various types of states in the empty and filled parts of the conduction band. Such measurements were carried out in [35,36] and showed that V3d-states appear at the Fermi surface in all V_3X compounds, and it is apparently these states which form the indicated narrow peak in the density of states. The electronic states of the x-component are, as a rule, located at the bottom of the valence band, where the degree of their localization depends on the nature of the location of the X-element relative to vanadium in the periodic table.

The extraction of detailed information from optical spectra runs into great difficulties connected with non-unique interpretation of the experimental data. However, from optical experiments one can obtain other important parameters such as, for example, the frequency of electron collisions or the values of the energy gap. The effective electron-collision frequency for the compound Nb_3Sn, determined from optical spectra, was found to be $\nu_{eff} = 1.85 \times 10^{14}$ sec^{-1}. [37] Furthermore, the electron-phonon collision frequency was calculated, $\nu_{ep} = 1.1 \times 10^{14}$ sec^{-1}, from this value and by using the data concerning the measured values of the residual and room-temperature resistances, and the electron-phonon coupling constant was found to be $\lambda = 0.46$. The effective Coulomb potential μ^* was obtained by substituting this value of λ into McMillan's formula [38] for the superconducting transition temperature; the resulting value unexpectedly turned out to be negative in sign: $\mu^* = -0.12$. This value for λ cannot give so a high value of T_c (~18°K) for conventional values of the effective Coulomb potential μ^*. Therefore, the authors of [37] propose that a nonphonon superconductivity mechanism may perhaps also exist in Nb_3Sn.

Optical measurements are also valuable in that they enable us to determine the energy gap in superconductors. Thus, for example, from a measurement of the optical properties of the compound Nb_3Sn in the infra-

TABLE III. Temperature of the structural transformation in binary compounds of β-W structure

Compound	Structural transformation temperature, °K	Tetragonality, c/a	Reference
V_3Si	21	1.0024	51
Nb_3Sn	43	0.9939	51
V_3Ga	50	—	53

red region of the spectrum the relative value of the energy gap was found to be $2\Delta/kT_C = 3.77$, which is close to the value which follows from the BCS theory ($2\Delta/kT_C = 3.53$). However, the method of infrared reflectivity is not the only way to measure the energy gap; therefore, a comparison of the values of $2\Delta/kT_C$, determined by using different methods, is of interest. Examination of these data,[39-49] which are summarized in Table II, indicates that there is a great deal of scatter in the values of this parameter for the compounds Nb_3Sn and V_3Si. For Nb_3Sn the relative values of the energy gap $2\Delta/kT_C$ fluctuate between 0.2 and 4.8, and for V_3Si they fluctuate between 1.8 and 3.8. What is the reason for the different values of the energy gap, which are obtained even when the same method of investigation is used (for example, tunneling)? On the one hand, as is indicated in[43], this may be related to the anisotropy of the energy gap as a function of the orientation of the crystal with respect to the tunneling contact. In the case of polycrystalline samples a set of different orientations will exist and, as a consequence of this, there will be several values for the gap, as observed, for example, in[42]. On the other hand, since tunneling experiments measure the energy gap within a distance of the order of the coherence length ξ from the surface, it is possible that in the compounds of β-W structure under consideration, which have small values of ξ ($\xi \sim 100$ Å for Nb_3Sn), the values of the energy gap are to some extent determined by the state of the surface and by the impurities present on it. For example, it is shown in[44] that damaging the surface of the Nb_3Sn sample leads to a reduction of the relative values of the gap ($2\Delta/kT_C$) from 3.77 to 1.9.

Quite original measurements of the energy gap in superconducting Nb_3Sn were performed by Axe and Shirane.[48] They used inelastic neutron scattering to study the phonon damping at low temperatures, and it was found that for certain transverse phonons the phonon linewidth decreases sharply when the temperature is below T_C. Such behavior of the phonon damping can be explained by processes involving the decay of the phonon into two quasiparticles in the superconductor. This process obviously has a threshold equal to $2\Delta(T)$; therefore, when the phonon energy is less than the indicated threshold, its damping should fall off sharply. The data for $2\Delta(0)$, which is given in the Table, corresponds to a phonon with wave vector $\sim [1\ 1\ 0]$; therefore, the obtained value for the gap corresponds to precisely this direction in k-space. However, the majority of the remaining methods give certain characteristics of the gap which are averaged over the anisotropy.

Measurements of the energy gap, of course, give valuable information; however, the obtained data are unfortunately inconsistent, especially for the compound Nb_3Sn. If the multiple-valued nature of the tunneling experiment results is due to the existence of a strongly anisotropic Fermi surface, it would be desirable to de-

termine which directions in k-space the obtained data pertain to, by performing measurements on single crystals.

Now let us proceed to a consideration of the lattice properties.

4. Structural transformation. In 1963, in connection with neutron diffraction studies of the compound V_3Si, Shull observed a broadening of the diffraction lines on cooling the sample below the superconducting transition temperature. This is regarded as the first observation of a structural transformation in compounds of the β-W type. Later Batterman and Barrett[50] performed a careful, low-temperature, x-ray structure analysis of a single crystal of V_3Si and established that the crystal undergoes a transformation from a cubic to a tetragonal structure at a temperature of the order of $\sim 21°$K. A similar structural transformation was soon observed in another compound having the β-W structure—namely, Nb_3Sn [51,52] (Table III).

The basic characteristics of this transformation are as follows:

1) The absence of diffusion, that is, the compositions of the phases—the initial (cubic) phase and the final (tetragonal) phase—are identical. This implies that only a realignment of the crystal lattice occurs during the transformation, without any changes of the composition due to diffusion of the component atoms.

2) No noticeable change in the crystal volume is detected in the transformation process.

3) The temperature of the structural transformation always exceeds the superconducting transition temperature.

4) The transformation is reversible, i.e., upon heating above the structural transition point the crystal always returns to its original orientation (the absence of hysteresis effects).

5) The temperature of the structural transformation may vary from sample to sample: for V_3Si it occurs in the interval between 18 and 30°K, and for Nb_3Sn in the interval between 35 and 50°K. The structural transformation was not observed in a number of samples of V_3Si and Nb_3Sn.

6) The single-crystal nature of the material is not preserved during the transformation from a cubic to a tetragonal structure. A twinning domain structure is detected in the tetragonal state.

There is one essential difference in the general features of the compounds V_3Si and Nb_3Sn enumerated above, which lies in the fact that if the ratio $c/a > 1$ in V_3Si the same ratio will be less than unity in the tetragonal structure for Nb_3Sn (see Table III).

The nondiffusive nature of the transformation, the absence of changes in the volume, and certain other features recall the martensitic transformation in the alloy In-Te,[54] which was thoroughly investigated earlier; in connection with this Batterman and Barrett also called the structural transformation in V_3Si and Nb_3Sn martensitic.

In addition to V_3Si and Nb_3Sn, the martensitic transformation has also been detected in the compound V_3Ga on observation in an electron microscope.[53] No structural transformation of any kind has been observed in
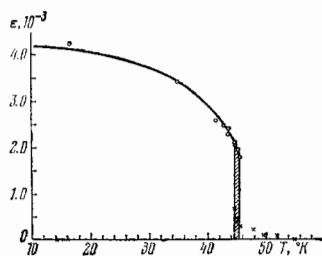
FIG. 8

Nb₃Sn   • – Nb
        o – Sn

FIG. 9

FIG. 8. Temperature dependence of the tetragonal strain $\epsilon = (a/c) - 1$ for the compound Nb₃Sn. The solid curve gives the results of a calculation of the indicated dependence according to the data from article [55].

FIG. 9. The atomic displacements in a β-W type lattice which correspond to the irreducible representations $\Gamma_{25}(-)$, $\Gamma_{15}(-)$, $\Gamma_{15}(+)$, and $\Gamma_{12}(+)$.
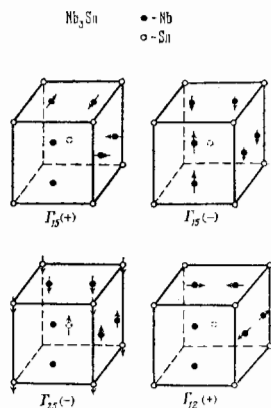
the other binary compounds of β-W structure at low temperatures. Thus, the martensitic transformation has so far been observed only in those compounds which have high T_C. Is this transformation related to high-temperature superconductivity? This question will be discussed below.

X-ray structure measurements first established[50,51] the fact that the ratio c/a increases rapidly below the temperature of the martensitic transformation, reaching saturation at temperatures of the order of T_C. (The impression is gained that the onset of the superconducting state prevents any further growth of the tetragonal deformation.) A sudden change in the value of c/a was not detected in these articles, and in this connection it was assumed that the transformation in question can be regarded as a second-order phase transition. However, more careful measurements by Vieland and coworkers[55] showed that a temperature range exists where the tetragonal deformation undergoes a jump (Fig. 8), which indicates a first-order phase transition.

Since the question of the nature of the transition was not solved in the indicated experiments, subsequent attempts were made to investigate the tetragonal phase. It followed from the analysis by Anderson and Blount[56] that, if a second-order phase transition occurs in the compounds V₃Si and Nb₃Sn, the tetragonal deformation cannot be homogeneous. Four types of atomic displacements, corresponding to the irreducible representations of the cubic group, are possible within the limits of the unit cell, namely, $\Gamma_{25}(-)$, $\Gamma_{15}(-)$, $\Gamma_{15}(+)$, and $\Gamma_{12}(+)$ (Fig. 9). An x-ray structural investigation of V₃Si did not detect these displacements;[57] however, the neutron scattering investigation of single-crystal Nb₃Sn, carried out by Shirane and Axe,[58] showed that displacements of the Nb atoms with respect to each other corresponding to the representation $\Gamma_{12}(+)$ appear below T_m. The spatial structure which arises is D_{4h}^9. It is remarkable that the displacement δ of the Nb atoms with temperature identically coincides with the temperature dependence of the tetragonality parameter determined from x-ray structural measurements. Thus, a linear relation exists between the two parameters:

$$\delta^2 \sim \left(\frac{a}{c} - 1\right)^2. \tag{4.1}$$

The influence of residual stresses on the transition of a number of binary compounds with β-W structure and their alloys into the superconducting state was investigated in[118-120]. Broadening of the superconducting transition and the formation of an additional low-temperature step on the transition curves, which is connected with the large development of the martensitic transformation in the samples under the influence of the stresses, were observed in the stressed samples. The low-temperature step on the transition curve is attributed to a transition of the martensitic phase into the superconducting state. This agrees with the general nature of the processes going on in ordinary martensitic transformations, when plastic deformation in the initial state raises T_m, thus increasing the amount of martensitic phase which is formed at one and the same temperature of measurements. However, direct x-ray structure analyses are required in order to reach a final conclusion about the influence of residual stresses on the martensitic transformation in the indicated compounds and alloys.

An interesting experimental study of the effect of a magnetic field on the martensitic transformation in V₃Si was recently made by Maita and Bucher.[59] They measured the specific heat in zero field and in a field of 90 kOe, which was applied along the [0 0 1]-direction of the crystal. Upon applying the magnetic field, a shift of the martensitic transformation point towards lower temperatures was observed: $\Delta T_m = -0.26°$K. The very concept of the effect of a magnetic field on the position of the martensitic transformation point in β-W compounds might have originated from the known (in the literature) shift of the martensitic transformation temperature range in steels and carbon-free alloys of iron base when a pulsed magnetic field is applied.[60] The observed effect of a magnetic field on T_m apparently once again confirms the martensitic nature of the structural transformation in compounds of β-W type.

It is interesting to note that, near the temperature of the structural transformation, anomalies are observed in such physical properties as the following: the electronic specific heat,[61] the magnet susceptibility,[59] nuclear magnetic resonance,[62] and the Mössbauer effect.[63] For example, large relative changes of the electric field gradient were observed in NMR studies of V₃Si; the observed field-gradient change was two orders of magnitude greater than the changes in lattice constant and differs from the predictions of the point-charge model by almost 60 times.[62] The experimental data on the temperature dependence of the probability for resonance absorption of γ quanta in Nb₃Sn indicate strong anharmonicity of the lattice in this compound.[63]

5. Anomalies of the acoustic properties. Some high-temperature superconducting compounds with β-W structure, and certainly those in which a structural transition is observed, exhibit anomalies in their elastic properties. The temperature dependences of the velocity of sound for polycrystalline samples of a number of compounds with β-W structure, measured in the range between 4.2 and 300°K,[64] are shown in Fig. 10. Examination of this data leads to the conclusion that, for compounds with relatively high T_C (> 14°K) the velocities of sound fall anomalously as the temperature decreases, which indicates a "softening" of the lattice moduli.

