Superfluidity of compounds based on transition elements, and its connection with lattice instability

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The experimental and theoretical research on the physical properties of superconducting compounds based on transition elements are reviewed. The discussed classes of compounds are those having the highest superconducting transition temperature T_c, frequently reaching 15°K and higher. Two types of such compounds are considered in detail: intermetallic and covalent-ionic. The first type includes compounds with the structures of β-tungsten, CsCl, α-Mn, σ-phase, and Laves phase. The second type includes numerous compounds with NaCl structure (carbides, nitrides, etc.) and chalcogenides. The superconducting, electronic, and lattice properties of each class of compounds are reviewed, and models of their electronic structures or calculations of their electronic spectra are presented. Not only compounds of stoichiometric composition, but also their alloys are considered. The extensive empirical material on the influence of alloying and of the composition on T_c is systematized. The same properties are compared in various classes of compounds, and this makes it possible to establish a number of correlations between T_c and the lattice symmetry, the electron density (the Matthias rule), and the anomalies of the lattice properties. A particularly substantial role is found to be played by the correlations with the lattice properties, namely, the largest T_c of the various compounds of a given class are possessed as a rule by those representatives which exhibit some lattice instability. The review analyzes the lattice instability types that can appear in the compounds. The authors attempt to base the observed correlation on the existing theory of superconductors with tight binding. The last chapter of the review is devoted to a theoretical investigation of lattice phase transitions (observed in superconducting compounds with structures A-15, C-15, and B-2) as one of the forms of the lattice instability. A symmetry analysis is given for transitions that proceed in accord with an irreducible representation of the point Γ of the O_h group. The electronic mechanism of the lattice instability of the compounds A-15 and C-25 is described on the basis of the model of L. G. Gor'kov. This review is a continuation of the one which appears in Usp. Fiz. Nauk **113**, 193, (1974) [Sov. Phys. Usp. **17**, 356, (1974)] dealing with the superconducting compounds having a β-tungsten structure.

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CONTENTS

1. INTRODUCTION

The highest superconducting-transition temperatures by far have been observed not in pure metals or their alloys, but in chemical compounds based on transition metals. Until recently, the only high-temperature superconductors were compounds with A-β15 (or β-tungsten) structure, to which belong the well-known superconductors V_3Si and Nb_3Sn, and also Nb_3Ge, which has at present the highest transition temperature T_c = 23.2 °K. This best-known class of superconductors has been under intensive study in recent years, and its physical properties have recently been the subject of three large reviews. [1-3]

By now, however, about ten other types of transition-metal compounds with high superconducting transition temperatures, say with $T_c > 10$ °K, are known. [1] These compounds can be either intermetallic similar to the A-15 or α-Mn structures, Laves phases or σ phases, or else include nonmetallic elements such as C, N, P, S, O, and others. The latter include the typically covalently-ionic compounds such as carbides, nitrides, sesquicarbides, chalcogenides, etc. for which T_c on the order of 15 °K is far from rare, and in individual cases, as in NbN, it exceeds 17 °K.

High-temperature superconductivity was discovered in a number of classes of compounds which were regarded even a short time ago as utterly hopeless in this respect, for examples in oxides of the spinel type. In one of them, with composition close to $LiTi_2O_4$ the value of T_c is almost 14 °K! As a rule, high T_c in compounds are accompanied by large critical fields.

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[1] Following V. L. Ginzburg (see, e.g.,[183]), high-temperature superconductivity is taken to mean superconductivity at > 30 °K. In this review we are dealing with actually produced superconductors and have in mind substances with $T_c > 10$ °K.

It is indicated in a recent communication that in the sulfide $PbMo_{5.1}S_6$ ($T_c = 14.4\,°K$) the second critical field H_{c2} reaches the record value 510 kOe at $4.2\,°K$.

During the last few years, a colossal amount of empirical material has been accumulated on various properties of these new superconductors, and this entire research field goes over gradually from the "metallurgical" stage, in which the principal attention is paid to methods of synthesizing the compounds, which as a rule are obtained via complicated reactions, to the stage of a systematic investigation of their physical properties. For this last stage the picture we see is still far from complete, but it is clear that the program for the study of compounds of each new class of superconductors should duplicate to a considerable degree the logic followed in the research of the compounds most thoroughly studied at present, with the $β$-tungsten structure.

What should be the aim in the experimental studies? To ascertain the mechanisms that lead to high T_c in these compounds, it is necessary to know a wide range of properties, at least the density of states on the Fermi surface, the phonon spectrum, and the matrix elements of the electron-phonon interaction. No such systematic studies have been made so far, and it is very important to study the correlations between T_c and many other easily-measured properties. One of the tasks of the present review is indeed the establishment of such correlations between T_c and the lattice symmetry, the crystal-chemistry of the compounds, the electron density, etc.

The most important question, however, is: why do only individual representatives of the isomorphic compounds of this class have very high superconducting transition temperatures? From the very start of the study of A-15 compounds the attention was focused on the fact that the high values of T_c in these compounds are accompanied by lattice-property anomalies that have the character of lattice instability. Later, in the study of other classes of compounds, numerous examples of this correlation were observed, and have by now been incorporated in the idea advanced by Matthias, [5] Phillips, [6] Testardi, [3,7,8] Alekseevskiĭ, [9] Collings, [10] Lawson, [11] and others, namely: *high superconducting-transition temperatures appear in compounds having unstable lattices.*

We shall show below that manifestations of lattice instability can be different.

It should be noted from the outset that there is still no rigorous theory that establishes this correlation (see, e.g., [12]) but some theoretical arguments can be advanced on the basis of the well-known McMillan formula[13] for T_c, which gives an analytic representation of the numerical results of the solution of the Éliashberg equation for superconductors with tight binding[14] (which undoubtedly include all the high-temperature compounds):

$$T_c = \frac{\langle \omega \rangle}{1.2} \exp\left[-\frac{1.04\,(1+\lambda)}{\lambda - \mu^*\,(1+0.62\lambda)} \right];$$

here $\langle \omega \rangle$ is the average phonon frequency, and λ is ex-

pressed in terms of the distribution function $F(\omega)$ of the frequencies in the phonon spectrum and the effective square $\alpha^2(\omega)$ of the matrix element of the electron-phonon interaction:

$$\lambda = 2 \int_0^\infty \frac{\alpha^2(\omega)\,F(\omega)}{\omega}\,d\omega. \tag{2}$$

The dimensionless parameter λ characterizes the magnitude of the attraction of the electrons on the Fermi surface because of the virtual phonon exchange, whereas μ^* represents the Coulomb repulsive pseudopotential. In[13] μ^* is estimated at 0.10–0.15 for transition metals, while λ is of the order of 1 for superconductors with tight binding.

Taking into account the smallness of μ^* we arrive at the conclusion that according to McMillan's formula T_c is expressed principally by the parameter λ, which contains the characteristics $\alpha^2(\omega)$ and $F(\omega)$ of the superconductor. Although formula (1) was obtained by using for $F(\omega)$ the experimentally determined density of the phonon states of niobium, and also the assumption that $\alpha^2(\omega)$ does not depend on the frequency, nonetheless its use for an analysis of T_c in transition metals and their alloys has shown good agreement between the values of T_c calculated from it and experiment. It should be noted in addition that the analytic expression obtained by Karakozov, Maksimov, and Mashkov[15] for T_c from Éliashberg's equation agrees in fact with formula (1) in the case of intermediate binding. All this allows us to regard McMillan's formula as a basis for a theoretical analysis of T_c in superconductors with tight binding.

McMillan has shown further that in the case of a monatomic lattice with ion mass M we can represent λ in the form of a simple product of factors that depend on the electron or phonon characteristics:

$$\lambda = \frac{N(0)\,\langle I^2 \rangle}{M\,\langle \omega^2 \rangle}, \tag{3}$$

where $N(0)$ is the density of states on the Fermi surface, $\langle I^2 \rangle$ is the square of the electron-interaction matrix element averaged over the Fermi surface, and $\langle \omega^2 \rangle$ is a certain mean-squared frequency of the phonon spectrum. By definition,

$$\langle I^2 \rangle = \int \frac{d^2p}{v_p} \int \frac{d^2p'}{v_{p'}} |\langle p|\,e\nabla U\,|p'\rangle|^2 \,\Big\backslash\, \int \frac{d^2p}{v_p} \int \frac{d^2p'}{v_{p'}} \tag{4}$$

where U is the potential of the ion, and e is the vector of polarization of a phonon with momentum $p - p'$; the integration is carried out over the vectors p and p' which lie on the Fermi surface; v_p is the electron velocity on the Fermi surface, so that $\int v_p^{-1}d^2p = N(0)$.

A comparison of the values of λ calculated from (1) using the experimental values of T_c with relation (3), carried out by McMillan for many superconducting transition metals, has shown that the values of $N(0)$ and $\langle I^2 \rangle$ vary significantly from metal to metal, but their product remains practically constant in a series of superconductors of the same type having the same crystal lattice and the same structure of the electronic

states. It turned out thus, for example, that for the series of transition metals Nb, Ta, and Mo we have $WN(0)\langle I^2\rangle \approx 7$ eV/Å^2. There exists thus a certain empirical rule

$$\lambda = \frac{\text{const}}{M\langle\omega^2\rangle}, \tag{5}$$

from which λ in a series of similar metals is determined principally by the mean-squared value of the phonon frequency. This result allows us to advance the following opinion: if the lattice of some metal is subject to an instability that leads to a softening of the phonon spectrum and to a decrease of $\langle\omega^2\rangle$, then its corresponding value of λ is larger and consequently its T_c is higher. At the present state of the theory, relation (5) is in essence the only expression for the correlation between high T_c and lattice instability.

The theoretical basis of this empirical rule for transition metals was provided by Hopfield from an analysis of the matrix element of the electron-ion interaction. He used an expansion of the wave functions that determine the matrix element $\langle p\,|\,e\,\nabla\,U\,|\,p'\rangle$ in terms of the eigenfunctions of the angular momentum, assuming the potential to have spherical symmetry. Since ∇U transforms like a vector, there should exist for this matrix element a selection rule of the type $l=l\pm 1$, where l and l' are the orbital angular momenta in the states p and p'. This means that the electron-phonon interaction in the transition metals leads to a transition between the d and p states. This leads to the relation

$$\langle I^2\rangle = \frac{N_p(0)\,N_d(0)}{N^2(0)}\left(\frac{dU}{ds}\right)^2, \tag{6}$$

where $N_p(0)$ and $N_d(0)$ are the contributions of the partial states of p and d symmetry to the total state density $N(0)=N_s(0)+N_p(0)+N_d(0)+\ldots$ on the Fermi surface. The gradient of the potential seems to vary little within a given series of transition metals, for which furthermore $N(0)\approx N_d(0)$. By virtue of these circumstances we get from relation (6)

$$N(0)\langle I^2\rangle \approx N_p(0)\left(\frac{dU}{ds}\right)^2 = \text{const.} \tag{7}$$

We note also that the constancy of the quantity $N(0)\langle I^2\rangle$ for a metal whose electronic states on the Fermi surface can be described in the tight-binding approximations (i. e., more readily in the approximation of a transition metal with a narrow d-band) was demonstrated also by Barisic, Labbe, and Friedel,[17] who connected this quantity with the metal cohesive energy E_c

$$N(0)\langle I^2\rangle = q_0^2 E_c, \tag{8}$$

where q_0 is the Slater coefficient (defined in terms of the spatial part of the d functions $\sim\exp(-q_0 r)$). The cohesive energy E_c varies little for similar transition metals, apparently in the same manner as the atomic property q_0, and this ensures constancy of $N(0)\langle I^2\rangle$.

Thus, owing to relation (5), the difference between the values of T_c of metals within a given class is due to

differences in the phonon spectrum, namely in the value of $\langle\omega^2\rangle$. This quantity cannot be regarded as a pure lattice property, since an important role in the formation of the phonon spectrum in a metal is played by the conduction electrons via the electron-lattice interaction. Consequently $\langle\omega^2\rangle$ should reflect in some manner the properties of the electron system. In a number of recent theoretical papers[18, 19] show that $\langle\omega^2\rangle$ depends on the electron density of states on the Fermi surface and on the electron concentration. In the latter case it becomes possible to justify Matthias's empirical correlation whereby two values of electron density exist and favor high T_c in transition metals.

Whereas the situation in transition metals and their alloys has been clarified to a considerable degree and it has been established that McMillan's formulas (1) and (4) account not only qualitatively but in many cases also quantitatively for the behavior of T_c as a function of the characteristics of the normal phase of the metal, the question of compounds based on transition metals is not yet clear. The phonon spectrum of compounds can differ greatly from the bcc-metal spectrum that is incorporated in the Éliashberg equation, when the McMillan formula (1) is derived, but one can hope that the general structure of expression (1) (e. g., the fact that $T_c \sim \exp[-(1+\lambda)/(\lambda-\mu^*)])$, will be preserved. As to the empirical expression (3) for λ, it is valid, of course, only for a monatomic lattice, and separation of λ into multiplicative pure-electron and pure-phonon factors is hardly possible in the general case. Nonetheless, there exists one general property of λ.

Maksimov[20] was the first to show that λ does not depend on the mass in a lattice with isotopic impurities. The most inclusive generalization of this result was obtained by Taylor and Vashishta,[21] who have shown that, owing to a certain sum rule pertaining to the phonon spectrum, the value given by formula (2) for λ of any complex lattice does not depend on the ion masses and is expressed, in term of force constants of the lattice in accordance with the formula

$$\lambda = \int\frac{d^3p}{v_p}\int\frac{d^3p'}{v_{p'}}\sum_{\alpha\beta}\sum_{\varkappa\varkappa'}\Phi_{\varkappa\varkappa'}^{-1\alpha\beta}(p-p')\langle p\,|\,\nabla_\alpha U_\varkappa\,|\,p'\rangle\langle p'\,|\,\nabla_\beta U_{\varkappa'}\,|\,p\rangle\Big/\int\frac{d^3p}{v_p}. \tag{9}$$

Here $\Phi^{-1}(p-p')$ is the Fourier component of the inverse matrix of the force constants; $\varkappa$ and $\varkappa'$ number the atoms in the unit cell, and α and β are Cartesian projections on the axes x, y, and z.

We assume that formulas (1), (2), and (9) can serve as a basis for a discussion of T_c in complex compounds.

Our review is devoted exclusively to an analysis of experimental facts pertaining to the properties of superconducting compounds of transition metals. In the first part we review the experimental data on each class of compounds separately, and in the second part we compare the same properties in different classes and establish different correlations, in particular between high T_c and the anomalies of the lattice properties, in which lattice stability sets in. In the last part of the review we give a theoretical analysis of the most important manifestations of lattice instability—the struc-
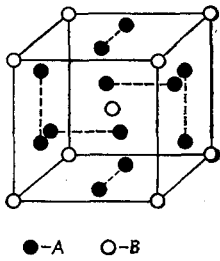
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FIG. 1. Structure of A-15 intermetallic A_3B compound.

●-A   O-B

tural phase transition—in all classes of compounds in which it takes place, and offer on its basis recommendations for further experimental research.

2. TYPES OF SUPERCONDUCTING COMPOUNDS AND THEIR PROPERTIES

A. Intermetallic compounds

1. Compounds with A-15 structure

Since a detailed analysis of various properties of this class of compounds was given in our previous review,[1] we merely recall here briefly their most important lattice properties and present the results of the latest experimental papers published after the review.[1]

The compounds that crystallize into the A-15 structure are of the A_3B type. The atoms B form in these compounds a body-centered cubic lattice, while atoms A are located pairwise on the faces of the cube parallel to the coordinate axes (Fig. 1). The unit cell contains eight atoms; the space group is $O_h^3 - Pm3n$. The atom A must be a transition element of group IV, V, or VI, whereas the atoms B can be either nontransition elements (Al, Si, P, Ga, Ge, As, In, Sn, Pb, Sb, Bi) or transition elements of group VIII.

A characteristic feature of this structure is that atoms A form families of intersecting linear chains, wherein the distance between the atoms in one chain is much less than the distance between the A atoms in the different chains. This circumstance has led Weger, Labbe, and Friedel to the assumption that the electronic spectrum of the d states in this structure is quasi-one-dimensional (see, e.g.,[1,2]). The quasi-one-dimensional model has made it possible to explain qualitatively the anomalies of the different physical properties of the most thoroughly studied compounds V_3Si and Nb_3Sn, namely, a strong temperature dependence of the magnetic susceptibility and of the Knight shift, the softening of some of the lattice moduli, the high temperatures of the superconducting transition, etc. It must be borne in mind, however, that no direct measurements of the structure of the electronic spectrum, for example of the Fermi surface, have been made so far, and on the other hand the model calls for parameter values that are too extremal, viz., a Fermi energy on the order of 100 °K and a ratio $\sim 10^{-2}$–10^{-3} of the matrix elements of electron transport from chain to chain and along the chain, which are not very realistic.

The compounds A-15 were the first in which a correlation was observed between high values of T_c and the lattice instability. This instability manifests itself in

a number of compounds in a softening of certain lattice moduli, primarily the shear modulus $C_s = (C_{11} - C_{12})/2$, thus pointing to instability of the phonons that propagate in the [110] direction with a transverse polarization as the temperature is lowered from room temperature to several dozen °K (Fig. 2). It is definitely known that in two compounds, V_3Si ($T_c = 17.1$ °K) and Nb_3Sn ($T_c = 18$ °K) this softening of the lattice terminates (in sufficiently pure samples!) in a structural transformation into the tetragonal phase at temperatures T_m equal to 21 and 43 °K, respectively. The tetragonal distortion $|c - d|/a$ amounts to only $\sim 10^{-3}$, and it is curious that $c/a > 1$ in V_3Si but $c/a < 1$ in Nb_3Sn.

It was noted that a number of attributes of this transition (lack of diffusion, dependence of T_m on the magnetic field, etc.) brings it closer to the martensitic transition in iron-carbon and other alloys; the absence of latent heat of the transition, of changes in volume, and of hysteresis points to a second-order transition, but at the point T_m there is observed a finite discontinuity in the spontaneous deformation, and this is an attribute of a first-order transition. Researches of last year, which were not included in the review,[1] were devoted to a detailed study of these martensitic transformations and to the correlation of T_m with T_c. We now proceed to deal with them.

Measurement of the temperature dependence of the derivatives of the shear modulus with respect to pressure $\partial G_s/\partial P$ for V_3Si samples undergoing and not undergoing structural transitions[22,23] has shown that these relations coincide only in the region 296–90 °K, where $\partial C_s/\partial P$ is positive and decreases in magnitude, reaching zero at 80–90 °K (Fig. 3). With further decrease of temperature, $\partial C_s/\partial P$ reverses sign and decreases continuously to − 5 at 13.5 °K in the non-transforming V_3Si sample (Fig. 3b). For the sample that exhibits a structural transformation, $\partial C_s/\partial P$ also reverses sign at $T < 80$ °K, but then decreases only to 62 °K, and with further decrease of temperature it again reverses sign and increases in magnitude already in the region of positive values (Fig. 3a).

This difference in the behavior of $\partial C_s/\partial P$ at low temperatures means that in one case (in the nontransforming V_3Si sample) the pressure softens greatly the shear mode, and in the second case (in the transforming sample) it hardens it. It was therefore proposed[22] that the pressure dependence of T_c should differ considerably in these cases ($\partial T_c/\partial P$ of the nontransforming
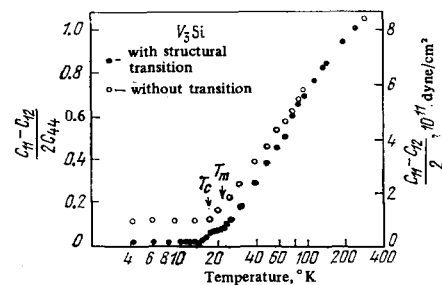

FIG. 2. Temperature-induced softening of the shear modulus in V_3Si.
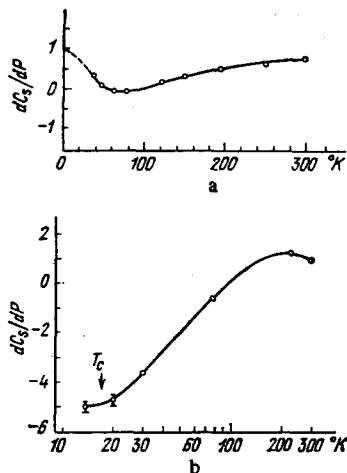
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FIG. 3. Temperature dependence of the first derivative of the shear modulus on the pressure in transforming (a) and non-transforming (b) V_3Si samples.

sample should be approximately 16 times larger than that of the transforming V_3Si sample according to the estimates of[22]). The direct experiments, however, did not confirm this assumption. Measurements made on the same samples as used to study the $\partial C_s/\partial P_1$ temperature dependences in Fig. 3 have yielded not an appreciable increase but, to the contrary, a 30% decrease of $\partial T_c/\partial P$ for the V_3Si sample that undergoes no transformation. [130]

The presence of negative values of $\partial C_s/\partial P$ at definite temperatures indicates that the shear mode can become annihilated and that a structural transformation can take place at these temperatures if the hydrostatic pressure is high enough. The behavior of $\partial T_m/\partial P$ is then determined entirely by the change of $\partial C_s/\partial P$ in this temperature region. From the condition $C_s(P, T_m) = 0$ we can obtain[22]

$$\frac{\partial T_m}{\partial P} = -\left(\frac{\partial C_s}{\partial P}\right)_T \Big/ \left(\frac{\partial C_s}{\partial T}\right)_P.$$

Since $(\partial C_s/\partial T)_p = 20$ kbar/°K for V_3Si,[22] the sign of $\partial T_m/\partial P$ depends only on the sign of $\partial C_s/\partial P$. For the transforming V_3Si sample we have $\partial C_s/\partial P > 0$ at $T < 50$ °K, therefore $\partial T_m/\partial P = 0$. Experiment[162] has yielded $\partial T_m/\partial P = -1.5 \times 10^{-4}$ °K bar^{-1}, in full agreement with this prediction (Fig. 4). The same figure shows the change of T_c with pressure. [143] It is seen that in the considered region of pressures we have $\partial T_c/$
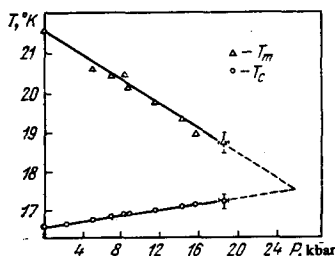

FIG. 4. Effect of pressure on the temperature of the super-conducting and structural transitions in V_3Si.
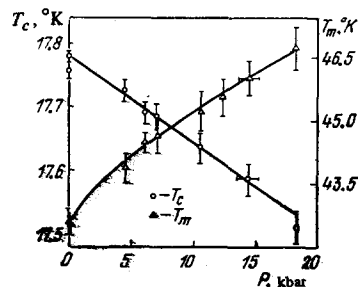

FIG. 5. Effect of pressure on the temperatures of the super-conducting and structural transitions in Nb_3Sn.