The elastic moduli C_{ij} were calculated from measurements of the velocity of sound in single crystals of
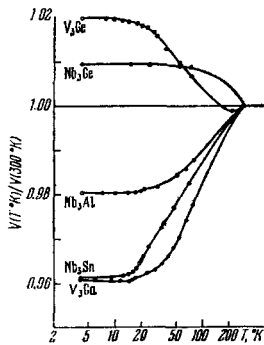
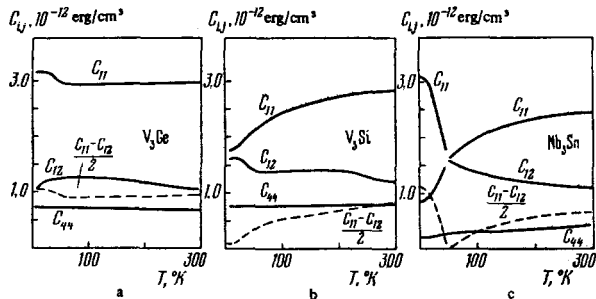FIG. 10. Temperature dependence of the velocity of sound for the compounds A_3B.
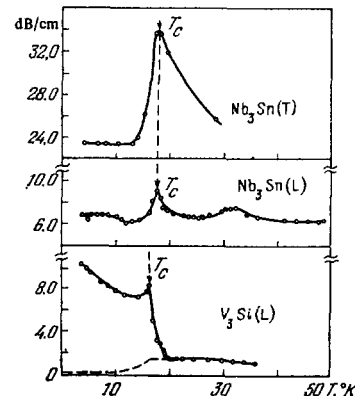

FIG. 12. The attenuation of sound as a function of the temperature in the compounds Nb_3Sn and V_3Si. The dashed line indicates the attenuation for a typical superconductor.


FIG. 11. Temperature dependence of the elastic moduli for V_3Ge (a), V_3Si (b), and Nb_3Sn (c).

the compounds Nb_3Sn and V_3Ge for different directions and polarizations. This data from[65-66] are presented in Fig. 11.[2] The completely anomalous temperature dependence of the elastic moduli C_{11} and $(C_{11} - C_{12})/2$ in V_3Si and Nb_3Sn at low temperatures should be noted, whereas in V_3Ge their temperature dependence is similar to that observed for the majority of metals. For all three compounds, the modulus C_{44} turns out to exhibit the most weakly-expressed dependence. It is necessary to separately note the large temperature variation of the shear modulus $(C_{11} - C_{12})/2$, which almost vanishes in the compound V_3Si and is markedly "softened" in Nb_3Sn. "Softening" of the shear modes has also been detected in measurements of the temperature dependence of the derivative of the shear modulus with respect to the pressure,[121] and in a very unique experiment by Testardi in which the generation of second-harmonic ultrasound by shear waves in V_3Si is observed.[122] The softening of the lattice in V_3Si and Nb_3Sn and the instability of the shear phonon modes apparently leads to a martensitic phase transition in these compounds. Also the change in the value of dC_{ij}/dT at $T = T_C$, due to the transition from the normal state into the superconducting state, was found to be anomalously large in the compounds V_3Si and V_3Ge. (The normal state was maintained in these compounds by applying a magnetic field of the order of 23 kOe, which destroyed the superconductivity at low temperatures.) The discontinuity in the derivative of the shear modulus with respect to temperature in V_3Ge and V_3Si was found to be two and four, respectively, orders of magnitude larger than typical values for the majority of superconductors.

The temperature dependence of the attenuation of sound is also anomalous for the compounds V_3Si and Nb_3Sn[66,69] (Fig. 12). At temperatures of the order of several tens of degrees Kelvin, the attenuation is small and slowly increases with decreasing temperature. There is a spike in the attenuation curve for Nb_3Sn at a temperature of the order of $36°K$, which is apparently
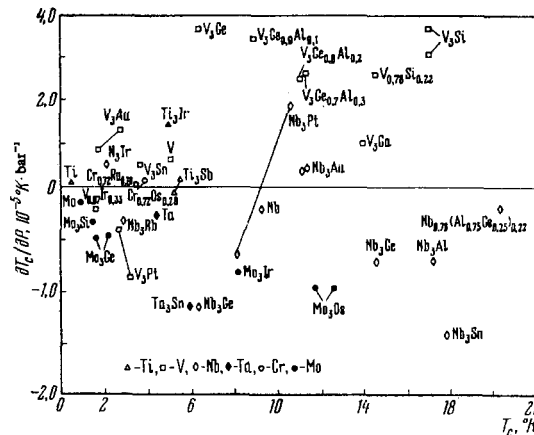
FIG. 13. Values of $\partial T_C/\partial p$ for a number of compounds with β-W structure.

due to the structural transformation from a cubic into a tetragonal phase. A second spike in the attenuation curve for this compound occurs at the superconducting transition temperature ($\sim 18°K$). For V_3Si the martensitic transformation temperature T_m and the superconducting transition temperature T_C are separated by only $4°K$, so that here the two bumps in the attenuation curve may overlap.

Thus, it follows from an analysis of the propagation and attenuation of sound that quite unusual behavior of the crystal's elastic properties is observed in compounds with β-W structure. In this connection it is very interesting that many anomalies of the elastic properties are observed just in the high-temperature superconductors. This may mean one of two things, either the high values of T_C in these compounds are related to an instability of the lattice (in the cubic phase) or else both are consequences of one and the same cause, for example, anomalies of the electronic spectrum. We shall discuss this alternative in Chapter III of the review.

6. The effect of pressure on the superconducting transition temperature. Under conditions closely approximating hydrostatic pressure conditions, Smith recently measured the superconducting transition temperatures of approximately thirty compounds with β-W structure.[70,71] His data are shown in Fig. 13. Examination of these results indicates the interesting features of the behavior of $\partial T_C/\partial p$ in these compounds. The investigated compounds of chromium and most of the vanadium compounds indicate a positive sign for $\partial T_C/\partial p$ (V_3Pt and V_3Ir are exceptions). At the same time a decrease of T_C with increasing pressure is

registered for all molybdenum compounds and for most of the niobium compounds. Our attention is drawn to the substantial difference in the behavior of $\partial T_C / \partial p$ for compounds of vanadium and niobium with identical second components and, consequently, identical electron concentrations (V_3Ga and Nb_3Ga, V_3Ge and Nb_3Ge, V_3Sn and Nb_3Sn, V_3Ir and Nb_3Ir, $V_3(Al - Ge)$ and $Nb_3(Al - Ge)$). One more interesting feature can be noted. A_3B compounds with β-W structure, in which the transition 3d-metals (Ti, V, Cr) appear as the A atoms, exhibit, as a rule, positive values of $\partial T_C / \partial p$, whereas a reduction of T_C with increasing pressure is observed for the analogous compounds of 4d- and 5d-metals (Nb, Mo, and Ta). Deviation from stoichiometry in the compound V_3Si and the presence of disorder in the compound V_3Au lead to a drop in the value of T_C with increasing pressure.

Thus, the depicted experimental data on the effect of pressure on T_C conclusively demonstrate that there is no universality in the behavior of $\partial T_C / \partial p$ for the different compounds. It is difficult to distinguish a parameter with respect to which it might be possible to establish some kind of regularity in the fluctuations of $\partial T_C / \partial p$.

It should be noted that the application of hydrostatic pressure also leads to changes in other crystalline properties and, in particular, to a reduction of the volume and also of the lattice parameter. Let us see whether such an effect can be achieved by other methods, for example, by doping. In this connection, how will the superconducting properties be modified? The experimental data indicate that, by doping the compounds V_3Si, V_3Ge, and V_3Ga one can, in contrast to compression, obtain either an increase or a decrease of the lattice parameter. However, in order to compare with the experimental data on pressure we shall only be interested in that part of the doping data which pertains to a decrease of the lattice parameter. Let us examine these results. The experimental points shown in Fig. 14 correspond to the dependence of T_C on lattice parameter in ternary alloys based on V_3Si, V_3Ga, and V_3Ge.[72] It is evident that in V_3Si and V_3Ga the superconducting transition temperature decreases as the lattice parameter becomes smaller, but the transition temperature increases in V_3Ge. From these data one might anticipate that $\partial T_C / \partial \rho$ would be positive for V_3Ge and negative for V_3Si and V_3Ga. But in all three cases, as we have seen in Fig. 13, the change of T_C under high pressure indicates that $\partial T_C / \partial p$ has a positive sign. Thus, the comparison which has been made implies that it is impossible to reduce the effect of doping to just changes of the volume.

The dependence of T_C on hydrostatic pressure is a special case of the question of the strain dependence of $T_C = T_C(\epsilon)$. In a number of articles[64,72,73] Testardi has attempted to systematize the extensive experimental data on the basis of a phenomenological expansion of T_C in powers of the strain tensor, where the ϵ_j with $j = 1, 2, \ldots, 6$ label the independent components of the strain tensor, namely, ϵ_{xx}, ϵ_{yy}, ϵ_{zz}, ϵ_{xy}, ϵ_{yz}, and ϵ_{zx}. It is postulated that $T_C(\epsilon)$ can be represented in the form of the series

$$T_c(\varepsilon) = T_c(0) + \sum_{j=1}^{6} \Gamma_j \varepsilon_j + \sum_{i,j=1}^{6} \Delta_{ij} \varepsilon_i \varepsilon_j + \ldots \quad (6.1)$$

The coefficients Γ_j and Δ_{ij} in this expansion can be determined independently from a series of experiments.
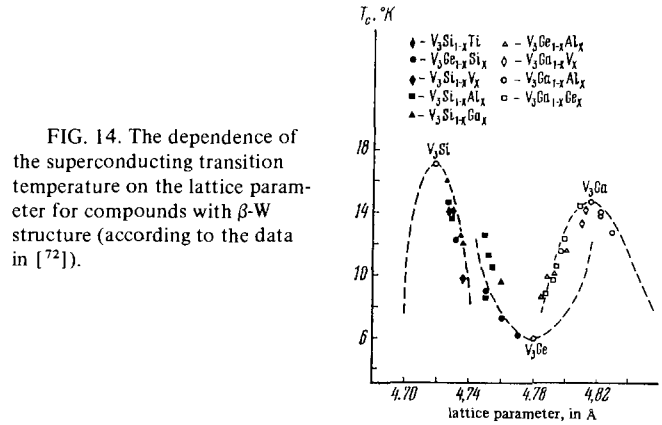

FIG. 14. The dependence of the superconducting transition temperature on the lattice parameter for compounds with β-W structure (according to the data in [72]).

For this purpose it is necessary to utilize the following expression for the difference between the free energies of the system in the normal and superconducting states near T_C:

$$F^N - F^S = \frac{H_c^2(T, \varepsilon)}{8\pi} = \frac{\alpha^2(\varepsilon)}{8\pi} [T_c(\varepsilon) - T]^2. \quad (6.2)$$

By differentiating this expression with respect to the strains and with respect to the temperature, we obtain three equations relating the experimentally observable quantities at the point T_C to the coefficients Γ_j and Δ_{ij}:

$$\left. \begin{aligned} C_{ij}^S - C_{ij}^N &= -\frac{\alpha^2}{4\pi} \Gamma_i \Gamma_j, \\ \frac{dC_{ij}^S}{dT} - \frac{dC_{ij}^N}{dT} &= -\frac{\alpha^2}{4\pi} \Delta_{ij}, \\ C_V^N - C_V^S &= -\frac{\alpha^2 T_c}{4\pi} ; \end{aligned} \right\} \quad (6.3)$$

here C_{ij}^N and C_{ij}^S are the elastic constants in the normal and superconducting phases, which are related to the free energy by the relation

$$C_{ij} = \frac{\partial^2 F}{\partial \varepsilon_i \partial \varepsilon_j}, \quad (6.4)$$

and C_V^N and C_V^S are the corresponding specific heats.

Having made complete measurements of the elastic properties of single crystals of V_3Ge and V_3Si,[65,72] Testardi determined the expansion coefficients Γ_j and Δ_{ij}, which for V_3Si turned out to be given by: $|\Gamma_1| < 50°K$, $\Delta_{11} = -24 \times 10^{4°}K$, $\Delta_{12} = -5 \times 10^{4°}K$, $\Delta_{44} = -1 \times 10^{4°}K$; and for V_3Ge he found: $|\Gamma_1| < 45°K$, $\Delta_{11} = 9.4 \times 10^{4°}K$, $\Delta_{12} = -1.8 \times 10^{4°}K$, and $\Delta_{44} = 0.4 \times 10^{4°}K$. Such small values of the coefficients Γ_j relative to the values of the coefficients Δ_{ij}, obtained for both compounds, indicate that the strain dependence of T_C is mainly quadratic; this is shown in Fig. 14 by the parabolas with branches directed downward for V_3Si (since $\Delta_{11} < 0$) and with branches directed upward for V_3Ge ($\Delta_{11} > 0$). This means that all strains should increase the superconducting transition temperature in V_3Ge and, conversely, decrease T_C in V_3Si. Are these predictions in agreement with the experimental data?