$\partial P > 0$, and $\partial T_m/\partial P < 0$. For the Nb_3Sn compound, the behavior of T_c and T_m in the same pressure region turned out to be entirely different[142]: T_c decreased, and T_m increased with applied pressure (Fig. 5). Unfortunately, for Nb_3Sn there are no measurements of the temperature dependences of the elastic moduli under pressure. By analogy with V_3Si we can only assume that $\partial C_s/\partial P$ will have a negative sign in this temperature region.

Another question that has been raised recently is the dependence of the martensitic-transition temperature T_m on the magnetic field. Estimates by Dieterich and Fulde, [144] obtained using the Labbe–Friedel model, yielded for V_3Si the value $\Delta T_m = -0.31$ °K in a field $H = 90$ kOe. The experimental temperature shift in this field turned out to be close enough: $\Delta T_m = -0.26$ °K.[145] A more complete measurement of $T_m(H)$ was made recently, up to 156 kOe, [157] and a quadratic dependence of ΔT_m on H was observed:

$$\frac{\Delta T_m}{T_m(0)} = -\alpha\left|\left(\frac{\mu_B H}{kT_m(0)}\right)^2\right|,$$

where α turned out to equal 0.10. In an earlier study, Maita and Bucher obtained $\alpha = 0.15$. The difference is apparently due to the different degress of purity of the V_3Si samples.

The sign of the effect $(\Delta T_m < 0)$ denotes stabilization of the cubic state in a strong magnetic field; this stabilization should be accompanied by an increase (at the given temperature) of the shear modulus. Measurements of the speed of the sound corresponding to the soft mode in the nontransforming V_3Si sample as a function of the magnetic field have shown[158] that this speed indeed increases quadratically with the field, in exact accordance with the theoretical predictions. [144]

What is the role of alloying in these effects? Vieland[24] investigated the superconducting and structural transitions in the alloy $Nb_3(Sn_{1-x}Sb_x)$ with $0 < x \leqslant 0.15$. It turned out that alloying the Nb_3Sn compound lowers T_c, but hardly changes T_m. However, when small amounts of Sb are added (at $x = 0.15$), the value of c/a becomes larger than unity, whereas $c/a < 1$ for pure Nb_3Sn. Thus, in this case the reversal of the sign of $(c/a) - 1$ is due to the alloying. It is interesting to note that theory[25] also predicts a reversal of the sign of $(c/a) - 1$ in V_3Si when the latter is placed in a sufficiently strong magnetic field $H = 275$ kOe at $T = 17.4$ °K and
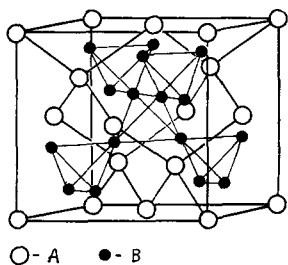
FIG. 6. Crystal structure of type C-15.

O- A ●- B

$H = 298$ kOe at $T = 0\,°K$.

In the $Nb_3(Sn_{1-x}Sb_x)$ alloys, the alloying of Nb_3Sn led to replacement of nonmetal atoms occupying bcc positions. What will be the effect of alloying on T_c and T_m if the atoms in the chains are replaced? The answer to this question was obtained in[26], where the superconducting and elastic properties of the alloys $(V_{1-x}Ti_x)_3Si$ were investigated $(0 < x < 0.10)$. When the compound V_3Si was alloyed, the decrease of T_c was accompanied by a shift of the minimum of the sound velocity v_{min} towards lower temperatures.

The available data on the effect of alloying on T_m and on the temperature dependences of the lattice moduli are far from sufficient to be able to draw any conclusions at present. In contrast to the question of the effect of alloying on T_c, for which there is an extensive literature (see[1]), the influence of alloying on T_m is the subject of only isolated studies. It should be noted that the correlation between T_c and T_m in alloyed compounds may turn out to be very indeterminate, for in addition to the changes that alloying produces in the lattice elastic properties that influence T_c, the superconducting temperature can also be changed by purely electronic transitions, for example by the interband scattering by impurities. However, a study of only the change of the elastic properties of alloyed A-15 compounds is of considerable interest, particularly in connection with the theoretical models considered in the last part of the review.

2. Laves phases

Laves phases are the most numerous groups of metallic compounds: by now about 270 binary compounds of this type are known.[27]

These compounds have a general chemical formula AB_2 and can belong to three different structure types—$MgNi_2$ (structure C-14), $MgCu_2$ (structure C-15) and $MgZn_2$(structure C-36). The largest number of binary Laves phases (~ 140) are of type C-15. The structure C-15 has cubic symmetry and belongs to space group $O_h^7 - Fd3m$. The next largest group is of type C-36 (112 compounds).[27] This structure has hexagonal symmetry and belongs to the space group $D_{6h}^4 - P6_3/mmc$. The remaining compounds have the C-14 structure, which, just as C-36, belongs to a hexagonal symmetry (space group $D_{6h}^4 - P6_3/mmc$) but, unlike the C-36 structure, contains 24 rather than 12 atoms in the unit cell.

The three structure types indicated above have one common element—tetrahedra of the atoms of sort B, forming a three-dimensional framework, in the voids of which are located the atoms of sort A (Figure 6 shows the C-15 structure).

The atoms that enter as components in these compounds are all metals of subgroups "a" of the periodic system (with the exception of mercury), and also Al, Pb, and Bi. There is no regularity whatever in the distribution of the A and B components among the indicated metals—both A and B components are encountered in all the subgroups (except IIIa and IVa).

The superconducting properties of only some of the compounds have been investigated, and 75 out of the 100 investigated compounds exhibit superconductivity (Table 1).[28,42,101,187] The superconductors with highest transition temperatures were those with A metals of groups III and IV (ZrV_2 ($T_c = 8.8\,°K$); $HfV_2(T_c = 8.7\,°K$); $LaOs_2(T_c = 8.9\,°K)$). In two out of the three examples listed above, the B-partner of these compounds is vanadium. However, in contrast to compounds with A-15 structure, where the niobium compounds have the highest T_c, no superconducting Laves phases with niobium were observed at all, let alone high-temperature ones. All the observed superconductors belong to two structure types, C-15 or C-14. So far, not a single superconductor with C-36 structure has been observed. It can be noted that T_c of the C-14 compounds is in most cases lower than that of the C-15 compounds. They include no high-temperature superconductors—the T_c of any binary Laves phase is lower than 10 °K. Recently, however, it was shown that the alloy $(Hf_{0.5}Zr_{0.5})V_2$ has $T_c = 10.1\,°K$ and relatively high critical fields (on the order of 230 kOe at $4.2\,°K$[29]).

The lattice properties of Laves-phase compounds turned out to be very interesting. In 1972, Lawson and Zachariasen observed at 120 °K a structural transition in the compound HfV_2, from cubic (type C-15) to body-centered orthorhombic (space group) $Imm2(C_{2v}^{20})$.[30] When the HfV_2 was cooled from 120 °K to 6 °K, its volume increased by as much as 0.35%. A similar structural transition was observed soon afterwards in ZrV_2 at 90–116.7 °K. There is a difference of opinion, however, with respect to the character of the transition in ZrV_2. While x-ray structure investigations show that ZrV_2, just like HfV_2, has at low temperatures a body-centered orthorhombic structure ($a = 5.22$, $b = 5.12$ and $c = 7.57$ Å),[31] according to Moncton's neutron-diffraction measurements[32] the low-temperature phase of ZrV_2 has not an orthorhombic but a rhombohedral structure without any changes whatever in the volume of the crystal. No structural transitions whatever were observed in TaV_2 at low temperatures, down to 4.2 °K.

Lawson and co-workers[33] have recently discovered a structural transition in one more compound with C-15 structure. This compound was $LaRu_2$, which exhibited at 30 °K a tetragonal distortion of the initial cubic structure with lattice parameters $\sqrt{2}a = 7.663$ Å and $c = 7.773$ Å. This transformation takes place without a change in the crystal volume.

TABLE 1. T_c in compounds of the Laves-phase type (the underscored values of T_c pertain to Laves phases with structure C-14; the crosses mark Laves phases whose superconducting properties were not investigated).

B₂ \ A	Be	Mg	Al	Zn	Ge	La	Lu	Bi	Hf	V	Tc	W	Re	Fe	Ru	Os	Co	Rh	Ir	Pd	Pt	Cu	Au	Mo
Na K Rb Cs								3.6 1.2 4.7															<1.0	
Be Mg Ca Sr Ba		<1.0	<1.0		<1.7	<1.0									6.4 6.2 6.0	6.1 5.7		<1.0 <1.0	<1.0 <1.0 <1.0	<1.0				
Al Pb Bi						<1.0																	1.2 1.8	
Sc Y La			<1.0 <1.0 3.2									4.2 1.8		2.2 2.4 4.4	4.6 3.7 8.9		<0.3	1.0 2.1 <1.0	0.7 1.6				
Ce Pr Nd Cd Tb Ho Er Lu Th U		<1.0										<4.2 <4.2 <4.2 <4.2 <4.2 5.0	<1.0	4.9 x x <1.2 0.9 3.5	x x 3.5 <1.0 <0.4		<0.3 x x x	<0.4 x x x	<1.0 x x <1.1 6.5 <0.3				
Ti Zr Hf	<1.0		<0.3 <0.1	<1.0						8.8 8.7	7.6 5.6	<0.03 <0.03	6.8 5.6	1.8	3.6 2.7	<1.0		4.1						<0.125 0.08
Ta Mo W Re Rh	<1.7 <1.7 <1.7 <1.7							1.9	<1.0															

Measurement of the temperature dependence of the resistivity of HfV_2, ZrV_2, and TaV_2 has shown that in the case of HfV_2 and ZrV_2 there are anomalies[11,34] in temperature regions that coincide with the temperature of the structural transition in HfV_2 and ZrV_2. At the same time, in TaV_2 (where no structural transition is observed), no singularities were seen in the temperature dependence of the resistivity. Anomalies in other physical properties of HfV_2 and ZrV_2 were observed in the temperature region 100–120 °K. Figure 7 shows the measured values of the specific heat, which exhibits a sharp peak between 105 and 128 °K in the case of HfV_2.[35] Anomalies were noted also in the behavior of the magnetic susceptibility of ZrV_2,[36] of the nuclear magnetic resonance in HfV_2,[37] and of the internal friction in ZrV_2 at low temperatures.[36] Very interesting results were obtained recently in experiments on ultrasound in polycrystalline HfV_2, ZrV_2, and TaV_2 samples.[38] These data are shown in Fig. 8. It is seen that the velocities of the longitudinal waves in HfV_2 and $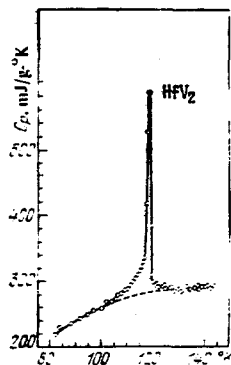ZrV_2$ first decrease when cooled from 300 °K, and then increase abruptly near 115 °K. At the same time, TaV_2 exhibits the increase, typical of metals, of the lattice rigidity with decreasing temperature. These data offer definite evidence of softening of the lattice moduli in ZrV_2 and HfV_2 in a temperature region close to the temperature of the structural transition. Thus, superconducting transition temperatures that are relatively high for this class of compounds were observed in those compounds in which softening of the lattice moduli at low temperatures and a structural transition occur, indicating that a connection exists between the high-temperature superconductivity and the lattice instability.

Since the anomalies of the resistivity and of longitudinal sound wave propagation, as well as the struc-
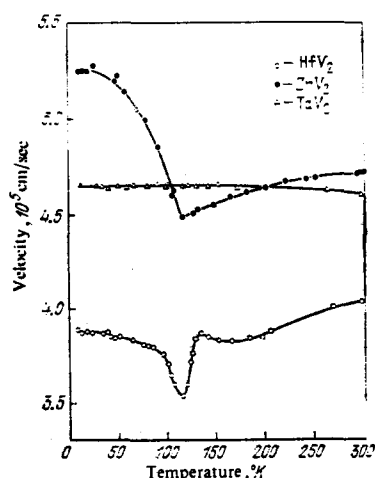

FIG. 7. Specific heat of the compound HfV_2.