For V_3Si the different methods of producing deformations give a drop in the value of T_C. Thus, for example, the application of uniaxial stress[74] and also the doping with different components, indicated in Fig. 14, lead to a decrease in the values of T_C. Furthermore, the spontaneous deformation which arises in connection with the structural transition in V_3Si also gives a reduction of T_C by 0.1 to 0.4°K[72] for samples under-

going a structural transformation in comparison with samples in which a martensitic transition was not observed. This number is very close to the value $0.38°K$ which Testardi's estimate gives.[65] As for V_3Ge there are no direct experiments involving uniaxial pressure, but a decrease of the lattice parameter caused by doping leads to an increase of T_C (Fig. 14). It should be noted that the experimental points obtained from the dependence of T_C on the lattice parameter (the data with respect to doping) fit very well on the curves predicted by Testardi from his analysis of the elastic properties of V_3Si and V_3Ge.

In spite of the successful interpretation of a set of experimental data, it must be noted that Testardi's treatment is not rigorous and not unique. The very possibility of expanding T_C in powers of the strain is problematic because it may not be an analytic function of ϵ.

In addition, V_3Si and V_3Ge compounds with extreme values of the superconducting transition temperature were chosen as the objects on which the experimental verification of the strain dependence of T_C is based. As we have seen from the material presented in Chap. I, arbitrary doping of high-temperature superconductors (including V_3Si and V_3Ga) leads to a decrease of T_C and the reverse situation is very often observed (V_3Ge). Furthermore, some of the experimental data is not included in Fig. 14, for example, the data concerning $(V - Pd)_3Si$ and $(V - Mo)_3Si$ alloys,[2] which clearly does not fit a parabolic dependence of T_C on the lattice parameter. Therefore, it is possible that the above described correlation between the dependence of T_C on the lattice parameter predicted by Testardi and the selected experimental data on the variation of T_C in A_3B alloys is accidental.

In order to reach final conclusions about the adequacy of such a treatment, an investigation of the intermediate case is of interest—namely, superconductors with transition temperatures of the order of 9 or $10°K$, in which doping might lead to either a decrease or an increase of T_C.

III. THEORETICAL MODELS

7. Calculations of the electronic spectrum. The cited experimental data indicate that high values of the magnetic susceptibility and of the electronic specific heat are observed for high-temperature superconducting compounds such as V_3Si, V_3Ga, Nb_3Sn, etc.; this fact indicates a high density of states near the Fermi surface. In these compounds there is apparently a peak in the density of states and the Fermi level falls on it.

It is characteristic that, it is only for these high-temperature compounds that appreciable temperature dependences of the magnetic susceptibility and of the Knight shift are observed; this indicates that the peak in the density of states, existing near the Fermi level, is extremely narrow with a width comparable to the energy kT of thermal motion. What kind of atomic electron states can produce such a peak? Certain arguments can be given in this respect if all the anomalies of the considered compounds are analyzed with respect to the Knight shift (in order to be definite, we shall have in mind the compound V_3Ga in mind). They are the following:
1) The Knight shift K_V of the vanadium atoms is positive and decreases with decreasing temperature;
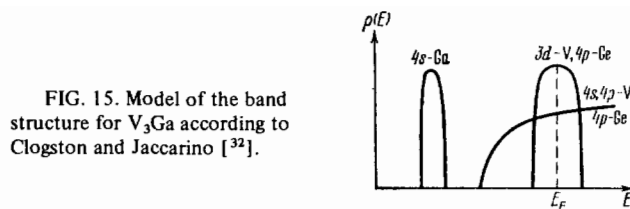

FIG. 15. Model of the band structure for V_3Ga according to Clogston and Jaccarino [32].

2) The Knight shift K_{Ga} for gallium atoms is negative and increases with decreasing temperature. We also recall that the susceptibility increases with decreasing temperature.

In order to explain these facts, Clogston and Jaccarino[32] proposed the following model for the electronic spectrum of V_3Ga. There is a wide electron conduction band formed principally from vanadium 4s and 4p and gallium 4p-type atomic states. This band overlaps a narrow band formed from the vanadium 3d-type states, and the Fermi level occurs somewhere inside this band (Fig. 15). It is also assumed that the 4s states belonging to the Ga atoms form a very narrow band lying far below the Fermi surface. This assumption reflects the fact that the Ga atoms are distributed in the lattice at considerable distances from one another so that their levels will be broadened only slightly. Finally it is assumed that the 4p states of Ga lie sufficiently close to the Fermi surface so that they are strongly intermixed with the vanadium bands. To explain the strong temperature dependence of the susceptibility, for V_3Ga it is necessary to assume that the width of the peak in the density of states at the Fermi surface amounts to about 0.04 eV. We shall see below how numerical calculations of the spectrum for vanadium compounds confirm the correctness of the proposed structure. We also note that the proposed model for the band structure of vanadium compounds is in complete agreement with the results of x-ray spectroscopy for these compounds, which were given in Sec. 3.

To verify the correctness of the Clogston-Jaccarino model, in 1965 Mattheiss[75] made detailed calculations of the electronic spectrum of a number of compounds having the β-W structure. The calculations for the compounds V_3X (X = Al, Si, Co, Ga, Ge, As) were made using the augmented-plane-wave (APW) method; the spectrum was calculated at all symmetry points in the Brillouin zone and, in addition, along symmetry lines for V_3Ga so as to be able to construct the density of states as a function of the energy for this compound.

The results of the calculations turned out to be in qualitative agreement with the Clogstron-Jaccarino model. The following structure of the spectrum was recognized in detail. Lowest of all are the bands which are mainly associated with the 4s states of the Ga atoms and which lie well below the Fermi surface. They are separated by an energy gap from the overlapping conduction bands. The 3d bands, formed by the atomic states of vanadium and having a width of approximately 7 eV, lie in the midst of bands which represent the vanadium 4s, 4p, and gallium 4p-type states. These 3d bands are divided roughly into two sub-bands separated by a minimum in the density of states $\rho(E)$ between them (Fig. 16). The calculation of the density of states showed that the Fermi level for V_3Ga falls at the peak in $\rho(E)$. Analysis of the APW wave functions for V_3Ga in the vicinity of the Fermi energy suggests that they
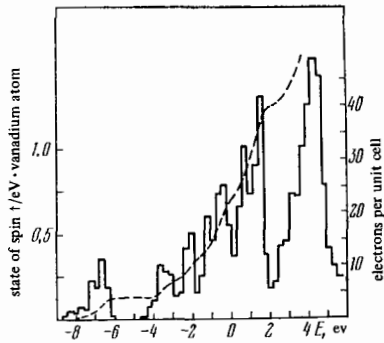
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FIG. 16. Density of states for V_3Ga according to Mattheiss [75]. The dashed line is the integrated number of electrons per unit cell, the scale to the right indicating the number of electrons that can be accommodated at a given energy.

are predominantly 3d states of vanadium with a small admixture (of the order of 5%) of gallium 4p states.

Thus, the calculation led to a high value for the density of states at the Fermi surface; for V_3Ga it gives 1.3 spin states per eV for one atom and one spin direction. The experimental values for the density of states are 7.1 and 5.6, obtained respectively from measurements of the electronic specific heat and the magnetic susceptibility. The calculated values turn out to be several times smaller. Clogston[76] pointed out that a possible cause of this discrepancy is a renormalization, due to the electron-phonon interaction of the density of states, which determines the electronic specific heat.

Although Mattheiss's calculations confirmed the Clogston-Jaccarino model for V_3X compounds, a new attempt was recently made to theoretically investigate the electronic band structure in these compounds. Goldberg and Weger[77] performed a calculation using the tight binding method, allowing for interchain coupling between the chains of vanadium atoms. The tight binding calculation also led to the existence of a peak in the density of states near the Fermi level. Typically the parameters of the interchain coupling turn out to be of the same order of magnitude as the interaction of the V atoms inside the chains. From the point of view of these results, one gains the impression that the appearance of the indicated peak is not due to the weak interaction of the chains in V_3X compounds, but rather to a cancellation of the interaction with the eight next nearest neighbors due to symmetry.[77]

8. The Labbé-Friedel model of noninteracting chains. Although numerical calculations of the electronic spectrum demonstrate the existence of a narrow peak in the density of states near the Fermi surface, they are not convenient to use since they do not give an analytic expression for the density of states. It would be desirable to obtain an approximate analytic expression for the spectrum of the compounds under investigation even at the cost of using a very crude model; this is what Labbé and Friedel[78] were able to accomplish by considering the characteristics of the crystalline structure of A_3B compounds. As indicated above, in these compounds the A-type atoms (transition element) are located on straight lines directed along the axes of the type [1 0 0], and moreover the distance between neighboring atoms on such a straight line is considerably smaller than the distance between atoms belonging to different lines. In other words, the A-type atoms form three mutually perpendicular systems of linear chains in the crystal.[79] It is assumed, in the first place, that the s-electrons of the transition atoms and of the B-type atoms undergo collective motion in the crystal, forming a wide band (valence p-electrons of the B-type atoms

may also appear in this band), and in the second place it is assumed that the d electrons form a narrow band and can be described in the tight binding approximation. Thus, from an electronic point of view, a crystal of the V_3Ga type can be represented as an assembly of one-dimensional chains, immersed in s electrons which stabilize the system.[78]

For a linear chain one can write down the energy of the d electrons in the tight binding approximation in the following form:

$$E_k = E_0 - E_m \cos(ka), \qquad (8.1)$$

where E_0 is the atomic level of a d electron, E_m is the doubled matrix element for a transition between nearest neighbor atoms in the chain, the atoms being spaced a distance a apart, and k is the quasimomentum.

Thus, in the model under consideration the motion of the d electrons in the crystal turns out, in the first place, to be one-dimensional and, in the second place, multiply degenerate (according to the number of chains). It is obvious that the Fermi surface for such a system consists of three mutually perpendicular plane sheets.

One can easily verify that the density of states $\rho(E)$ of the one-dimensional motion has a square root singularity at the band edges. In fact, let us substitute expression (8.1) into the formula for the density of states per single atom of a chain,

$$\rho(E) = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} \delta(E - E_k)\, dk \qquad (8.2)$$

and then by integrating we obtain the dependence on E:[78]

$$\rho(E) = \frac{1}{\pi} [E_m^2 - (E - E_0)^2]^{-1/2}. \qquad (8.3)$$

Near the bottom of the band, expression (8.3) gives exactly a square root singularity of the form

$$\rho(E) = \begin{cases} \dfrac{B}{\sqrt{E - E_m}}, & E > E_m, \\ 0, & E < E_m, \end{cases} \qquad (8.4)$$

where the energy reference point is chosen such that $E_0 = 0$.

Now it is necessary to take the angular nature of the atomic d-states into consideration. In a linear chain the five-fold degenerate atomic term can be decomposed into three degenerate terms, combining the states according to the principle

$$d_{3z^2-r^2}, \quad (d_{xz}, d_{yz}), \quad (d_{xy}, d_{x^2-y^2}) \qquad (8.5)$$

(the z axis is directed along the chain). In a chain, each of these orbital levels is smeared into a one-dimensional band with the dispersion law (8.1), where the parameter E_m will still depend on the type of orbital (8.5). Let us assume that the structure of the electronic spectrum for compounds of β-W structure with high T_c, such as V_3Si, Nb_3Sn, and so forth, has the form of three bands which are "nested" inside one another, corresponding to the one-dimensional motion of the d electrons, and a wide band associated with the collective motion of the s electrons throughout the entire crystal (Fig. 17).

For vanadium compounds, where the number of d electrons is equal to 3 or 4 per vanadium atom, the d band is less than half full and the Fermi level may turn out to be near the bottom of the upper d band, thereby ensuring a high density of states near it. Precisely such
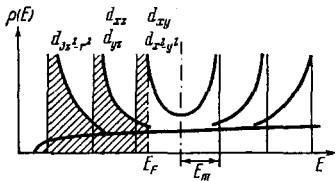
FIG. 17. The band structure for compounds of the type V_3Si, V_3Ga, Nb_3Sn, etc., according to the Labbé-Friedel model.

a situation is assumed for V_3Si, Nb_3Sn, and for a number of other compounds with high superconducting transition temperatures. The contribution to the density of states from the other d sub-bands and also from the s band near the Fermi level can be neglected, and thus the electronic spectrum of these compounds can be approximated by the one-dimensional dispersion law (8.1) and by a density of states in the form (8.4).