FIG. 8. Temperature dependence of the velocity of longitudinal sound waves (10 MHz) in ZrV_2, HfV_2, and TaV_2.
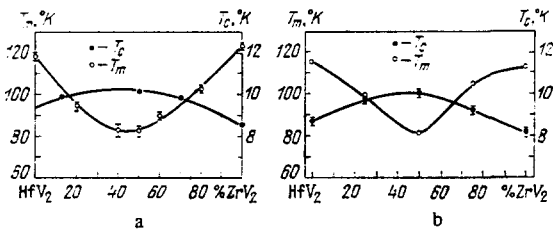
FIG. 9. Dependence of the superconducting transition tempera-
ture and of the start of the lattice instability in compounds
based on HfV_2 and ZrV_2.

FIG. 11. Change of temperature of the start of the lattice in-
stability in alloys based on HfV_2 and ZrV_2.

tural transition in ZrV_2 and HfV_2, are all observed at
the same temperature, no structural measurements
were made in the subsequent studies of ternary C-15
Laves-phase compounds based on ZrV_2 and HfV_2, and
the existence of the phase transition was deduced from
the anomaly of the resistivity or of the ultrasound prop-
agation velocity. Figure 9 shows plots of T_c against the
compositions in alloys of the HfV_2-ZrV_2 system as
taken from[39,40]. The figure shows also the variation
of the structural transition temperature T_m determined
from the temperature dependences of the resistivity
(Fig. 9a) and the ultrasound propagation velocity (Fig.
9b). In both cases, the maximum value of T_c corre-
sponds to a minimum of T_m. Thus, in high-temperature
superconductors of the Laves-phase type the tempera-
tures T_c and T_m exhibit a pronounced tendency to ap-
proach each other.

Replacement of the hafnium with tantalum in HfV_2
rapidly eliminates the resistivity anomaly. At 20% Ta,
the function $R(T)$ has practically no singularities.[11]
X-ray measurements have established that the vanish-
ing of the anomaly of the resistivity is accompanied by
a decrease in the degree of lattice distortion, which in
final analysis tends to zero at 15% Ta. The suppression
of the structural instability is even faster when the sec-
ond component of HfV_2, vanadium, is replaced by mo-
lybdenum.[11] It is interesting that in both cases no sig-
nificant change of T_c takes place in this range of alloys
in comparison with superconducting transition tempera-
ture of the initial compound HfV_2.

The question of the influence of alloying on the super-
conducting properties and lattice instability in HfV_2 and
ZrV_2 was considered in detail in[31]. In all cases there
was observed an inverse proportionality of T_c and T_m,
i.e., wherever the temperature of the start of the lat-
tice instability decreased, the superconducting transi-
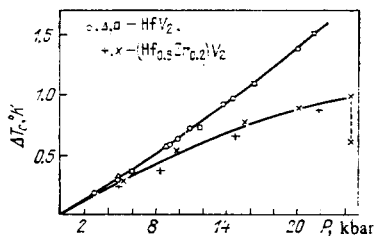tion temperature increased, and vice versa.
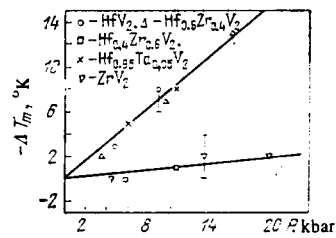
Interesting results were obtained in the study of the
influence of high pressure on the transition tempera-
ture and on the structural instability of cubic Laves
phases.[41] Simultaneously with measuring T_c, the
temperature dependence of the resistivity of the same
samples was measured. For the alloy systems HfV_2
-ZrV_2 and HfV_2- TaV_2 it was observed that the increase
of T_c with increasing pressure is accompanied by a de-
crease in the temperature at which the lattice becomes
unstable.

It turned out furthermore that even though T_c and T_m
of HfV_2 and of alloys rich in HfV_2 show strong depen-
dences on the pressure, these dependences become
much weaker when HfV_2 is alloyed with ZrV_2 (Figs.
10 and 11). Thus, in spite of the fact that both HfV_2
and ZrV_2 undergo structural transitions at low tempera-
ture and their elastic moduli soften, the stability of the
cubic phase of ZrV_2 is less sensitive to application of
pressure than HfV_2. It is possible that this difference
in the behavior of these compounds is due to differences
in the character of the structural instability. It can be
assumed on the basis of the pressure experiments that
the structural transition of ZrV_2 is not accompanied by
a noticeable change of volume. This agrees with neu-
tron-diffraction measurements, according to which the
transition in ZrV_2 is not from cubic to orthorhombic
but from cubic to rhombohedral lattice, and this transi-
tion is actually not accompanied by a change in vol-
ume.[32]

3. Compounds with CsCl (B-2) structure

Only three transition-metal compounds with CsCl
(B-2) structure have been observed (Fig. 12). These
are $TiRu(T_c = 1.07\,°K)$ $(T_c = 0.46\,°K)$[42] and $VRu(T_c$
$= 1.07\,°K)$.[43] Greatest interest among them attaches
to the compound VRu. According to the data of[44,45],
V and Ru form in a relatively narrow concentration in-
terval (near equi-atomic composition) alloys that pass
through the bcc, CsCl (cubic), CsCl (tetragonal), and

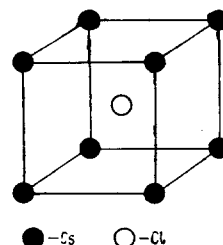FIG. 10. Pressure dependence of superconducting transition
of HfV_2 and of $(Hf_{0.8}Zr_{0.2})V_2$.

FIG. 12. Crystal structure of B-2
type (CsCl).

●—Cs   ○—Cl

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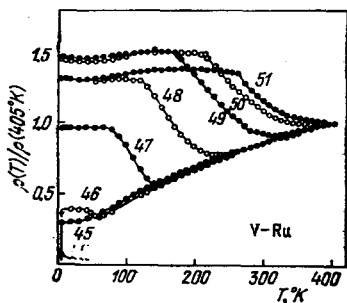Yu. A. Izyumov and É. Z. Kurmaev   33

FIG. 13. Temperature dependence of the resistivity of VRu alloys. The number on each curve indicates the Ru concentration in the alloy.

hcp structures.

Marezio and co-workers[46] observed a structural transition from CsCl (cubic) to CsCl (tetragonal) for samples of $V_{0.51}Ru_{0.49}$ and $V_{0.50}Ru_{0.50}$ in the temperature region 360–110 °K. Approximately one-third of the material in the $V_{0.50}Ru_{0.50}$ samples had a tetragonal structure at room temperature. With decreasing temperature, the tetragonal Bragg reflections increased in intensity, whereas the cubic reflections became weaker. Measurements have shown that the transition from the cubic to the tetragonal phase in ordered V-Ru alloys is accompanied by an increase in the volume of the lattice. For the $V_{0.50}Ru_{0.50}$ sample, this increase was from 0 to 1.4% on going from 360 °K to 300 °K, and subsequently remained unchanged down to 110 °K. It appears that the change of volume does not depend on composition, since a similar change (on the order of 1.5%) was observed for $V_{0.51}Ru_{0.49}$ at 110 °K.

The instability of the CsCl structure in the equi-atomic VRu alloy to changes in temperature is reflected also in the behavior of various physical properties. When the VRu alloy was cooled from 400 °K, a rapid increase of the resistivity, an abrupt drop of the susceptibility, and an increase of the Knight shift measured on the vanadium nuclei was observed.[43] A characteristic feature is that the temperature region of the anomalies of the physical properties coincides with the region of tetragonal distortion of the structure.[46] It is shown in[43] that the temperature region in which the anomalies noted above are observed is very sensitive to the composition of the alloy. With changing ruthenium concentration in the alloy, from 51 to 46%, i.e.,
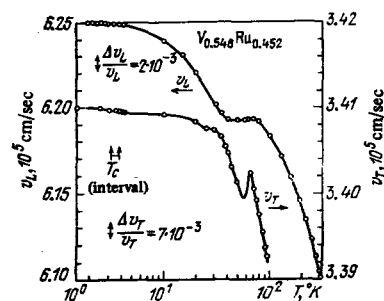

FIG. 14. Temperature dependence of the velocities v_L and v_T of the longitudinal and transverse sound waves in polycrystalline $V_{0.548}Ru_{0.452}$.
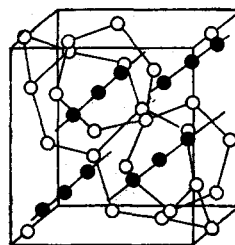

FIG. 15. Structure of β-U type (σ phase).

by merely 5%, the temperature of the observed jump of the resistivity drops from 300 to 50 °K (Fig. 13).

Interesting results were obtained recently by measuring the speed of sound in $V_{0.60}Ru_{0.40}$ $(T_c < 1$ °K$)$, $V_{0.548}Ru_{0.452}$ $(T_c \sim 4$ °K$)$ and $V_{0.51} \sim Ru_{0.49}$ $(T_c < 0.4$ °K$)$ at temperatures from 1 to 120 °K.[47] The change of the longitudinal-wave velocity with temperature in the samples $V_{0.60}Ru_{0.40}$ and $V_{0.51}Ru_{0.49}$ (which exhibit no superconductivity) is of the usual type, increasing monotonically by $\frac{1}{2}$ and 3% in the two samples, respectively, on cooling. The measured longitudinal and transverse sound velocities of $V_{0.548}Ru_{0.452}$ $(T_c = 4$ °K$)$ are shown in Fig. 14. The results show that near 55 °K there is an anomaly in the propagation of both the longitudinal and the transverse waves, thus demonstrating instability of the lattice.

Interesting data were obtained recently on the behavior of T_c and T_m in V-Ru compounds of near-equiatomic composition under hydrostatic pressure up to 21 kbar.[159, 160] It was observed that in the compound with composition $V_{0.54}Ru_{0.46}$ the structural transition is suppressed and the superconducting transition is enhanced by pressure. We note that a similar situation was observed for V_3Si (see Fig. 4). Complete suppression of the structural transition was observed at a certain critical pressure $P_{cr} = 14$ kbar. It is interesting that $\partial T_c/\partial P$ decreases at this very pressure. The pressure dependences of T_c and T_m turned out to be very sensitive to the compositions of these compounds.[48, 159, 160]

4. σ phases and compounds with α-Mn structure (A-12)

Compounds of the σ-phase type were observed in 50 binary systems in which both components are mostly transition elements.[28, 49] The σ-phase structure is isomorphic to the β-uranium structure (space group $P4nm$). The tetragonal lattice of this structure (Fig. 15) contains 30 atoms per unit cell.[30] A feature of the arrangement of the atoms in this structure is the presence of quasi-hexagonal grids (singled out by us in Fig. 15), which lie one on top of the other and are rotated 90° relative to one another. These grids are centered about atomic chains parallel to the tetragonal axis [001]. The distance between the atoms in the chain is equal to half the lattice parameter $(c/2)$.