In such a model it is possible to explain[80,81] the strong temperature dependence of the magnetic susceptibility and of the Knight shift in the compounds under investigation. The magnetic susceptibility consists of two main contributions: The Pauli susceptibility $\chi_d(T)$, which is connected with paramagnetism, and the orbital susceptibility χ_0:

$$\chi = \chi_0 + \chi_{d(T)}.$$

In view of the large contribution of d electrons to the density of states at the Fermi surface, one can neglect the contribution to χ from the s electrons; then $\chi_d(T)$ can be written in the form

$$\chi_{d(T)} = -2\mu_B^2 \int f'(E)\,\rho(E)\,dE, \qquad (8.6)$$

where $f'(E)$ is the derivative with respect to E of the Fermi distribution function, μ_B is the Bohr magneton, and $\rho(E)$ is the density of states of the nearly empty d band, which is approximated by expression (8.4). The chemical potential of the system at any given temperature is determined by the equation

$$Q = 2\int f(E)\,\rho(E)\,dE, \qquad (8.7)$$

where Q is the number of electrons in this band. We choose the values of the basic parameters for V_3Si— namely, the width of the band $2|E_m|$, the Fermi energy E_F, and Q (the number of electrons per vanadium atom)—as follows:

$$2|E_m| = 9\,\text{eV}, \quad E_F = 1.8 \cdot 10^{-3}\,\text{eV}, \quad Q = 0.036. \qquad (8.8)$$

Formula (8.6) leads to a temperature dependence $\chi_d(T)$ which agrees with the experimentally observed behavior of χ in the temperature interval from 50 to $400°K$. However, at room temperature the numerical value of $\chi_d(T)$ differs from the experimental value by a factor of seven. The experimental value amounts to 8×10^{-4} emu/mole, whereas $\chi_d(T) \approx 1.1 \times 10^{-4}$ emu/mole. Thus, the orbital contribution should amount to approximately 6×10^{-4} emu/mole. The orbital contribution χ_0 is of the order of μ_B^2/Δ, where Δ is the mean separation of the energy levels connected by the orbital angular momentum. Since Δ is of the order of 1 eV, the orbital contribution must be almost temperature-independent and amounts to $\sim 10^{-4}$ emu/mole.

Labbé's calculations[80] gave a value $\chi_0 \approx 2.3 \times 10^{-4}$ emu/mole, which is substantially smaller than the experimentally observed value. These calculations should be regarded only as order-of-magnitude estimates. We note that satisfactory agreement between the calculated values for the Knight shift[81] and the experi-

mental values is obtained upon using the chosen values (8.8) of the parameters for V_3Si.

In order to clarify the qualitative features of superconducting compounds of type V_3Si in the Labbé-Friedel model, let us first attempt to use the ordinary BCS theory of superconductivity,[82] taking into account only the substantial energy dependence of the density of states near the Fermi level.[83] The equation for the determination of the transition temperature T_c

$$1 = g \int_{-\hbar\omega_D}^{\hbar\omega_D} \rho(E + E_F)\,\frac{\text{th}\,(E/2T_c)}{2E}\,dE \qquad (8.9)$$

(g is the BCS coupling constant) must be solved together with the equation for the chemical potential E_F of the system

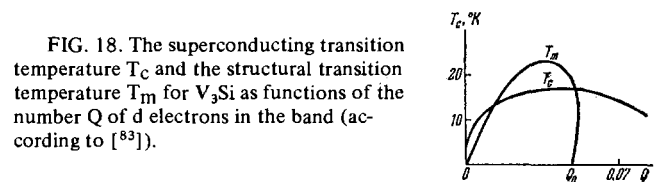$$Q = 2\int_{-\infty}^{\infty} \rho(E + E_F)\,\frac{1}{\exp(E/T_c) + 1}\,dE, \qquad (8.10)$$

where $\rho(E)$ is the electron density of states for one spin direction. In view of the large density of states in the nearly empty sub-band, we neglect the contribution to (8.9) and (8.10) from other sub-bands and also from the s band. Thus, in the model under consideration[83] it is assumed that only the d electrons of the nearly empty d sub-band play a significant role in the superconductivity of the present compounds; therefore, it is necessary to substitute expression (8.4) into the equation under investigation instead of the total electron density $\rho(E)$. Taking the narrowness of the electron spectrum into consideration, i.e., assuming the inequality

$$E_F - E_m \ll t\omega_D, \qquad (8.11)$$

one can extend the upper limit in the integral (8.9) to ∞. The results of a numerical solution of Eqs. (8.9) and (8.10) are shown in Fig. 18, where T_c is plotted as a function of the number Q of d electrons in the nearly empty sub-band.

The curve for T_c typically has a maximum at the value $Q_M = 7.5\,B^2$. The variations of T_c are slight throughout a wide neighborhood of the maximum. Thus, in the strong-coupling limit (8.11) under consideration, the dependence of T_c on the electron concentration Q is weak. In the opposite weak-coupling limit, when $Q \gg Q_M$ and $(E_F - E_M) \gg \hbar\omega_D$, Eqs. (8.9) and (8.10) lead to an exponential dependence of T_c on Q according to the well known BCS formula, $T_c \sim \exp[-1/g\rho(E_F)]$. It is quite remarkable that the dependence of T_c on the Debye frequency ω_D drops out in the strong-coupling limit (8.11), i.e., the isotope effect disappears, which is characteristic for the high-T_c compounds under investigation.

If we take for V_3Si the parameters (8.8), which were used for the calculations of the susceptibility and of the Knight shift, and if we add to them the value g = 0.15 eV (instead of the value 0.4 eV usually assumed for transition metals), we then obtain a transition temperature $T_c = 17°K$. Thus, the assumed quasi-one-dimensional

FIG. 18. The superconducting transition temperature T_c and the structural transition temperature T_m for V_3Si as functions of the number Q of d electrons in the band (according to [83]).

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model of the spectrum leads to high values of T_c for a reasonable choice of the physical parameters.

It is necessary to make a comment about the applicability of the BCS theory to models of noninteracting chains. It has been rigorously shown that superconductivity is impossible[84] in a one-dimensional system due to the destructive action of the electron density fluctuations[85] and the fluctuations in the phase of the ordering parameter. The density fluctuations can be suppressed due to the long-range nature of the Coulomb interaction by considering, for example, a model for a metal which consists of a parallel system of linear chains spaced at distances from each other which are much greater than the interatomic distance inside a chain.[86] In such a system the long wavelength fluctuations in the density remain essentially the same as in an ordinary three-dimensional metal.

In order to limit the influence of the phase fluctuations, we need to take real transitions from chain to chain into account; in the model of a quasi-one-dimensional metal[86] they are described by a dispersion law of the form

$$E_k = \frac{k_z^2}{2m} + \alpha \left(\cos a k_x + \cos a k_y \right) \qquad (8.12)$$

(the z axis is directed along the chain), where $\alpha \ll k_F^2/2m$ and k_F is the Fermi momentum. It was found[86] that, for very small values of $\alpha \ll T_c$ the formula for the superconducting transition temperature essentially agrees with the formula which was obtained for the case of a purely one-dimensional metal[87] (within the framework of the "logarithmic" approximation, without taking the fluctuations into consideration). For larger values of $\alpha \gtrsim T_c$, superconductivity is described by the usual formulas of the BCS theory. Since, as we have seen above, the matrix element for a transition from one chain to another is not very small even for the compounds V_3Si and Nb_3Sn, it should be possible to use the BCS equations to estimate the value of T_c, by substituting into them an expression for $\rho(E)$ with a singularity corresponding to the quasi-one-dimensional spectrum. The justification of the qualitative correctness of the results of such an approach was undertaken by Kats.[88]

The chain model enables us to give a theoretical explanation of the lattice phase transition.[78,89] As the experiment described in Sec. 5 shows, this transition is connected with a "softening" of the elastic shear modulus $C_{11} - C_{12}$, the vanishing of which must determine the lattice instability temperature, which is identified with the temperature T_m of the structural transformation. On the basis of the quasi-one-dimensional model one can show (detailed calculations of the elastic constants in a similar model are presented in Sec. 10) that the interaction of the d electrons with the strained lattice leads to a strongly temperature-dependent term in the free energy, which ensures the "softening" of the modulus $(C_{11} - C_{12})$ as the temperature decreases. The results of calculations of T_m for V_3Si as a function of the number Q of d electrons are shown in Fig. 18 (side by side with the results for T_c). A similar curve is obtained for Nb_3Sn.[90] It is seen from the figure that the lattice instability occurs only for sufficiently small values of Q, not exceeding the value Q_0, which for typical values of the parameters amounts to between 0.01 and 0.1 electron per atom. But small values of Q can also lead to large values of T_c. The

FIG. 19. Splitting of the upper d sub-band in the chain model in the tetragonal phase for c/a > 1 (a) and for c/a < 1 (b).
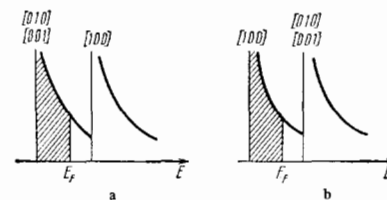
converse statement does not hold, that is, large values of T_c are not necessarily related to a softening of the lattice and to the possibility of a phase transition. Apparently this is the reason why martensitic transitions are not observed in all A_3B-type compounds, but only in some of them. Incidentally, the strong temperature dependence of the martensitic transition temperature on stoichiometry already becomes clear from the results of the calculation presented in Fig. 18. If the value of Q for the pure compound turns out to be close to Q_0, a deviation from stoichiometric composition may cause the value of Q to shift to the other side of Q_0 and thus lead to the appearance or disappearance of the phase transition, while T_c changes very little in this connection. The temperature T_m, determined from the conditions for instability of the cubic phase, is the point of the phase transition into the tetragonal structure. A spontaneous deformation of the tetragonal type appears below T_m. This deformation has different signs for the compounds V_3Si (c/a > 1) and Nb_3Sn (c/a < 1). It is easy to understand how the electronic spectrum is modified in this connection. For V_3Si the band spectrum of the d electrons in the cubic phase is described (according to Labbé-Friedel) by Fig. 17. The upper, almost empty sub-band turns out to be doubly degenerate with respect to the magnetic quantum number and, which is now most important, triply degenerate with respect to the directions of the chains. Let us associate the [1 0 0] direction with the tetragonal axis; then the two perpendicular directions [0 1 0] and [0 0 1] will be equivalent. For V_3Si the cell turns out to be elongated; therefore, in the [1 0 0] direction the band narrows, but it broadens in the perpendicular directions. Thus, a splitting of the spectrum appears so that the Fermi level may fall in the region between the bottom edges of the sub-bands (see Fig. 19). It is conjectured that just such a situation occurs in the compounds V_3Si and Nb_3Sn at T = 0°K. It is clear that as soon as the tetragonal deformation appears below T_m and the sub-bands begin to separate, there is a very rapid redistribution of the electrons between them, which leads to an abrupt increase of the spontaneous deformation with decreasing temperature. As soon as the Fermi level emerges beyond the edge of the upper, split sub-band, the rearrangement of the electron redistribution is completed, and the growth of the deformations must cease. The temperature dependence of the spontaneous deformation observed experimentally (Fig. 8) is of precisely such a nature.

By comparing the conclusions of the Labbé-Friedel model with the experimental data pertaining to compounds of the type V_3Si and Nb_3Sn, we arrive at the conclusion that it qualitatively describes the complete set of their anomalous properties: The temperature behavior of the elasticity moduli and of the magnetic susceptibility, the lattice transition, high-temperature superconductivity, and their connection with each other. The model is, of course, too crude for a quantitative description.

Now let us pose the following question: To what extent do the explicit assumptions about the one-dimensional nature of the motion of the d electrons pertain to the compounds with β-W structure under consideration? In order to quantitatively explain the observed properties of the compounds V_3Si, Nb_3Sn, and so forth, it would be necessary to assume a very low Fermi energy of the order of 0.005 eV relative to the bottom of the upper, nearly empty band. A reasonable value for the width of the whole band is 2.5 eV; therefore, the parameter l_1 characterizing the intrachain interaction of the atoms must have the same order of magnitude. In order that the interchain interaction l_2 should not strongly change the value of the Fermi energy, it is necessary that $l_2^2/l_1 \lesssim (E_F - E_m)$, that is, l_2 must be two orders of magnitude smaller than l_1. However, such a ratio of the interaction parameters for nearest neighbors and next-nearest neighbors is very improbable in the structure under consideration (at a difference of 20% between the corresponding interchain distances). Estimates of the ratio of the nearest neighbor interaction integral to the next nearest-neighbor interaction integral, made by using the structure of the d-state wave functions and of the potentials, indicate that l_2 is either roughly the same order of magnitude as l_1 or else is only one order of magnitude smaller.[91]

In order to understand the effect of interchain coupling on the electronic band structure, Weger[92] numerically investigated a model consisting of two families of mutually orthogonal chains. Of course, this model is a very simplified idealization of the spectrum in the β-W structure; however, by investigating it the author reached the conclusion that the quasi-one-dimensionality is apparently a topological property of a lattice with interpenetrating chains, but anisotropy of the interatomic interaction parameters by itself is still not sufficient to cause appreciable one-dimensionality. It would be of great interest to investigate this question in general form and establish the analytic nature of the density of states in the energy regions corresponding to states of quasi-one-dimensional character.