As a rule, the A component of an AB compound (of the σ-phase type) can be only elements of groups situated to the left of the manganese group in the periodic system. The largest number of σ phases was observed in alloys whose A component was Nb or the B component was rhenium. The range of compositions for which σ phases were observed can fluctuate greatly, from A_4B
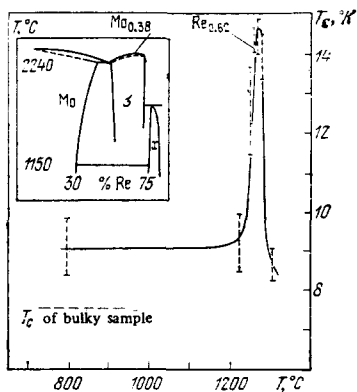
FIG. 16. Dependence of T_c on the settling temperature for the alloy $Mo_{0.38}Re_{0.62}$. The insert shows part of the Mo—Re phase diagram.

to AB_4.[49] It is reported that the component atoms are ordered in a number of compounds of this type in the alloys Cr–Fe,[51] Cr–Ru,[52] Cr–Os,[52] Nb–Al,[53] Ta–Al,[54] and others.

According to the data given in[28,42,102], 33 compounds of the σ-phase type were tested for superconductivity, and 25 were superconducting, with T_c exceeding 10 °K in two of them, $Mo_{0.3}Tc_{0.7}$ and $Mo_{0.38}Re_{0.62}$ (Table 2).[2]

The highest value, $T_c = 14.6$ °K, was obtained for the σ phase in the Mo—Re system. We note that the compound with the highest T_c ($Mo_{0.38}Re_{0.62}$) was synthesized by evaporation on a sapphire substrate heated to 1250 °C.[55] In a bulky sample of the same composition, prepared by ordinary arc melting, T_c did not exceed 6–7 °K.[55,56] The superconducting properties of an $MO_{0.38}Re_{0.62}$ sample obtained by sputtering turned out to be very sensitive to the settling temperature, which was regulated by heating the substrate. It is seen from Fig. 16 that the dependence of T_c on the settling temperature exhibits for this material a sharp maximum at 1250 °C.

The rise of T_c in film samples of the compound $Mo_{0.38}Re_{0.62}$ is attributed in[55] to the structural instability of the σ phase in the Mo—Re system, wherein at the settling temperature 1250 °C the σ phase with this composition is located near a boundary with a phase having a different structure (of the α-Mn type). It is interesting that the σ phase obtained in this manner has unit-cell dimensions different from the cell dimensions of the bulk material.[55]

About 20 transition-metal compounds crystallize with an α-Mn type structure (space group $T_3^d - I\,\overline{4}3m$). The components A of such compounds are transition metals of the start of the period (groups III–VI), and the components B are transition metals of the end of the period, predominantly from the manganese groups. The composition intervals in which compounds with structure α-Mn (A-12) are encountered are quite large,

[2] σ phases exist in a wide range of compositions in each binary system, and the T_c corresponding to each concrete composition is different in value. The table lists the highest T_c obtained for the σ phase of each binary system.

TABLE 2. Superconducting transition temperature in σ phases.

A \ B	Al	Mn Tc Re	Fe Ru Os	Co Rh Ir	Ni Pd Pt	Au
V Nb Ta	 <1.3 <1.02	× 6.26 × 2.5 1.4	× × 1.85 <1.2	× 4.04 9.8 2.35 1.2	× 2.0 4.01 × 1.0	 <1.2
Cr Mo W		× × 2.50 12 14.6 7.9 4.9	× 2.10 × × 7.0 5.05 5.12 4.4	× × 6.8 4.46		
Mn Tc Re	 <1.0	<4.2	× 6.55			
Zr		<4.2				<1.02
Hf		<4.2				

from 50 to 90 at.% of the component B.

The α-Mn structure is derived from the β-U structure (see Fig. 15). An α-Mn bcc cell is obtained if two β-U cells are deposited in such a way that the point 000 of the second cell is at the point $\frac{1}{2}$ $\frac{1}{2}$ 1 of the first cell; two atoms then coincide, so that α-Mn contains 58 atoms in the cell.[50]

The superconducting properties of 14 binary compounds of transition metals with structure α-Mn (A-12) were investigated. All turned out to be superconducting (Table 3[28,42]). The highest T_c (~ 9–10. 5 °K) were observed in compounds whose A components are Nb, Mo, and W, and the B components are T_c and Re. It should be noted that practically no studies were made of the physical properties of these compounds.

B. Covalent-ionic compounds

5. Compounds with NaCl (B-1) structure

The crystal structure of compounds of this class, with chemical formula AB, has the following singularities: The atoms of the metal A form a cubic face-centered lattice, and the non-metal atoms B occupy octahedral voids. The result is a structure identical with that of NaCl (B-1), i.e., two cubic face-centered imbedded in each other (Fig. 17). Each metal atom is surrounded by an octahedron of atoms of the other type, and vice versa, i.e., the coordinations of the different atoms are identical.

The atoms A are usually transition metals of subgroups III, IV, V, and VI of the periodic system, and the atoms B are nontransition elements of the same subgroups. Most considered compounds have a variable composition, i.e., deviations from stoichiometry
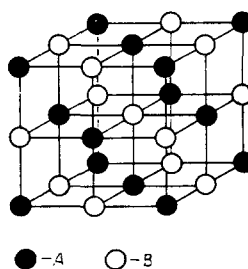

FIG. 17. Structure of B-1 (NaCl) type.

●–A   ○–B

TABLE 3. T_c in compounds with α-Mn structure.

A \ B	Tc	Re	Os	Pd
Sc	×	2.2		
Ti	×	6.6		
Zr	9.7	7.40		
Hf	×	5.86		
Nb	10.5	9.7	2.86	2.47
Ta	×	6.78	1.95	
Mo		9.89		
W		9.0		
Al		3.35		

TABLE 5. T_c in compounds with NaCl structure.

B \ A	Sc	Y	La	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W	Re
B						3.4	3.1						
C	<1.38	<1.38		3.42	<0.05	<1.20	0.03	12	10.35		14.3	10.0	3.4
N	<1.38	<1.4	1.35	5.49	10.7	8.83	8.5	17.3	6.5	<1.28	5.0	<1.38	
P			<1.68										
Sb		<1.02	<1.02										
O				2.0			<0.3	1.39					
S	<0.33	1.9	0.87		3.3								
Se	<0.33	2.5	1.02										
Te		2.05	1.48										

in either direction can be observed within the limits of one and the same crystal structure (NaCl in our case). For example, a compound of the TiO_x type has a homogeneity range $x = 0.7–1.25$. When referring to a compound with variable compositions, we shall henceforth use a notation that reflects exactly the degree of completeness of the metallic or metalloidal sublattice, for example, we shall write $Ti_{0.8}O_{1.0}$ when the metalloid sublattice is completely occupied by oxygen, and the titanium atoms in the metallic sublattice occupy approximately 80% of the places.

The physical properties of compounds with NaCl structure cannot be understood without taking into account the fact that they always contain a certain number of vacancies. In fact, a comparison of the pycnometric and calculated (with allowance for the lattice parameter) densities has shown that even in the series of stoichiometric compounds of this type (see Table 4), compiled from the data of[57,58] there can exist simultaneously both the metal and nonmetal atoms, in a very wide range of compositions. It turns out that the equiatomic TiO corresponds not to the formula $Ti_{1.0}O_{1.0}$, but to $Ti_{0.85}O_{0.85}$, or that NbO corresponds to $Nb_{0.75}O_{0.75}$, meaning in fact 15 and 25% of vacancies respectively in both sublattices.

As a rule, the vacancies are distributed over the lattice randomly, but structural investigations have shown that at certain compositions of these compounds an ordering of the vacancies may be observed, with formation of a superstructure both in the metalloidal sublattice ($Ti_{1.0}O_{0.7}$[59], $V_{1.0}C_{0.875}$, $V_{1.0}C_{0.84}$[60-64], $V_{1.0}N_{0.75}$[65], $Nb_{1.0}C_{0.75}$, $Ta_{1.0}C_{0.76}$[66]), and in the metallic one ($V_{0.783}O_{1.0}$[67,68]). In the compounds $Ti_{0.85}O_{0.85}$ and $Nb_{0.75}$ and $O_{0.75}$, ordering of the vacancies was observed in both sublattices.[69]

We proceed now to consider the superconducting properties of transition-metal compounds with NaCl structure. Out of the 40 investigated compounds, 26

turn out to be superconducting.[70-87,180] In six of them T_c exceeds 10 °K (Table 5). These high-temperature superconductors are made up of transition metals of groups IV, V, and VI, the compounds of the 4d and 5d metals (Zr, Nb, Mo, Ta, W) having higher T_c than those of 3d metals (Ti, V, Cr). On the other hand, it must be noted that the group of the second partners of the compounds of these metals, which are favorable to high-temperature superconductivity, reduces in essence to two elements, carbon and nitrogen, so that the number of combinations is greatly limited in the search for new high-temperature superconductors.

Just as in the A-15 structures, the superconducting properties of compounds with NaCl structure turned out to be very sensitive to deviations from stoichiometry.[88-92]. Figure 18 shows experimental data on T_c in Nb carbide and Ti nitride,[88-92] which show that T_c decreases with decreasing carbon-metal or nitrogen/metal ratio.

The first attempts to alloy transition-metal compounds with NaCl structure yielded promising results. In 1953 Matthias obtained a superconducting transition temperature 17.8 °K in the NbC–NbN system.[90] In the succeeding 14 years this was one of the highest T_c among all the investigated superconductors.

When a compound AB is alloyed with a compound A'B', three cases are possible: a) replacement of the atoms A by the atoms A' with the sort of atoms B un-

TABLE 4. Vacancy concentration in compounds of stoichiometric composition with NaCl structure (in each of the sublattices).

Compound	Vacancy concentration,%	Compound	Vacancy concentration,%	Compound	Vacancy concentration,%
TiC	2.0	TiN	4.0	VO	11—15
ZrC	3.5	ZrN	3.5	NbO	25
HfC	4.0	VN	1.0	ZrS	20
VC	8.5	NbN	13	ZrSe	16
NbC	0.5—3.0	TaN	2.0	YS	10
TaC	0.5	TiO	15		

The exact compositions of the compounds are not reported in[57-58], the data of which were used to compile the table.
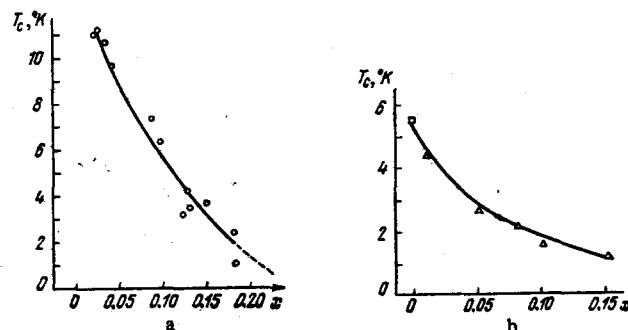
FIG. 18. Influence of deviations from stoichiometry on the superconducting properties of the transition-metal compounds $Nb_{1.0}C_{1-x}$ (a) and $Ti_{1.0}Ni_{1-x}$ (b) with NaCl structure.
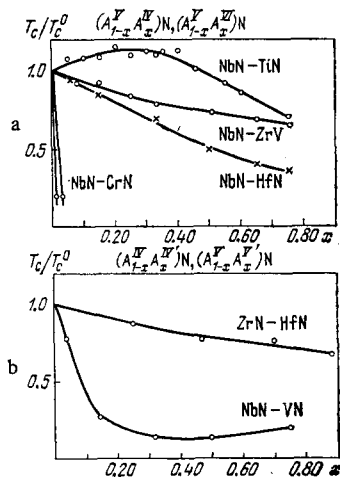
FIG. 19. Plot of T_c/T_c^0 against the alloy composition $(A_{1-x}A_x^{\prime})N$. A and A′ in Fig. a are transition metals from different groups of the periodic system; A and A′ in Fig. b are transition metals from the same group.

changed—(A – A′)B (Fig. 19); b) replacement of the atoms B with atoms B′ with the sort atoms A unchanged—A(B – B′); c) replacement of both sorts of atoms—(A – A′)(B – B′).