9. The model of interacting chains and the effect of impurities on T_C. The essential feature of the Labbé-Friedel model of noninteracting chains is the one-dimensionality of the electronic spectrum, leading to a singularity in the density of states near the Fermi surface. However, as has been indicated above, the matrix elements for electron transitions from chain to chain turn out to be fairly large, and the inclusion of these transitions restores the "three-dimensionality" of the d-electron spectrum and "smoothes over" the singularity of the one-dimensional spectrum. This fact must lead to results which are very sensitive to the value of the parameter characterizing the interchain transitions.

First let us approach this problem phenomenologically. We add to expression (8.1), which gives the spectrum of the chain in the tight binding approximation, a term that allows for interchain transitions and corresponding to the spatial symmetry of the β-W structure:[93]

$$E_k = E_0 - E_m \cos \frac{k_x a}{2} - 2\xi_0 \left(\cos^2 \frac{k_y a}{2} + \cos^2 \frac{k_z a}{2} \right) \quad (9.1)$$

(we also have two other branches, obtained by cyclic permutation of the momentum components k_x, k_y, and k_z). Here ξ_0 is the parameter characterizing the interchain coupling, a is the lattice parameter (it exceeds

twice the distance between atoms in a chain; therefore, there is a formal difference between expression (8.1) and the first term in Eq. (9.1)). To be definite, we assume that E_m and ξ_0 are positive.

The density of states per unit cell and for one spin direction is given by

$$\rho(E) = 3 \frac{a^3}{(2\pi)^3} \int\int_{-\pi/a}^{\pi/a}\int \delta(E - E_k) \, dk_x \, dk_y \, dk_z. \quad (9.2)$$

The factor three appears because there are three branches of the type (9.1). We shall only be interested in energies E near the bottom of the band, i.e., $E \ll E_m$. Assuming that $\xi_0 \ll E_m$, we may expand $\cos(k_x a/2)$ in (9.1) in a series in powers of k_x and immediately carry out the integration over this variable in Eq. (9.2). Then it is convenient to write $\rho(E)$ in the form

$$\rho(E) = \frac{3}{\pi^3 \sqrt{E_m \xi_0}} I(\mathscr{E}), \quad (9.3)$$

$$I(\mathscr{E}) = \int_0^\pi \int_0^\pi \frac{\theta[\mathscr{E} + \cos^2(y/2) + \cos^2(z/2)]}{\sqrt{\mathscr{E} + \cos^2(y/2) + \cos^2(z/2)}} \, dy \, dz, \quad (9.4)$$

where

$$\mathscr{E} = \frac{E - E_0 + E_m}{2\xi_0}. \quad (9.5)$$

In the integrand in Eq. (9.4), $\theta(z)$ is equal to unity for $z > 0$ and vanishes for $z < 0$. As follows from Eq. (9.4), $I(\mathscr{E})$ does not vanish for $\mathscr{E} > -2$; the point $\mathscr{E} = -2$ defines the lower edge of the spectrum. The asymptotic behavior of the quantity $I(\mathscr{E})$ can be easily determined:

$$I(\mathscr{E}) = \begin{cases} 2\pi\sqrt{2+\mathscr{E}}, & (2+\mathscr{E}) \ll 1, \\ \frac{\pi^2}{\sqrt{\mathscr{E}}}, & \mathscr{E} \gg 1. \end{cases} \quad (9.6)$$

In the last case the density of states turns out to be independent of ξ_0:

$$\rho_0 = \frac{B}{\sqrt{E - (E_0 - E_m)}}, \quad B = \frac{3}{\pi \sqrt{E_m/2}}, \quad (9.7)$$

and corresponds to a system of quasi-one-dimensional chains with a singularity at the edge of the spectrum. Thus, for interacting chains $\rho(E)$ has the square root dependence at the edge of the band which is typical for three-dimensional motion, and exhibits quasi-one-dimensional behavior well inside the band. The energy parameter, separating these two regimes of the behavior of $\rho(E)$, is ξ_0.

A numerical calculation of the quantity (9.4) is necessary for intermediate values of $I(\mathscr{E})$; the results are shown in Fig. 20. As we might have anticipated, upon taking the interaction between chains into account the singularity of the quasi-one-dimensional motion gets "covered over" and in its place appears a maximum, shifted downwards from the edge of the band spectrum for noninteracting chains.

Now let us investigate how the superconducting transition temperature T_C changes as a function of ξ_0. Numerical solution of the basic equations (8.9) and (8.10), determining T_C in the BCS theory with the calculated density of states (9.3), gives the dependence of T_C on ξ_0 shown in Fig. 21, where T_C^0 denotes the transition temperature in the same crystal but with $\xi_0 = 0$ (noninteracting chains). The calculations were performed for three values of the parameter $\eta_0 = (E_F - E_m)/2T_C^0$, characterizing the model of noninteracting chains.

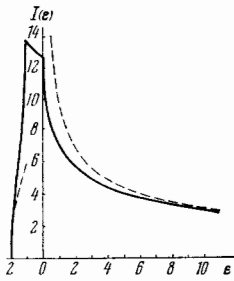Thus, we reach the conclusion that this model[83] gives an overestimate of the superconducting transition

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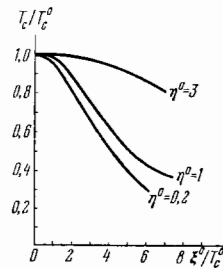FIG. 20. The function I(E) which determined the density of states in the interacting chain model.

FIG. 21. T_c as a function of the interchain coupling parameter ξ_0.

temperature. In addition, taking account of the interchain coupling eliminates the difficulty in the theory[83] associated with the fact that superconductivity is impossible in a one-dimensional system. As follows from[86], the superconductivity of a quasi-one-dimensional system can still be described by the BCS theory for $\xi_0 \geq T_c^0$. Hence the curves shown in Fig. 21 should correctly describe T_c as a function of ξ_0 for values of $\xi_0 \geq T_c^0$; however, T_c^0 must be understood not as a physical quantity—the superconducting transition temperature in a one-dimensional model, but as the mathematical limit for T_c, given by Eqs. (8.9) and (8.10) of the BCS theory, as $\xi_0 \to 0$.

The investigation which has been made of the dependence of T_c on ξ_0 permits us to understand in principle why the transition temperatures are so different in the same type of compounds (for example, in V_3X, where X = Si, Ge, and Sn) even though the electron concentration and the chemical nature of the compounds remain the same for the whole series. One of the causes of such a difference may be a difference in the strength of the interchain coupling. The other possibility lies in a variation of the parameters characterizing the splitting of the d band into sub-bands, in connection with which the Fermi level may be displaced from the edge of one of the sub-bands, giving a singularity in the density of states. The relative role of these factors in each specific compound is, of course, unknown.

The analysis of the interchain coupling which has been made enables us, possibly, to understand the nature of the effect of impurities on the value of T_c in high-temperature compounds of β-W structure. The extensive experimental data described in Sec. 3 indicates that in almost all cases a strong decrease of T_c with increasing impurity concentration is observed, independently of whether the impurity replaces a B-type atom or an A-type atom occurring in the chains. To be sure, the presence of impurities in the chains generally strongly reduces T_c.

Apparently one can suggest two fundamental mechanisms for the effect of impurities on T_c in these compounds: a change of the density of states due to impurities, and interband scattering. The first mechanism can be effective only for compounds with high T_c in which there probably exists a narrow peak in the density of states at the Fermi surface, so that small impurity concentrations can lead to an appreciable distortion of this peak, thus causing a change in the value of T_c. If we start from a model of weakly interacting chains for the pure compound, the presence of impurities may

modify the effective interchain coupling, thereby leading to a change in the degree of "three-dimensionality" of the quasi-one-dimensional electronic spectrum. This problem was investigated in article[93], where expression (9.1) was obtained in the tight binding approximation for the electronic spectrum of weakly interacting chains; here the parameter ξ_0 turns out to be related to the transition matrix elements l_1 (between neighboring atoms on the same chain) and l_2 (between neighboring atoms on different chains) in the following way:

$$\xi_0 = \frac{4l_2^2}{|l_1|} \qquad (|l_2| \ll |l_1|). \qquad (9.8)$$

Analysis of the spectrum, taking the angular nature of the atomic d functions and the twofold degeneracy of the nearly empty band into account, leads to the same result (9.1) but with another expression for ξ_0. Thus, the essential feature of the utilized spectrum consists in allowing for the spatial structure of the lattice, not the angular nature of the atomic wave functions.

One can show[93] that in the presence of impurities substituted into the chains, the results remain the same but the parameters l_1 and l_2 in expression (9.8) for ξ_0 are replaced by average values. Thus, the graphs shown in Fig. 21, giving the dependence of T_c on ξ_0, now in fact also determine the dependence of T_c on the impurity concentration C_A in the chains.

A different situation arises when A-type atoms replace B-type atoms. In this case an additional interchain coupling appears through the transition atoms occupying positions outside the chains; as a result the parameter ξ_0 is replaced by $\xi = \xi_0 + \xi'$,[93] where ξ' denotes the correction associated with the additonal interaction of the chains, and moreover ξ' increases with increasing concentration C_B.

One can understand the nature of the variation of T_c as a function of the stoichiometric composition of a binary alloy on the basis of this last result. For example, in the alloys V − Si[14] and Ti − Sb[15] the maximum transition temperature is reached near the stoichiometric composition, i.e., for 25% type-B atoms. Upon increasing their content (when the excess number of these atoms get into the chains) T_c is changed only slightly; however, an abrupt decrease of T_c is observed when the transition-metal atoms A occupy the sites of B atoms. Perhaps this is related to an increase of the parameter ξ (due to the growth of ξ' with concentration), i.e., with the additional "three-dimensionality" of the electronic spectrum which is, as we have seen, accompanied by a decrease in the value of T_c.

The other mechanism which decreases T_c—namely, interband scattering of the electrons by impurities—was investigated in[94] for the Labbé-Friedel model; the following two cases were considered: The transition of an electron from the d band to the wide s band, and the scattering between two degenerate d sub-bands. Acting together with the above considered mechanism for "three-dimensionalization" of the spectrum, it leads to an effective decrease of T_c with increasing impurity concentration.

However, a number of the compounds shown in Fig. 2 give an especially strong decrease of T_c with increasing impurity concentration. Among them, for example, the compound V_3Si with admixtures of Mo and Cr. It cannot be excluded that, in these compounds the impurity atoms Mo or Cr may have weak localized moments or

they may be found near the critical condition for the appearance of this moment when paramagnetic scattering of the electrons by the impurities arises, strongly lowering the superconducting transition temperature. In this case the dependence of the magnetic susceptibility of such alloys on the impurity concentration must be very substantial, which is observed experimentally.[23]

Another example, which does not fit into the schemes under consideration, is the alloys of vanadium with gold. The pure compound V_3Au has $T_C = 2.40°K$ (see Table I). It is well known that small surplus amounts of Au atoms, replacing V atoms in the chains, change T_C by factors of tens.[95] Labbé and van Reuth[96] proposed the idea that the Au atoms, having completely filled d shells, protrude in the V chains like ion-like atoms, thus breaking the chains in which the one-dimensional motion of the d electrons occurs. Within the limits of each segment of a chain of vanadium atoms, containing Au atoms at each end, the electronic spectrum is discrete with the distance between the levels inversely proportional to the number of vanadium atoms in such a segment. The authors of this idea calculated the density of states of the system for a given concentration of randomly distributed Au atoms and showed that, for a finite concentration the singularity in $\rho(E)$, corresponding to the quasi-one-dimensional spectrum, gets "smoothed out," leading to an exponential behavior of $\rho(E)$ at the edge of the band. However, calculations of T_C using the expression found for the density of states were not made, so it is still difficult to say what the concentration dependence of the transition temperature will be on the basis of the proposed mechanism of broken chains.

The cited theoretical analysis refers to compounds of β-W structure with high values of T_C for which the quasi-one-dimensional model of the spectrum is apparently valid, and leads to qualitative agreement with the experimental data in regard to the effect of impurities on T_C. The latter exist only for the original high-temperature compounds. It would be desirable to experimentally investigate the effect of impurities on T_C in compounds with low transition temperatures in order to verify, in comparison with the existing data for high-temperature compounds, the particular role of the quasi-one-dimensional nature of the electronic spectrum for the behavior of T_C in compounds with impurities.