An examination of the concentration dependence of the relative transition temperature $T_c/T_c^0 = t$ (where T_c is the superconducting transition temperature of the initial compound) in all the foregoing three cases[71,88,91,93,94] leads to the following conclusions:

Replacement of a $4d$ metal (A) by a $5d$ metal (A′) has little effect on the superconducting transition temperature in the (A – A′)B system. To the contrary, when the $4d$ metal is replaced by a $3d$ metal the transition temperature decreases rapidly. When the B atoms are replaced by B′ in the A(B – B′) system the situation for compounds of transition metals of the V group, V(C–N) and Nb(C–N), is quite favorable and $t > 1$ for a large range of concentrations. For compounds of the transition metals of group IV (Ti(C–N), Hf(C–N)), to the contrary, substitution of the nonmetal atoms greatly lowers the temperature of the superconducting transition, and t drops sharply.

For alloys of the system (A–A′)(B–B′) the decisive influence is exerted by substitution of the transition metals. Just as in the case of the (A–A′)B alloys, replacement of a $4d$ metal by a $3d$ metal makes the superconducting properties of the material much worse.

Concluding the examination of the superconducting properties of transition-metal compounds with NaCl structure and their alloys, we can note that those compounds for which high T_c were obtained by alloying are based mainly on the NbN compound. The superconducting transition temperatures in these ternary systems (~ 17.8–18.0 °K) and in the pure compound NbN (17.0–17.3 °K) are very close in magnitude. Further attempts at alloying the most "successful" ternary alloy $(NbN)_{0.75}(NbC)_{0.25}$, which has $T_c = 17.8$ °K, with various additives (TiN, TiC, HfN, HfC, ZrN, VN)[91] yielded no significant positive results. On the other hand, we

note that $T_c = 17.3$ °K was obtained for a not strictly stoichiometric composition of the NbN compound. It therefore becomes obvious that further attempts to improve the superconducting properties of compounds with NaCl structure should not be limited to alloying alone. Until compounds of stoichiometric compositions are obtained, the inherent possibilities of pure compounds cannot be regarded as exhausted.

If we plot the superconducting transition temperature against the electron density of the compound, then we note easily that the most favorable for high-temperatures superconductivity are two values of the electron density, $N_e = 4.5$ and $N_e = 5.0$ electrons/atom. The first value holds for nitrides of transition metals of group IV (ZrN, HfN) and carbides of transition metals of group V (NbC, TaC). Most of them have T_c on the order of 8–10 °K. The second value corresponds to nitrides of transition metals of group V (VN, NbN) and carbides of transition metals of group IV (MoC, WC) with values $T_c = 8.5–17.3$ °K.

Examination of the other physical properties (electronic specific heat, γ paramagnetic susceptibility χ[79,82,95]) as functions of the electron density shows that high values of T_c are not necessarily accompanied by increased values of γ and χ. For example, the value of γ in the compound TiO exceeds the value in TiN, whereas the superconducting temperature of TiN, to the contrary, is 2.5 times higher than that of TiO. Again, just as in compounds with A-15 structures, a significant difference can be observed between the behavior of γ and χ for compounds of vanadium and niobium. For example, at high T_c (~ 17 °K), relatively low values of the electronic specific heat and of the magnetic susceptibility of NbN are observed, whereas the situation is reversed for VN($T_c = 8.5$ °K).

Self-consistent calculations of the electron-energy spectrum were carried out for the following compounds: TiC[103], VC[104], NbC[105], NbN[106], TiN, TiO, VN, VO[163]. From an examination of the results of these studies we can draw the following general conclusions on the electron-energy spectrum of the considered compounds. Regardless of the type of metal atom (Ti, V, Nb) and of the metalloid atom (C, N), three main bands can be separated in the occupied part of the energy spectrum. In increasing order of energy, these bands are populated by $2s$, $2p$ and nd electrons. The energy separation of the $2s$ and $2p$ bands coincides almost exactly with the separation of the energies of the $2s$ and $2p$ levels of the free atoms of the nontransition element.[107,108] The band with highest energy is the nd band, the electrons of which are apparently responsible for the superconducting properties of these compounds. In all the cases listed above, self-consistent calculations have shown a certain transport of electrons from the metal atoms to the nonmetal atoms.

All the self-consistent calculations of the electron-energy spectrum, referred to above, pertain to compounds of stoichiometric composition with complete occupation of the atoms in both sublattices. Yet the results of Table 4 show that even compounds with stoichiometric composition always contain a certain num-
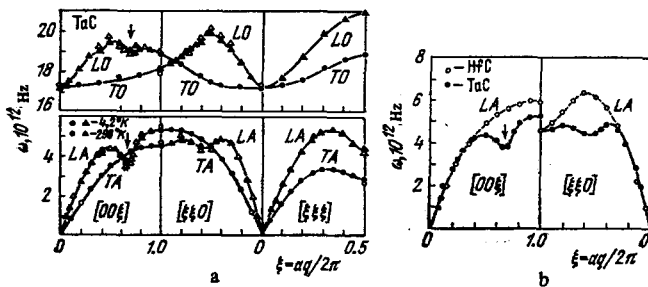
FIG. 20. Dispersion curves of the phonon spectrum $\omega(k)$ of the compounds TaC (a) and HfC (b).

ber of vacancies. In the case of deviations from stoichiometry, the number of vacancies increases appreciably. This raises the question of the applicability of the conclusions concerning the electronic structure of complex compounds of stoichiometric composition to the actually existing stoichiometric and nonstoichiometric compounds with vacancies.

Gel'd and his co-workers[109, 110] advanced the hypothesis that in nonstoichiometric carbides of transition metals the vacancies in the carbon sublattice can be regarded as a perturbation of the electronic state of the crystal, leading to formation of energy levels. At vacancy concentrations on the order of 25%, vacancies separated from one another by a distance on the order of the lattice parameters appear, and here, in the authors' opinion, one can expect them to become ordered, and the local levels to be transformed into an energy band. However, no actual calculations of the spectrum in this model were made.

We proceed now to a discussion of the properties of compounds of transition metals with NaCl structure. We consider first the results of neutron-diffraction investigation of the phonon spectra of the compounds ZrC, $Nb_{1.0}C_{0.97}$, $Nb_{1.0}C_{0.76}$, HfC and TaC, which were carried out by Smith.[111, 112] Figure 20 shows the dispersion curves of the phonon spectrum $\omega(k)$ for the stoichiometric compounds of TaC and HfC, which differ in their superconducting properties (T_c of TaC and of HfC are ~ 10 °K and ~ 1 °K, respectively). The most interesting is that anomalies of the longitudinal and acoustic modes were observed in the high-temperature superconductor TaC near the boundary of the band (marked by the arrow). At the same time these anomalies do not occur in nonsuperconducting HfC.

The spectra shown in Fig. 20b were obtained at room temperature. In connection with the correlation of the observed anomalies of the phonon spectra with the superconducting properties, it was of interest to perform low-temperature measurements. For the TaC compounds, these measurements were made at 4.2 °K. Figure 20a shows the low-temperature data together with the spectra obtained at room temperature. We see that lowering the temperature does not lead to any noticeable changes in the phonon spectra.

The influence of deviations from stoichiometry on the structure of the phonon spectra was considered by Smith with NbC as an example.[112] In almost-stoi-

chiometric niobium carbide, $Nb_{1.0}C_{0.97}$, just as in the compound TaC, a softening of the longitudinal acoustic and optical modes was observed. At negative deviation from stoichiometry ($Nb_{1.0}C_{0.76}$) these anomalies vanished and the spectrum became similar to that of HfC or ZrC.[112] It is remarkable that $Nb_{1.0}C_{0.97}$, just as TaC, is a high-temperature superconductor with T_c ~ 11 °K while $Nb_{1.0}C_{0.76}$, like HfC and ZrC, is not superconducting down to 1 °K. Thus, the connection between the high-temperature superconductivity and the softening of the phonon modes, and hence with the lattice instability, is further confirmed.

Interesting information on the distribution of the phonon density of states was obtained by Zeller from experiments on tunneling in TaC.[113] He observed a strong nonmonotonic dependence of the second derivative of the tunnel characteristic d^2I/dV^2 in the region of the acoustic phonons. At the same time, in the region of optical phonons this dependence is very weakly pronounced. Zeller concludes from this fact that the main contribution to the electron-phonon interaction parameter is made by the acoustic phonons.

An attempt to explain the tremendous differences between T_c of the carbides NbC and TaC, on the one hand, and ZrC and HfC, on the other, as well as to explain the role of the lattice anomalies described above, was recently made by Weber on the basis of McMillan's formula (1).

Weber's calculations[114] based on McMillan's formulas (1) and (3) are given in Table 6 for several carbides. The value of λ was determined with formula (1) from data on T_c and on the Debye temperature; N(0) was determined from measurements of the electronic specific heat (with allowance for the corrections for the electron-phonon interaction); $\langle\omega^2\rangle$ was calculated from the dispersion curves of the phonon spectrum. Then, using formula (3), it is possible to determine $\langle I^2\rangle$. As seen from the table, the quantity $N(0)\langle I^2\rangle$ is not constant for carbides, despite the McMillan–Hopfield rule. Its values for carbide with 8 and 9 valence electrons per cell differ by a factor of two. One of the reasons, as noted by Weber,[114] may be the overlap of the d-functions of neighboring atoms, which was completely neglected in Hopfield's formula (6).

An important conclusion of these calculations is that it is impossible to attribute the large difference of T_c of the two carbide groups to softening of the phonon spectrum in the short-wave region of TaC and NbC. As seen from the data of Table 6, the difference between $\langle\omega^2\rangle$ of the compounds TaC and NbC, which have a pho-

TABLE 6. Values of $\langle I^2\rangle$ calculated by Weber for carbides from McMillan's formulas.

Compound	T_c, °K	λ	$N(0)$, (eV/atom)$^{-1}$	$\sqrt{\langle\omega^2\rangle}$, °K	$\langle I^2\rangle$, eV^2 Å^{-2}	$N(0)\langle I^2\rangle$, eV·Å^{-2}
ZrC	<0.25	0.3	0.14	295	30	4.2
HfC	<0.25	0.3	0.14	220	33	4.6
NbC	11.1	0.7	0.40	268	21	8.3
TaC	10.3	0.7	0.40	196	22	8.6

non anomaly, and ZrC and HfC, which do not have the anomaly, is only 30%.

A similar conclusion is arrived at in[115], where the authors calculated directly by the augmented plane wave method the matrix elements $\langle I^2 \rangle$ for the atomic components in the carbides NbC, TaC, and HfC, and then used the Phillips formula[117] for λ in a two-component system:

$$\lambda = \frac{[N(0)\langle I^2\rangle]_A}{M_A \langle \omega^2\rangle_A} + \frac{[N(0)\langle I^2\rangle]_B}{M_B \langle \omega^2\rangle_B}, \qquad (10)$$

where A and B stand for the metallic and nonmetallic atoms in a compound with chemical formula AB. This resolution of λ is valid only in the case of a large mass difference, as is the case in the carbides $(M_A \gg M_B)$. By virtue of this inequality, the heavy metallic atoms vibrate mainly in the acoustic frequency band, while the light carbon atoms vibrate in the optical band. In the same approximation, it turns out that $\langle \omega^2\rangle_A \sim 1/M_A$ and $\langle \omega^2\rangle_B \sim 1/M_B$, so that the denominators in (10) do not depend on the mass and are of the same order of magnitude. A numerical calculation by the augmented plane wave method has shown that the first term, connected with the vibration of the metallic atom, predominates in the expression for λ. This agrees with Zeller's tunnel measurements, which have shown that λ is determined mainly by the interaction of the electrons with the acoustic phonons. Calculation of λ from first principles led to values of T_c for NbC and TaC in good agreement with experiment (within 10%).

We find thus that the high T_c of NbC and TaC are not connected with the mode-softening mechanism, and more readily the phonon anomalies and the high T_c are the consequence of the large electron-lattice interaction.

6. Sesquicarbides

In this section we consider a group of carbides with chemical formula A_2C_3, in which the A component is the transition metal Y, a lanthanide (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, and Ho) or an actinide (Th, U. Np, Pu). These compounds have a structure of the type Pu_2C_3 and belong to the space group T_d^6-$I\bar{4}3d$.[118,119] A_2C_3 compounds with Pu_2C_3 structure have a complicated unit cell containing 16 atoms of sort A and 24 carbon atoms.
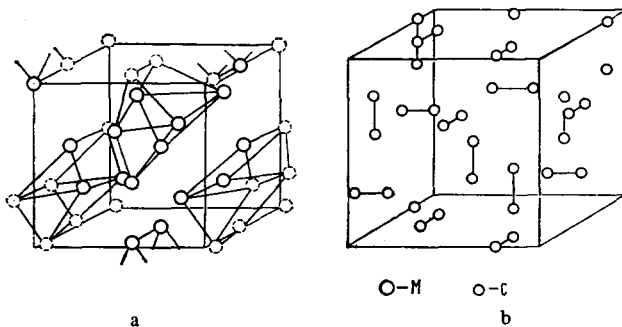

O—M   o—c

a   b

FIG. 21. Structure of Pu_2C_3 type: the sublattice made up of the metal atoms (a) and the carbon sublattice (b).

TABLE 7. T_c in sesquicarbides.

Compound	$Y_2C_{3.48}$ *	$La_2C_{2.70}$	Th_2C_3 *	$(Y_{0.7}Th_{0.3})_2C_{3.1}$ *
T, °K	11.5	11.0	4.1	17.0

*These compounds were synthesized by a high-pressure technique.

In the sublattice made up of the atoms A (Fig. 21) one can single out an atomic polyhedron made up of six tetrahedra. Translation of this polyhedron using three symmetry operations yields the positions of all the metal atoms in the Pu_2C_3 structure. The carbon atoms are pairwise disposed and separated by a gap amounting to only two tenths of the lattice parameter. Characteristically, the pairs of carbon atoms are oriented parallel to the coordinate axes. According to Schubert,[50] out of the eight metal atoms occupying the vertices of the cube, seven are shifted by 0.05 lattice parameter and actually belong to other unit cell (see Fig. 21a).

Most of the considered carbides are produced by ordinary arc melting of the A-elements and graphite, however, the sesquicarbides of V and Th and the ternary compounds on their basis, with Pu_2C_3 structure, cannot be obtained by the ordinary fusion technique. Their preparation calls for special conditions, under which the high-temperature processing of the fused components (1200–1500 °C) is effected at high pressure (15–30 kbar).[120–123]

In spite of the fact that the class of sesquicarbides is quite representative, the superconducting properties of only a limited number of pure compounds were investigated—V_2C_3, Th_2C_3, and La_2C_3.[121,124,125] In two of the three foregoing compounds T_c turned out to be higher than 10 °K (Table 7). This has immediately attracted attention to the study of the superconducting properties of the sesquicarbides, and high-temperature superconductivity was soon observed[122,126] in ternary compounds based on Y_2C_3 and La_2C_3 ($T_c \sim 14$–17 °K; see Table 7).

Further investigations have shown that, just as in carbides of transition metals with NaCl structure, the superconducting properties of sesquicarbides are very sensitive to deviations from stoichiometry. The maximal T_c are observed as a rule near stoichiometric compositions.[12] The electron density of the compounds Y_2C_3, La_2C_3, and Th_2C_3 is 3.6 electrons/atom, i.e., less than in the transition-metal carbides with NaCl structure.

In contrast to compounds with A-15 and B-1 (NaCl) structure, the T_c in alloys of sesquicarbides greatly exceed those in the initial compounds (see Table 7). Detailed investigations were therefore undertaken of the influence of alloying on the superconducting properties of sesquicarbides of Y and Th.[122,124] An analysis of these data leads to the conclusion that the improvement of the superconducting properties of Th_2C_3 is attained when the alloying elements have an unfilled or a nearly-filled f shell (La, Er, Lu).

Alloying with transition and nontransition elements was investigated in[122]. The initial compound was Y_2C_3 and the additives were transition d-metals (Ti, V, Cr, Nb, Mo, Ru, W) and nontransition elements predominantly of group IV (Si, Ge, Sn, Bi). On the whole, alloying with these elements produces a positive effect (for example, when W is used for alloying in a ratio $W/Y = 1/9$, the value of T_c increases approximately 2.5 times), but in a number of cases (when In or Zn is added), the ternary alloy becomes non-superconducting down to 4 °K.

Very interesting results were obtained in investigations of solid solutions of the sesquicarbides V_2C_3 and Th_2C_3. We have already noted above (see Table 7) that it is precisely among the ternary alloys of the $Y_2C_3-Th_2C_3$ system that the highest-temperature superconductors of all the sesquicarbides were observed. The body-centered cubic structure (of the Pu_2C_3 type), which is favorable for superconductivity in these compounds, is formed only under the combined action of high pressure and high temperatures. When the same samples are synthesized by usual arc melting, it was observed that the ternary $V_2C_3-Th_2C_3$ alloys have a body-centered tetragonal lattice and are not superconducting down to 4 °K.

Thus, even though under definite synthesis conditions one can obtain either bcc or bct structures, no direct transition from one structure to the other is observed in these alloys. Nonetheless, an analysis of the geometric relations between the tetragonal and cubic carbide phases shows[127] that such a transition can take place.

The foregoing material shows that sesquicarbides are very interesting research objects. Unfortunately, the physical properties of these compounds have hardly been studied. Particular interest attaches to the measurements of the magnetic susceptibility in alloys with rare-earths added, for the purpose of determining the magnetic moments in those cases when the alloying lowers T_c. On the other hand, it is necessary to search for the structural transition from the bcc to the bct structure and to investigate the phonon spectrum of the indicated compounds.

7. Chalcogenides

An unexpected recent superconductivity discovery is the high-temperature superconductivity in ternary chal-
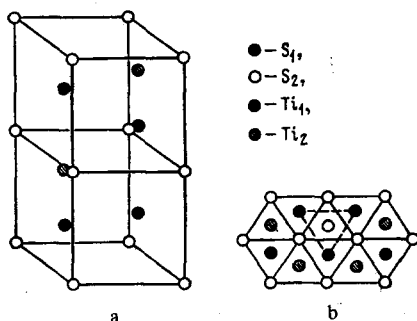

FIG. 22. Structure of Ti_3S_4 type.

cogendies of transition metals. In 1972 Matthias and co-workers[128] synthesized the compound $Li_xTi_{1.1}S_2$ $(0.1 < x \leqslant 0.3)$ with hexagonal structure of the Ti_3S_4 type and have found in it $T_c = 10-13$ °K. This is the first of the high-temperature noncubic superconductors. An interesting feature of this ternary compound is that none of its binary components, Li–S, Ti–Ti, or Ti–S is superconducting above 1 °K.

The Ti_3S_4 structure is of the space group Pt_3/mmc.[129] The sulfur atom in this structure (Fig. 22) occupy alternately two nonequivalent series of positions, in alternating hexagonal (S_1) and cubic (S_2) close packing. The layer of titanium atoms is at the center of the regular octahedra made up of the sulfur atoms ($3S_1 + 3S_2$) (Fig. 22b). Whereas the sites of type Ti_1 are fully populated, the sites of type Ti_2 are only partly occupied, not more than half of them.

Thus, one of the characteristic structural features of the compound $Li_xTi_{1.1}S_2$ is the presence of layers of metal atoms. This compound can nevertheless not be included in the known class of layered alkali-metal compounds synthesized on the basis MoS_2 (Na_xMoS_2, K_xMoS_2, and others).[131] Whereas in layered compounds there is practically no interaction between layers, in compounds with Ti_3S_4 structure the metal atoms of type Ti_2 from the partly filled layer interconnect the completely filled layers of atoms of type Ti_1, like "bridges," and thus ensure their interaction.

One of the important attributes of the compound $Li_xTi_{1.1}S_2$ is its instability in the temperature range 77–600 °K. First, after the synthesis of the indicated compound, the measurements have revealed high values of T_c ($T_c \sim 10-13$ °K), but then, after these temperatures were kept several hours at room temperature, T_c decreased by several degrees. After a week's delay, the superconductivity of the sample became even worse. A second annealing of the sample at 750 °C restored the superconductivity fully. On the other hand, if the sample was cooled immediately after its synthesis to helium temperature, then the high-temperature superconductivity was preserved for a long time. Whether the observed instability has a structural character is not yet clear, but its discovery cannot be disregarded. In Matthias's opinion, it is necessary to return to the study of that large number of compounds that previously exhibited poor superconducting properties, possibly because they lost their stability in the time between the synthesis and the measurements.[132]

Another representative of ternary chalcogenides of transition metals with high-temperature syperconductivity is the class of compounds with the general formula $A_xNo_3S_4$ (where A = Li, Na, Mg, Ca, Sr, Ba, Sc, Y, Cr, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, In, Tl, Sn, Pb).

From among the 21 compounds of this class, only nine were superconducting. Among these, the compounds whose A-component was Mg, Sc, and Y had low values of T_c.[133] More interesting turned out to be the superconducting properties of the compounds with heavier A-components (A = Cu, Ag, Zn, Cd, Sn, Pb), half of which had high-temperature superconductivity with $T_c = 10-15$ °K (Table 8) and high critical fields.[4] These

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TABLE 8. Superconducting properties of ternary Mo sulfides.

Compound	T_c °K	Lattice parameter, A		Compound	T_c °K	Lattice parameter, A	
		a	c			a	c
$Mo_{4.5}Cu_{1.5}S_6$	10.9—10.8	9.63	10.18	Mo_5SnS_6	11.3—10.9	9.19	11.34
Mo_4CuS_5	11.0—9.7	—	—	Mo_6SnS_7	13.0—12.6	—	—
$Mo_{4.8}Ag_{1.2}S_6$	8.9—8.4	9.32	10.83	$Mo_{5.1}Pb_{0.9}S_6$	13.2—12.5	9.20	11.43
Mo_5CdS_6	2.4—2.3	9.44	10.72	Mo_6PbS_7	14.0—13.6	—	—
Mo_5ZnS_6	3.0—2.7	9.54	10.28	$Mo_6Pb_{0.9}S_{7.5}$	15.2	—	—
$Mo_5Mg_{0.9}S_6$	2.5—2.4	9.49	10.55				

compounds have a rhombohedral structure of the type Mo_3Se_4 (space group $C_{3i}^5 - R\bar{3}$). The sulfur atoms are at vertices of distorted cube, every fourth of which contains the A-atom (or an octahedron made up of the Mo atoms) (Fig. 23).

The superconducting transition temperature is shown in Table 8, which is compiled from the data of[135,136]. It is seen from it that the highest values of T_c are observed in compounds in which the A-component is the transition element Sn, Pb, or Cu. Results of measurements of the magnetic susceptibilities of $CuMo_4S_5$, $PbMo_6S_7$, and $SnMo_6S_7$ are reported in[136]. According to these data, the electronic-state densities at the Fermi level of these compounds have rather moderate values.

However, measurements of the electronic heat capacity of the compounds $AgMo_4S_5$, $PbMo_6S_7$, and $SnMo_5S_6$, given in[137], have shown that the indicated ternary molybdenum sulfides have very high values of γ, exceeding in some case the corresponding values in high-temperature superconductors with A-15 structure.