10. Quasi-one-dimensional model with a constant density of states. We have seen that the Labbé-Friedel model of quasi-one-dimensional chains is able to give a qualitative explanation of many anomalous electronic and lattice properties of high-temperature superconductors of the type V_3Si and Nb_3Sn. The physical origin of these anomalies is the sharp decrease in the density of states near the Fermi level which, in the Labbé-Friedel model, is related to the fact that the quasi-one-dimensional d band is nearly empty. If the essential point here is the fact that there is an abrupt change in the density of states near the Fermi level, the model may be simplified. Cohen, Cody, and Halloran[97] proposed an electronic model of the compounds under consideration, postulating in it the following behavior of the density of states of the d electrons as a function of the energy:

$$\rho(E) = \begin{cases} N_0, & E > E_0, \\ 0, & E < E_0, \end{cases} \tag{10.1}$$

where N_0 is some constant, and E_0 is the edge of the band, which is assumed to be triply degenerate (corresponding to the three types of linear chains) in a cubic crystal. Thus, in its typical foundation this model is quasi-one-dimensional; however, instead of using an exact expression of the type (8.4) for the density of states, the approximation that $\rho(E)$ is constant is assumed. According to the chain model, the Fermi level passes near the edge of the band. It was found that such a model enables one to easily obtain analytic results, which are likewise in good agreement with experiment.

First of all let us see how the temperature behavior of the lattice moduli of elasticity is calculated in this model. We shall assume that the crystal is found at a temperature below the martensitic transformation temperature and has a tetragonal structure. In order to calculate the elastic constants C_{ij} according to formula (6.4), it is necessary to calculate the free energy of the crystal F as a function of the strain tensor $\hat{\epsilon}$. It is convenient to represent the free energy as consisting of two parts:

$$F = F_1 + F_2, \tag{10.2}$$

where F_1 refers strictly to the lattice and F_2 describes the system of d electrons existing in the deformed lattice. F_1 can be expanded in a series in powers of the strains, and for a tetragonal crystal this expansion has the form

$$F_1 = \tfrac{1}{2} A_{11}\epsilon_1^2 + \tfrac{1}{2} A_{22}(\epsilon_2^2 + \epsilon_3^2) + A_{12}(\epsilon_1\epsilon_2 + \epsilon_1\epsilon_3) \\ + A_{23}\epsilon_2\epsilon_3 + \tfrac{1}{2} A_{44}\epsilon_4^2 + \tfrac{1}{2} A_{66}(\epsilon_5^2 + \epsilon_6^2), \tag{10.3}$$

where the A_{ij} are the elasticity moduli of the lattice without the d electrons.

The electronic part of the free energy can be expressed in terms of the internal energy U and the entropy S: $F_2 = U - TS$, and for an electron gas

$$U = \sum_l \int \rho_l(E) f_l(E) \, dE, \tag{10.4}$$

$$S = -k \sum_l \int \rho_l(E) \{f_l(E) \ln f_l(E) - [1 - f_l(E)] \ln [1 - f_l(E)]\} \, dE, \tag{10.5}$$

where $\rho_l(E)$ is the density of states in the l-th band ($l = 1, 2, 3$ corresponding to the three types of orthogonal chains), and $f_l(E)$ is the Fermi distribution function for the electrons from the l-th band, which interact with the field of the strained lattice. We shall assume that this interaction is described in terms of a deformation potential, that is, the correction to an electron's energy due to strain has the form

$$\delta E_l = U_l \epsilon_l. \tag{10.6}$$

The deformation interaction obviously shifts the band edge in a strained crystal; therefore, in the case when the Fermi level lies near the edge it leads to a strong temperature dependence of the calculated quantities.

According to Eqs. (10.4) and (10.5), the free energy of the electronic system can be written down in the form

$$F_2 = QE_F - kT \sum_l \int_{-\infty}^{\infty} \ln(1 + e^{(E_F - E_l)/kT}) \rho_l(E) \, dE, \tag{10.7}$$

where $E_l = E_{0l} + \delta E_l$ denotes the edge of the band associated with a chain in the l-th direction in the deformed crystal (E_{0l} denotes the edge of the band in the undeformed tetragonal crystal), $\rho_l(E) = N_0/3$ for $E > E_l$ and vanishes for $E < E_l$.

We substitute expressions (10.3) and (10.7) in (10.2); after differentiation with respect to the strains, the integrals over energies are easily evaluated since the density of states is constant. As a result the following formula appears for C_{ij}:

$$C_{ij} = A_{ij} - \frac{N_0}{3} \sum_{l=1}^{3} f(E_{0l}) \left[\frac{\partial (E_F - E_l)}{\partial \epsilon_i} \frac{\partial (E_F - E_l)}{\partial \epsilon_j} \right]_{\hat{\epsilon}=0}, \quad (10.8)$$

where $f(E_{0l})$ is the Fermi function evaluated for energy $E = E_{0l}$.

In the derived expression E_{0l} and E_l, and E_{0F} and E_F denote the edge of the l-th band and the Fermi energy in the unstrained and strained crystals, respectively. The Fermi energy is determined from the condition for conservation of the number of electrons in the d band, which in this model takes the form

$$\frac{1}{3} N_0 kT \sum_{l=1}^{3} \ln(1 + e^{(E_F - E_l)/kT}) = Q. \quad (10.9)$$

Differentiating this equation with respect to ϵ_i and taking the dependence (10.6) of the deformation energy on the strain into account, we obtain the following expression for the derivative of the Fermi energy with respect to ϵ_i:

$$\frac{\partial E_F}{\partial \epsilon_i} = \sum_{l=1}^{3} \frac{\partial E_l}{\partial \epsilon_i} f(E_l) \Big/ \sum_{l=1}^{3} f(E_l). \quad (10.10)$$

Relation (10.8) together with (10.10) determine the temperature dependence of the elastic constants in the tetragonal phase:

$$C_{11} = A_{11} - \frac{2}{3} N_0 U_1^2 \frac{f_1 f_2}{f_1 + 2f_2}, \quad (10.11)$$

$$C_{22} = C_{33} = A_{22} - \frac{1}{3} N_0 U_2^2 \frac{f_2(f_1 + f_2)}{f_1 + 2f_2}, \quad (10.12)$$

$$C_{12} = C_{13} = A_{12} + \frac{1}{3} N_0 U_1 U_2 \frac{f_1 f_2}{f_1 + 2f_2}, \quad (10.13)$$

$$C_{23} = A_{23} + \frac{1}{3} N_0 U_2^2 \frac{f_2^2}{f_1 + 2f_2}; \quad (10.14)$$

here the notation $f_l = f(E_{0l})$ is used for brevity. The quantities A_{ij} can be assumed to be temperature independent; thus, the entire temperature dependence of the elastic constants C_{ij} is determined by the factors f_l.

The tetragonality arising in the compounds Nb_3Sn and V_3Si is small; therefore, in formulas (10.11)–(10.14) one can approximately set [68,98]

$$A_{11} = A_{22}, \quad A_{23} = A_{12}, \quad U_1 = U_2 \equiv U. \quad (10.15)$$

The tetragonal crystal itself can be assumed to be obtained by a spontaneous tetragonal deformation of the cubic crystal which keeps its volume unchanged:

$$\hat{\epsilon} = \left\{ -\epsilon_0, \frac{1}{2}\epsilon_0, \frac{1}{2}\epsilon_0 \right\}. \quad (10.16)$$

In this case the edges of the energy bands for the chains along the tetragonal axis and for the chains perpendicular to it are given by the expressions (Fig. 22)

$$E_1 = E_0 - U\epsilon_0, \quad E_2 = E_3 = E_0 + \frac{1}{2}\epsilon_0. \quad (10.17)$$

In the cubic phase the positions of the edges coincide for all three bands so that the elastic constants are determined by the same expressions (10.11)–(10.14) in which, together with (10.15), it is necessary to replace f_1 and f_2 by

$$f_0 = (1 + e^{(E_0 - E_F)/T})^{-1}, \quad (10.18)$$

so that we obtain

$$C_{11} = A_{11} - \frac{2}{9} N_0 U^2 f_0,$$

$$C_{12} = A_{12} + \frac{1}{9} N_0 U^2 f_0, \quad (10.19)$$

from which we find that the shear modulus is given by

$$C_{11} - C_{12} = (A_{11} - A_{12}) - \frac{1}{3} N_0 U^2 f_0. \quad (10.20)$$

Let us introduce the temperature T_0 which is a measure of the Fermi energy in the cubic phase: $kT_0 \equiv E_{0F} - E_0$. As follows from Eqs. (10.20) and (10.18), the temperature behavior of the shear modulus is characterized by the dimensionless quantity T_0/T since A_{11} and A_{12} are assumed to be temperature independent. The shear modulus decreases with falling temperature and vanishes at the point which is determined from the condition

$$\frac{1}{1 + e^{-T_0/T}} = \frac{3(A_{11} - A_{12})}{N_0 U^2}. \quad (10.21)$$

Careful experimental measurements of the temperature dependence of the elasticity moduli in monocrystalline Nb_3Sn ($T_m = 45°K$) were made in the work described in article [68] (Fig. 11c). The experimental data for C_{11} and C_{12} in the cubic phase and in the temperature interval $49°K < T < 300°K$ fits on the curves (10.19)–(10.20) for the following values of the theoretical parameters:

$$\left. \begin{array}{l} A_{11} = 2.94 \cdot 10^{12} \ \mathrm{erg/cm}^3, \\ N_0 U^2 = (7.47 - 7.86) \cdot 10^{12} \ \mathrm{erg/cm}^3, \\ A_{12} = 0.84 \cdot 10^{12} \ \mathrm{erg/cm}^3, \\ T_0 = 80 \ °K. \end{array} \right\} \quad (10.22)$$

Satisfactory agreement of the values of C_{11} and C_{12} calculated from formulas (10.11) and (10.13) with the experimentally measured values of the moduli in the tetragonal phase is obtained for these same parameters if the temperature dependence of the tetragonality parameter $\epsilon_0(T)$ is taken from experiment. [55] For the calculation of $\epsilon_0(T)$, one can set up the equation minimizing the free energy with respect to ϵ_0:

$$\frac{3}{2}(A_{11} - A_{12})\epsilon_0 - \frac{1}{2} N_0 U^2 \epsilon + \frac{1}{3} N_0 U kT \ln \frac{f_1}{f_2} = 0. \quad (10.23)$$

Together with Eq. (10.9) it determines the temperature behavior of the spontaneous deformation. We immediately see that Eq. (10.23) describes a phase transition of the first kind. [99] First let us write down the asymptotic form of this equation for $\epsilon_0 \to 0$. One can see that in this case Eq. (10.23) goes over into the equation

$$\left[\frac{3}{2}(A_{11} - A_{12}) - \frac{1}{2} N_0 U^2 f_0 \right] \epsilon_0 = \frac{1}{8} \frac{N_0 U^3 f_0 (1 - f_0)}{kT} \epsilon_0^2, \quad (10.24)$$

which has two solutions: $\epsilon_0 = 0$ and

$$\epsilon_0 = \frac{12 kT}{N_0 U^3} \frac{C_{11}(T) - C_{12}(T)}{f_0(1 - f_0)} \quad (10.25)$$

(we have used formula (10.20) for the shear modulus). This relation indicates that the temperature T_1, at which the shear modulus vanishes, is the temperature of absolute instability of the cubic phase. On the other hand, the temperature T_2, above which the tetragonal phase is ab-
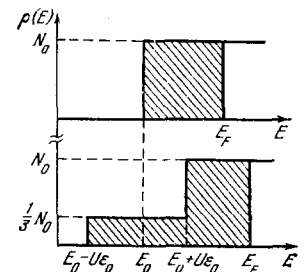

FIG. 22. The density of states in the d band of Nb_3Sn according to the model of Cohen, Cody, and Halloran [97] for the cubic (a) and tetragonal (b) phases. For $T = 0$, when the spontaneous deformation reaches a small value, it is assumed that the Fermi level lies totally within the first band.

$$\lambda \left(1 + \frac{\lambda}{2}\right) = \frac{N_0 U^2}{A_{11}}. \qquad (10.30)$$

The difference between expression (10.29) and the formula obtained for T_C in the strong-coupling method consists in the appearance of the coefficient $1/2$ in front of λ in the numerator of the exponential function's argument and the appearance of $\sqrt{\omega_D T_0}$ in place of ω_D in the factor appearing in front of the exponential function. Both of these changes arise as a consequence of the fact that in the adopted model the energy integration below the Fermi energy is cutoff at the value $T_0 \ll \omega_D$. Since here $T_0 = Q/N_0$, formula (10.29) gives $T_C \sim \sqrt{Q}$, in contrast to the Labbé-Friedel model where T_C and Q are described by a function with a maximum (see Fig. 18). This distinction is due to the difference in the behavior of the density of states $\rho(E)$ at large energies in the compared models.

If we take the parameters $N_0 U^2$ and A_{11} obtained from measurements of the temperature dependence of the moduli in the cubic phase, the values of λ and T_C turn out to be given by: $\lambda = 0.92$ and $T_C = 28°K$ for Nb_3Sn, and $\lambda = 0.72$ and $T_C = 21°K$ for V_3Si. The value of T_C obtained for Nb_3Sn is strongly overestimated. The discrepancy becomes even greater if T_C is calculated for the tetragonal phase ($T_C = 8°K$ for Nb_3Sn). This indicates that, in the model under consideration it is impossible to obtain numerical agreement with experiment in regard to T_C. Nevertheless, it is possible to establish some correlation between high values of T_C and the existence of a structural transition. The condition under which a structural transition should exist in Nb_3Sn and V_3Si follows from Eqs. (10.30) and (10.21): it has the form $\lambda > 0.7$. Thus, high values of λ (and hence, high values of T_C) are favorable to a structural transition.

11. Dynamical treatments. The nature of the lattice phase transition. The treatment of the martensitic phase transition described above used a static approximation in order to describe the coupling of the electronic system with the lattice deformations. Such an approximation leads to a uniform shift and a splitting of the d band, depending on the magnitude of the spontaneous deformation, which is calculated by a self-consistent method. However, one can develop a theory which also takes dynamical effects into consideration, i.e., the interaction of the d electrons with long-wavelength acoustic phonons.[102] The equation for the spontaneous tetragonal deformation obtained in such a treatment essentially agrees with Eq. (10.23) if only the renormalization of the electronic spectrum in the self-consistent field approximation is taken into account, i.e., take the static part of the electron-phonon interaction. Consideration of the dynamical part leads to renormalization of the phonons, described by the usual polarization term, which corresponds to the virtual creation of an electron and a hole by the phonon:

$$F_{lm}(q, \omega) = \frac{1}{N} \sum_k \frac{f_m(k) - f_l(k-q)}{\omega - E_m(k) - E_l(k-q)}, \qquad (11.1)$$

where $f_m(k)$ is the Fermi function for an electron with momentum k from the m-th sub-band.

If the nearness of the Fermi level to the edge of the band is taken into account in connection with the calculations in expression (11.1) and the model (10.1) is used for the density of states, one can easily obtain the explicit form of the temperature dependence of the acoustic phonon branches. One can verify[102] that, for pho-

solutely unstable, is determined from the condition $(d\epsilon_0/dT)_{T=T_2} = \infty$. Differentiation of Eq. (10.23) with respect to T gives the equation

$$\frac{f_1 f_2}{f_1 + 2f_2} = \frac{A_{11} - A_{12}}{N_0 U^2}, \qquad (10.26)$$

which together with the fundamental equation (10.23) determines T_2 and the value of the spontaneous deformation at this point. We note that if we set $\epsilon_0 = 0$ in Eq. (10.26), it goes over into Eq. (10.21).

The temperature range between T_1 and T_2 corresponds to metastable states, where T_1 is obviously the supercooling temperature and T_2 is the superheating temperature of the cubic and tetragonal phases. The phase transition point T_m, which must lie somewhere between T_1 and T_2 is determined by equating the free energies of the tetragonal and cubic phases, which leads to the equation

$$(A_{11} - A_{12})\, \epsilon_0^2\,(T_m) = \frac{4}{9}\, N_0 k T_m \left[2F(-U\epsilon_0) + F\left(\frac{1}{2} U\epsilon\right) - 3F(0) \right], \qquad (10.27)$$

where

$$F(\Delta) = \int_\Delta^\infty \ln\left(1 + e^{(E_F - E)/kT_m}\right) dE. \qquad (10.28)$$

The solution of Eq. (10.27) with Eq. (10.9) for the chemical potential determines the tetragonal transition and the jump in the spontaneous deformation. On the basis of a numerical solution of these equations by the authors of the model under discussion, the dependence of E_0 on T which is shown in Fig. 8 was obtained for the same parameters (10.22), together with experimental points for Nb_3Sn determined from x-ray measurements.[55] As we see, the magnitude of the jump in the spontaneous strain parameter at the point T_m is in good agreement with the theoretical predictions. A region of coexistence of the two phases near T_m (cross-hatched in the figure) is also clearly revealed in the experiment.

Thus, the model under consideration gives a reasonable explanation of the "softening" of the shear modulus and, as a consequence of this, the appearance of a lattice phase transition. However, the agreement with experiment is much worse for calculations of the other moduli. Thus, for example, one can easily see that in this model the modulus $C_{44} = A_{44}$, i.e., it does not depend on the temperature whereas in actual fact it experiences considerable "softening." Quantitative disagreement with experiment also appears in the calculation of the magnetic susceptibility, although the characteristic behavior of $\chi(T)$ near T_m (a sharp drop for $T < T_m$) is obtained from the present theory.

An estimate of the superconducting transition temperature T_C in this model was made in[100]. The authors assumed that the interaction of the d electrons in the nearly empty bands with acoustic phonons was responsible for the appearance of superconductivity. If it is postulated that this interaction is described by the matrix element of the deformation potential, the solution of the Éliashberg equations[101] for the strong-coupling method leads to the following expression for T_C:[100]

$$T_c = 1.14 \sqrt{\omega_D T_0} \exp\left[-\frac{1 + (1/2)\lambda}{\lambda - \mu^*}\right], \qquad (10.29)$$

where λ is the effective coupling constant for the electron-electron attraction due to electron-phonon coupling, which is determined from the equation

nons propagating in the [1 1 0] direction and with polarization along [1 1̄ 0] in the cubic phase, the frequency vanishes at a certain temperature T_1 (see Eq. (10.21)), at which the shear modulus disappears. Of course, the whole region of phonons with wave vectors adjacent to this direction should experience "softening". However, how far with regard to the value of the wave vector does this "softening" extend? For compounds of the type V_3Si and Nb_3Sn, the width of the d band amounts to several electron volts, and the Fermi level corresponds to $T_0 \approx 10^{2\circ}K$. This implies that the Fermi momentum $k_F \ll q_D$, where q_D is the Debye wave vector. For $q \sim q_D$ expression (11.1) decreases by the amount $(k_F/q_D)^2$ in comparison with the value which corresponds to acoustic phonons. This means that high-frequency phonons in these compounds should not be renormalized, and consequently they should not strongly depend on the temperature. The recent neutron scattering studies of the phonon spectrum in V_3Si[103] showed that the "softening" of some acoustic phonons (especially of the transverse type) is extended to approximately the middle of the Brillouin zone, although the degree of "softening" falls with increasing wave vector.

In the model under consideration, the instability of the individual phonon modes in the cubic phase leads to a phase transition of the first kind. We recall that in the compound Nb_3Sn a jump in the tetragonal stress parameter ϵ_0 is actually observed experimentally at the transition point T_m; however, the other characteristic signs of a first-order phase transition are absent: the specific volume does not change in practice, and no latent heat of transition or hysteresis is observed. All these facts compelled investigators to seek a model for these compounds which would give a phase transition of the second kind.

By applying Landau's theory of second-order phase transitions to the martensitic transformation in V_3Si and Nb_3Sn, Anderson and Blount[56] showed that if the tetragonal strain parameter is the only order parameter characterizing the system from the point of view of the phase transition, then the latter must, with absolute certainty, be a first-order transition. Therefore, if a second-order phase transition occurs in these cases it must be characterized by one more order parameter, for example, by the relative displacements of the atoms within the limits of a single unit cell. Such displacements might appear if one of the optical modes (for example, $\Gamma_{15}(-)$, $\Gamma_{25}(-)$ or $\Gamma_{15}(+)$[56]) were found to be soft and become unstable at the point T_m.

Klein and Birman[104] calculated the optical frequencies of A_3B compounds on the basis of a one-dimensional model of the electronic spectrum in the tight-binding approximation and reached the conclusion that, at $T = 0°K$ the optical modes $\Gamma_{15}(-)$ and $\Gamma_{25}(-)$ may become unstable for suitable values of the density of states due to an additional screening of the d electrons. However, later Sham[105,106], who was making first-principle calculations of the optical frequencies in this same model, pointed out an error in the calculations of Klein and Birman. The point is that, in the harmonic approximation the only source of a "softening" of the phonon modes is the interaction with the electrons, in the present case the interaction with the d electrons, which are treated in the chain model. In the modes of $\Gamma_{15}(-)$ or $\Gamma_{25}(-)$ symmetry the atoms of one chain vibrate as a whole; therefore, such motion cannot excite

the d electrons, which might renormalize the frequencies of these modes (Fig. 9). So in the present model the frequencies of the $\Gamma_{15}(-)$ and $\Gamma_{25}(-)$ modes cannot substantially depend on the temperature. The same remark also pertains to the mode $\Gamma_{15}(+)$, in which nearest-neighbor atoms of a chain can rotate about an axis perpendicular to the chain, but the associated change of the interatomic distance, which is what the electronic band parameters depend on in the tight-binding approximation, is extremely small.

For q = 0 the only optical mode, which excited electronic motion in the chain model and thereby turns out to be temperature dependent, is the mode Γ_{12} (Fig. 9). Sham's calculation[106] for Nb_3Sn showed that the frequency of the $\Gamma_{12}(+)$ mode is the largest of all optical branches. It actually depends on the temperature, decreasing with falling temperature; however, the frequency change amounts to only 10% for a reduction of the temperature from room temperature to T_m. Thus, this optical mode does not become unstable at any temperature. Nevertheless, it was found that its temperature variation is significant for the temperature behavior of the shear moduli. Owing to the electron-phonon interaction, the long-wavelength acoustic phonons, determining the transverse moduli $(C_{11} - C_{12})$, turn out to be coupled to the optical frequency $\omega(\Gamma_{12})$. Sham showed that in this situation the shear modulus can be expressed as the sum of three terms:

$$C_{11} - C_{12} = (A_{11} - A_{12}) + B - \frac{C}{\omega^2(\Gamma_{12})}, \qquad (11.2)$$

where the first term gives the contribution of the ionic interactions screened by the s electrons, the second contribution comes from the d electrons, and the third term—which is negative—describes the influence (via the d electrons) of the motion of the atoms in the chains relative to each other on the transverse acoustic phonons. The temperature dependence of $(C_{11} - C_{12})$ is determined by the last two terms of expression (11.2), where the negative contribution of each term increases with decreasing temperature. This dependence corresponds to the experimental behavior of the modulus $(C_{11} - C_{12})$. However, in contrast to the preceding theories[89,97] which also led to a "softening" of the shear modulus, according to Sham the loss of stability of the Nb_3Sn lattice is only related to some "softening" of the $\Gamma_{12}(+)$ mode. The latter, although it itself does not lose stability, nevertheless leads to a loss of stability of the shear acoustic vibrations.

Coupling of these vibrations with the mode $\Gamma_{12}(+)$ should lead to a nonuniform, tetragonal distortion of the lattice, described by the symmetry $\Gamma_{12}(+)$ of the mode, as if the latter were "frozen" into the lattice below the temperature T_m. In such a distortion the atoms must be displaced by an amount δ one with respect to the other, as indicated in Fig. 9. The neutron scattering study of the tetragonal phase by Shirane and Axe (see Sec. 4) actually revealed these displacements. Analysis of the temperature dependences of δ and of the tetragonal strain parameter ϵ_0 showed that they are linearly related (see Eq. (4.1)). Thus, there is actually only one parameter in the system, so that the lattice phase transition is a first-order transition. This transition is the result of a loss of stability of the acoustic shear modes of the lattice, which is the common conclusion of all the theories[89,99,102].

IV. CONCLUSIONS

Although the considered models[78,97], which are fundamentally based on the concept of the quasi-one-dimensional nature of the d-electron spectrum in compounds with β-W structure, give a qualitatively correct explanation of various anomalies in high-temperature superconductors of this type, they nevertheless turn out to be unable to explain the experiments on the effect of pressure,[73] and also on the strain dependence of T_c. Testardi[65] showed that the coefficient associated with the large quadratic term in the expansion of T_c in powers of the strain is determined by the quantity $\partial T_c / \partial Q$, but in the Labbé-Friedel model (see Fig. 18) the latter is extremely small for V_3Si, from which one concludes that the large strain dependence of T_c in V_3Si does not originate from a singularity in the electron density of states. Testardi[73,107] developed the idea that the anomalous behavior of the high-temperature superconductors among these compounds is connected with a lattice instability due to the strong anharmonicity. Although the source of the instability must finally result from singularities of the electronic bond in these compounds, Testardi places major emphasis on singularities in the phonon spectrum in the origin of high values of T_c.

Now let us return to the question of the connection between high values of T_c in a number of compounds with β-W structure and the presence of a martensitic transition in them, or a tendency towards such a transition, manifesting itself in the "softening" of the corresponding elastic moduli. In the theories[89,99,102] under consideration, both of these phenomena are a manifestation of singularities in the density of states near the Fermi level, that is, simply the existence of a sharp peak with a width comparable with T_c and T_m. This singularity arises from the quasi-one-dimensional nature of the d-electron spectrum, but by itself it does not specify a connection between superconducting and structural transitions. Gor'kov recently emphasized[108a] that the connection between these transitions results from the quasi-one-dimensional nature of the motion of the d electrons in the structure under consideration, the singularities of which do not simply reduce to singularities in the density of states of quasi-one-dimensional systems.

The point is that, according to[87] in the presence of an attraction between the electrons the metallic state of a one-dimensional chain is simultaneously unstable with respect to superconducting pairing and doubling of the period. In this connection it was shown by the authors of[87] that, at temperatures much greater than the phase-transition temperature (strictly speaking, the phase-transition temperature in a one-dimensional system must be equal to zero), the value of the effective electron interaction increases logarithmically with decreasing T; therefore, the corresponding observables should exhibit a logarithmic dependence on T. Precisely such a dependence was observed by Testardi for the elastic shear moduli in V_3Si. On the other hand, the neutron scattering experiment of Shirane[58] indicates a doubling of the period in the chain of niobium atoms in the compound Nb_3Sn. If one (but not two, as actually occurs) niobium atom from each chain were necessary per lattice period in a β-W structure, it would be possible to attribute the indicated doubling to the Peierls instability of a one-dimensional metal with one electron per site. Of course, if transitions of the electrons from

chain to chain are completely neglected, and also if the interaction of the electron with the nontransition-element atoms is ignored, we obtain a set of one-dimensional chains which are isolated from each other. However, in order to attribute the observed doubling to a manifestation of the Peierls instability, another difficulty exists: As a consequence of the degeneracy of the d-states of the transition atoms forming the chains, the type of possible instability, associated with the characteristics of the effective interelectron interaction in a one-dimensional system, must be more complicated than the Peierls instability.

The indicated facts only make the problem of a theoretical explanation of the structural phase transition in the investigated compounds more acute. The group-theoretical analysis of the β-W structure[108a] indicates that a second-order phase transition is possible within the limits of isolated chains. However, the weakness of the phase transition in the three-dimensional structure itself is due to the smallness of the interchain coupling.

From the point of view of the methods of treatment applied in[87], the structural and superconducting transitions in a linear chain, resulting from the attraction between the electrons, must take place simultaneously. However, in the compounds V_3Si and Nb_3Sn, in which the quasi-one-dimensional nature of the electron spectrum is assumed, T_m and T_c are different, although the difference between them is smaller than the temperature interval where there is a logarithmic dependence of the elastic moduli on T, and moreover the structural transition always precedes (for pure samples!) the superconducting transition.

In order to explain the connection between these two transitions, Gor'kov uses the quasi-one-dimensional model, assuming however that in the indicated compounds the Fermi surface passes near the point X (we recall that for the β-W structure, the reciprocal lattice is a simple cubic; the point X lies on the boundary of the Brillouin zone in the directions [1 0 0] and thus the coordinates $(\pi/a, 0, 0)$). Since two atoms of transition elements along the chain are required per lattice period in the β-W structure, one might expect complete occupation of the band of an individual chain. However, as Weger showed,[92] due to the presence of nontrivial translations in the β-W structure the levels are doubly degenerate at the point X, and this guarantees the metallic conductivity of the chosen model. At the same time it turns out that,[108b] the complete set of properties of superconductors with β-W structure can be understood as the result of an instability of the electron spectrum at the point X with respect to the interactions of the electrons with the lattice and among themselves. The nature of this instability is related to the twofold degeneracy of the levels at the point X and the linear dispersion law in its neighborhood. The latter circumstance leads to the result that the instability of such a spectrum is related to the instability of the spectrum of a one-dimensional metal, discovered in[87].

In this situation, by taking the interaction of the quasi-one-dimensional electronic states near the point X with the lattice deformations into account, Gor'kov showed that the lattice moduli C_{11} and C_{12} decrease logarithmically with falling temperature, which is in good agreement with Testardi's results[107] in V_3Si, and moreover the relation between these moduli has the correct character. At a certain temperature the shear

modulus $(C_{11} - C_{12})$ may vanish, which would correspond to the appearance of a tetragonal deformation in the lattice. However, consideration of an attraction-type interaction between the electrons may strongly shift the corresponding transition temperature. It turns out that in this case the logarithmic term, determining the temperature dependence of the modulus, is multiplied by a dimensionless factor proportional to the scattering amplitude which, as was shown in[87], sharply increases with decreasing temperature in a quasi-one-dimensional metal, determining the boundary of stability of the normal metallic phase, for example, the superconducting transition temperature T_c. The presence of this factor obviously leads to the result that, the vanishing of the modulus occurs at a temperature T_m close to T_c. This is then the connection between the two associated phenomena in the β-W structure, the martensitic transition and superconductivity, from the point of view of the electronic spectrum of the investigated model. One should add to this the fact that Gor'kov's model also explains the anomalous temperature dependence of the magnetic susceptibility for V_3Si, which turns out to be logarithmic over a wide range of temperature above T_m, according to calculation and experiment.[108b] A number of other properties of compounds with β-W structure, for example, the strain dependence of T_m, are in agreement with this model.

Thus, after the work of Gor'kov, which has shown that the "softening" of the lattice moduli in the superconducting compounds V_3Si and Nb_3Sn may be regarded as a "distant precursor" of the phase transition, which is the result of an instability of the quasi-one-dimensional system with respect to the interactions of the electrons with the lattice and with each other, the concepts concerning the quasi-one-dimensional behavior of the d electrons in these compounds find further confirmation.

However, we recall that there are two different models which utilize the concept of the quasi-one-dimensional spectrum for the chains—the Labbé-Friedel model[78] and the Gor'kov model,[108a] which differ first of all in the position of the Fermi level. In actual fact, where does the Fermi level occur for compounds of the type V_3Si and Nb_3Sn? One can reformulate this question as follows: is the Fermi momentum small ($k_F \ll \pi/a$) or, on the contrary, large ($k_F \sim \pi/a$) for these compounds? Right now a direct experimental determination of this quantity would be extremly important. Let us indicate one theoretical possibility, which is related to the study of inelastic neutron scattering by an electron Fermi gas in a metal. If the wave vector p of the incident neutron is much larger than the extremal diameter $2k_F$ of the Fermi surface, the differential cross section $d\sigma/d\Omega$ for the scattering of neutrons should have a cusp at a scattering angle $\theta_0 = 2k_F/p$.[109] For ordinary metals the fulfilment of the condition $2k_F \ll p$ requires neutrons with epithermal energies of the order of an electron volt or more, which does not allow us to use the indicated method in view of the small intensity of neutrons with such energies in reactor beams. However, if the Fermi momentum is small in comparison with the limiting wave vector, then one can satisfy the condition $2k_F \ll p$ even for thermal neutrons, so that the observation of a singularity in their angular distribution is actually possible in this case. As the calculations recently completed by Dieterich showed,[110] the corresponding cross section $d\sigma/d\Omega$ for V_3Si (under the assumption that $k_F \ll \pi/a$) should amount to 10^{-3} barn per vanadium atom—an effect which, unfortunately, is extremely small.

Another possibility for the investigation of the Fermi surface in this type of substances is connected with positron annihilation. An experiment performed on V_3Si[111] showed that the Fermi surface in it is sharply anisotropic, where the equal-energy surfaces have planar sections perpendicular to the directions of the type [1 0 0], as was first predicted by Weger.[79] It would be very valuable to carry such experiments further, since this technique also affords a possibility of determining the thickness of the plane layer between different segments of the Fermi surface, i.e., its position with respect to the points Γ and X.

Any experiment in which specific predictions of the two models under consideration might appear deserves a great deal of interest. In this connection let us turn our attention to the work concerning the influence of a magnetic field on the structural transition in V_3Si. In the Labbé-Friedel model the Fermi level for this compound is estimated, as we know, to be several tens of degrees. This means that magnetic fields of the order of 10^5 Oe can substantially shift it and cause noticeable effects. One of such effects is the reduction of T_m on application of the magnetic field. The predicted reduction of T_m in a field of 90 kOe was $0.30°K$;[112] the measured value was found to be $0.26°K$.[59]

Such surprising agreement with experiment, which, of course, might be accidental, caused the authors of[113] to go further. They predicted a new effect for V_3Si—the dependence of the spontaneous deformation ϵ_0 on the magnitude of the field, using the same values of the parameters which give agreement with experiment in regard to the entire set of properties of this compound (see Sec. 8). It was found that ϵ_0 slowly decreases upon application of the field, and moreover the effect depends on the temperature: The lower the temperature T, the smaller the derivative $|d\epsilon_0/dH|$. However, a certain critical temperature exists (for the parameter chosen, it turned out to be equal to $17.4°K$, and $T_m(H = 0) = 21.25°K$) below which a field of a definite value will suddenly transform the crystal from the state $\epsilon_0 > 0$ ($c/a > 1$) into the state with $\epsilon_0 < 0$ ($c/a < 1$). At the critical point $T = 17.4°K$ itself, the critical field $H \approx 275$ kOe. Of course, the observation of such an effect would indicate that the position of the Fermi level is near the edge of the one-dimensional band.

In spite of the fact that at the present time it is still impossible to make a final choice between the models under discussion, from an examination of the review of the experimental facts and by comparing them with these models, one must conclude that the different properties of such compounds as V_3Si and Nb_3Sn appear as if they can be understood on the basis of the concept of the quasi-one-dimensional nature of the d-electron states in the β-W structure.

However, it should be noted that there is a very clearly expressed difference between the compounds V_3Si and Nb_3Sn in regard to purely electronic properties. The experimental material presented in Sec. 2 of the present review indicates a high density of states at the Fermi level for V_3Si, whereas the density of states appears to be small for Nb_3Sn. Nevertheless, both compounds have high values of T_c and exhibit a marten-

sitic structural transition. Is this difference related to the fact that in V_3Si, let us say, the Fermi surface passes near the point Γ, but in Nb_3Sn it passes near the point X?

In order to definitely confirm this idea, it would be necessary to ascertain whether the special lattice properties of V_3Si and Nb_3Sn are unique, or whether other representatives exist in the series of high-temperature superconducting compounds with β-W structure for which the high values of T_C are accompanied by a "softening" of the lattice moduli and perhaps by a structural transition. Unfortunately, the elastic properties of compounds such as V_3Ga, Nb_3Al, Nb_3Ga, and Nb_3Ge ($T_C > 15°K$) have not been intensively studied. Nevertheless, the first acoustic experiments, performed on polycrystals, indicate (see Fig. 10) an appreciable softening of the lattice for V_3Ga and Nb_3Al. It would be of great interest to carry out a detailed measurement of the lattice moduli with variation of the temperature, as was done for V_3Si and Nb_3Sn, and also their investigation by neutron scattering experiments at very low temperatures on the subject of the existence of a structural transition.

Another aspect of the investigations, which have the goal of clarifying the validity of the model of a quasi-one-dimensional spectrum in compounds with β-W structure, is connected with the dependence of the lattice properties on doping or on stoichiometric composition. Since these factors may disturb the chains of A atoms (transition elements) in the A_3B compounds, one can anticipate considerable changes in a number of the properties of these compounds (for example, the temperature dependence of the elastic moduli) upon doping or the introduction of disorder if, in actual fact, the reason for the anomalous properties of the pure compounds of stoichiometric composition is due to the quasi-one-dimensional nature of the electronic states. A detailed comparative analysis of the properties of the various compounds with β-W structure should indicate how widely the model of weakly interacting chains can be utilized for them.

Note added in proof. Information about the synthesis of the compound Nb_3Si with β-W structure and its superconducting properties is communicated in [123]. The effect of a magnetic field on the structural transition in V_3Si was investigated in [124] and an interpretation is given of the experimental results within the framework of the Labbé-Friedel model. Further development of the theory of the structural transition in Nb_3Sn, which was started in [105,106], is carried out in [125]. We also call attention to review articles on structural transitions, [126] tunneling, [127] and an experimental article which investigates the softening of the lattice moduli in ternary systems [128].

[1)]An analysis of a number of the physical properties of compounds with a vanadium base is contained in the brief review by Levanyuk and Suris, [1] which was published in 1967. An extensive collection of empirical data of a metallurgical nature on compounds with β-W structure exists in the monograph by Savitskii and colleagues [2].

[2)]In Testardi's original article [66], the temperature dependence of the modulus of elasticity in V_3Si is plotted on a logarithmic scale. From the figures given in [66] one can see that a logarithmic dependence $C_{ij}(T) = a + b \ln T$ holds for temperatures T appreciably exceeding T_m.

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