Lawson has recently observed a structural transition in a number of ternary molybdenum sulfides.[138] The compounds $CuMo_4S_5$ ($T_c = 10.5$ °K) and $CoMo_3S_4$ (T_c was not measured) undergo transitions from the rhombohedral to the orthorhombic structure at temperatures 260 and 220 °K, respectively (Table 9). Thus, in this system of superconductors, too, a structural instability is observed and manifests itself in the form of a transition from a rhombohedral to an orthorhombic structure.

Coming close to the chalcogenide group are certain oxides. Usually oxygen compounds of transition metals do not reveal high T_c. Prior to 1973, the highest T_c reported for this class of materials was 6—7 °K for $Rb_{0.2}WO_3$.[139] In 1937, Johnston and co-workers[140] synthesized the compound $Li_xTi_{3-x}O_4$ ($0.8 \le x \le 1.33$), which had $T_c = 0$—13.7 °K, i.e., the first oxygen com-
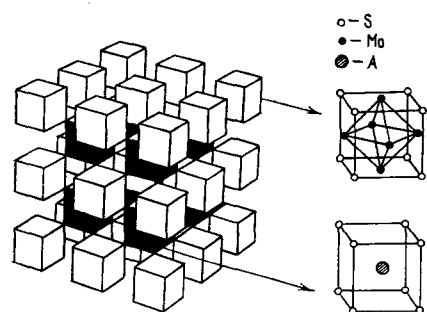

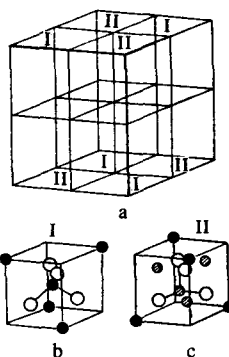FIG. 23. Structure of compounds of the $A_xMo_3S_4$ type.

FIG. 24. Structure of spinel type.

pound with high-temperature superconductivity.

The compound $Li_xTi_{3-x}O_4$ ($0.8 \le x \le 1.33$) crystallizes with a structure of the spinel ($MgAl_2O_4$) type (space group $H1_1 - Fd3m$). The spinel structure of an AB_2O_4 compound is very complicated and is usually subdivided into eight simpler structural elements—octants (Fig. 24a), half of which (octants of type I; Fig. 24b) contain A-cations in tetrahedral coordination, and in the remainder (octants of type II; Fix. 24c) the B-cations are in octahedral coordination, although the octahedra made up of the oxygen atoms go outside the boundaries of one octant.

It is interesting to note that an fcc structure of spinel type was hitherto regarded as unfavorable for superconductivity. From among the 200 known spinel compounds, only three were superconducting: $CuRh_2S_4$, CuV_2S_4, and $CuRh_2Se_4$, with $T_c = 4.8$, 4.5, and 3.5 °K, respectively.[141]

One of the features of the spinel phase in the Li–Ti–O system is that its homogeneity region includes both dielectrics ($Li_{1.3}Ti_{1.7}O_4$) and compounds with metallic conductivity ($Li_{1.0}Ti_2O_4$). Thus, the compound $Li_{1.0}Ti_2O_4$, for which the highest T_c was recorded (13.7 °K), is in the vicinity of spinel compositions at which a metal–insulator transition is observed.

3. HIGH-TEMPERATURE SUPERCONDUCTOR AND LATTICE INSTABILITY OF THE COMPOUNDS

8. Comparison of the superconductivity in various crystalline structures

8.1. Symmetry. It was considered in the literature for a long time that the most favorable for high-temperature superconductivity is cubic symmetry of the crystal lattice. The latest research has shown, however,

TABLE 9. T_c and T_m in ternary Mo sulfides.

Compound	T_m, °K	T_c, °K	Lattice parameter, A	
			Rhombohedral structure, 300 °K	Orthorhombic structure, 6 °K
Mo_4CuS_4	260	10.5	$a = 9.63$ $c = 10.21$	$a = 9.40$ $b = 16.98$ $c = 10.16$
Mo_3CoS_4	220	—	$a = 9.57$ $c = 10.15$	$a = 9.42$ $b = 17.11$ $c = 10.12$

TABLE 10. Comparison of T_c in various structures.

Structure type	Symmetry	Maximum T_c, °K	T_c (°K) of the compound components
A-15	Cubic	23.2 — Nb$_3$Ge	Nb : 9.2; Ge : 5.4
C-15	"	8.9 — LaOs$_2$	La : 5.9; Os : 0.65
C-36	Hexagonal	6.8 — ZrRe$_2$	Zr : 0.73; Re : 1.7
B-2 (CsCl)	Cubic	5.0 — VRu	V : 5.3; Ru : 0.49
A-12 (α-Mn)	"	10.5 — NbTc$_3$	Nb : 9.2; T$_c$: 8.2
σ-phase (β-U)	Tetragonal	14.6 — Mo$_{0.38}$Re$_{0.62}$	Mo : 0.92; Re : 1.7
B-1 (NaCl)	Cubic	17.3 — NbN	
		16 — (Pd — Ag) D	Nb : 9.2; Pd <0.01; Ag <0.01
Pu$_2$C$_3$	"	17.0 — (Y$_{0.7}$Th$_{0.3}$)$_2$C$_{3.1}$	Th : 1.37; Y <0.03
Ti$_3$S$_4$	Hexagonal	10—13	
		Li$_{0.1-0.3}$Ti$_{1.1}$S$_2$	Li : 0.08; Ti : 0.49
Mo$_3$Se$_4$	Rhombohedral	15.2	
		Pb$_{0.92}$Mo$_6$S$_{7.5}$	Pb : 7.2; Mo : 0.92
Spinel	Cubic	7—13.7	
		Li$_x$Ti$_{3-x}$O$_4$ $x=0.8$—1.3	Li < 0.08; Ti : 0.49

that this conclusion is premature. In fact, if we analyze the superconducting properties of the transition-metal compounds discussed above, then we arrive inevitably at the conclusion that high T_c (>10 °K) can be observed not only in a cubic system (A-15, B-1), but also in rhombohedral, tetragonal, and hexagonal systems. From the data represented in Table 10 it follows that the symmetry is not decisive in the formation of the superconducting properties of transition-metal compounds.

The same table lists the T_c of the components of the compounds in question. An analysis of these data leads to the conclusion that the components can have lower T_c or may not even be superconductors, while the compound exhibits good superconducting properties. Interesting examples in this respect are the systems Pd–Ag–D, [147] Pd–Cu–H, [179] and Li–Ti–S, [128] which have high-temperature superconductivity while the T_c of their components does not exceed 0.5 °K.

8.2. Crystal chemistry. A crystal-chemistry analysis of the considered compounds includes a determination of the type of chemical bond, the coordination method, the packing of the atoms in the crystal, etc. The following conclusion can be drawn with respect to the compounds of interest to us.

The presence of wide regions of homogeneities (an attribute of the metallic bond) and the metallic conductivity in the compounds with structure A-15 are combined with the appreciable brittleness that is inherent in covalent crystals. Favoring the presence of a covalent bond is also the low coordination number of the metal atoms in the A-15 structure. This indicates that a covalent-metallic type of bond is realized in these compounds.

In compounds with B-1 (NaCl) structure with the attributes listed above (presence of homogeneity region, metallic conductivity, brittleness), there is also, as established in experiments on x-ray and electron spectroscopy and by calculations of the electron-energy spectrum, a transfer of charge from the metal atoms to the nonmetal atoms. This is evidence of an ionic component of the binding forces. Thus, three types of bond coexist in compounds with NaCl structure—metallic, covalent, and ionic.

Compounds of the Laves-phase type have metallic conductivity, but their other "metallic" features are weak (very insignificant homogeneity regions or complete absence of such regions). Brittleness and high melting temperatures characterize the presence of a covalent component of the binding forces in these compounds. A number of workers point out the similarity in the geometrical arrangement of the atoms in Laves phases and in the diamond structure, which is characterized by rigid covalent bonds. [164] This makes it possible to classify these compounds as having predominantly covalent-metallic bonds.

Chalcogenides and sesquicarbides have been less studied than the compounds listed above. It can be assumed nevertheless that the presence of a homogeneity region in chalcogenides is a symptom of a metallic bond, and the charge transfer from the metal to the nonmetal atoms (as evidenced by some preliminary results of x-ray spectral investigations) points to an ionic component of the binding forces.

Both components of the σ phases and of the compounds with α-Mn and B-2 structure are metals with small resistivity differences, so that it is difficult to expect here ionic bond effects. The wide inhomogeneity regions, the high plasticity, and the metallic conductivity give grounds for assuming that the bond in these compounds is predominantly metallic.

The foregoing analysis of the character of the interatomic interaction in compounds of transition metals cannot lead to more than qualitative conclusions. On the other hand, the quantitative relations between the different types of bonds can be obtained from a quantum-mechanical treatment. Of particular convenience for the investigation of the chemical bond is the method of combination of atomic orbitals (LCAO), which in the case of molecular system is called the MO LCAO method, and in the case of crystals the tight-binding method (for an assessment of the LCAO method see Ziman's book[161]). By determining the population of the atomic orbitals, we can find the effective charges of the atoms of the components in the compound and the relation between the purely covalent and purely ionic states of the system. [165] For transition-metal compounds with NaCl structure (VC, VN, VO) such an analysis was recently carried out in[166]. No such quantitative calculations were carried out for the remaining compounds.

Most superconducting compounds of transition metals have structures with rather close packing of the atoms (A-15, C-15, etc.) In a number of cases this allows us to determine the effective radii of the components and to obtain interesting information on the crystal-chemical stability of the compounds. We examine this, using as an example A$_3$B compounds with A-15 structure, for which such an analysis was carried out recently in[167].

In the A-15 structure, the distance between neighboring atoms of sort A, which make up linear chains, is $R_{AA} = a/2$ (a is the lattice parameter). If it is assumed that the atoms of sort A touch each other, then we can determine the effective radius of the atom A, namely

$R_{eff}^A = R_{AA}/2 = a/4$. Comparison of the effective radii of the A components in A_3B compounds (calculated in this manner) with the values of the atomic, ionic, and covalent radii of the A elements shows that R_{eff}^A are close to covalent radii, thus indicating the presence of positive covalent bonds in the chains.

Starting from analogous assumptions concerning that the atoms A and B are in contact, we can (knowing that the distance between them is $R_{AB} = (\sqrt{5}/4)a$), determine the effective radius of the atom B:

$$R_{eff}^B = R_{AB} - R_{eff}^A = \frac{\sqrt{5}}{4}a - \frac{1}{4}a.$$

The condition for the crystal-chemical stability of the A-15 lattice, when the atom B is simultaneously tangent to all the surrounding 12 atoms A, is

$$\frac{R_{eff}^B}{R_{eff}^A} > \sqrt{5} - 1 = 1.23. \tag{11}$$

It follows from the data in[167] that none of the known superconducting compounds with structure A-15 satisfies this condition. In all cases we have $R_{eff}^B/R_{eff}^A < 1.23$, thus indicating that none of the indicated compounds is crystal-chemically stable. This follows from the fact that the A atoms are somewhat compressed, while the B atoms, to the contrary, are somewhat stretched in the A-15 structure.[167] The degree of compression of the A-sublattice or elongation of the Bp o-sublattice can serve as some measure of the crystal-chemical stability of the A-15 structure. The degree of elongation of the B-sublattice can be expressed by the ratio $\varepsilon = R_{eff}^B/R_B^c$, where R_B^c is the covalent radius of the B-element). If we now plot T_c as a function of ε, then we observe a tendency of T_c to increase with increasing degree of crystal-chemical disequilibrium of the A-15 structure (Fig. 25). Estimates made in[167] show that high T_c should be expected for Nb_3Si (this was recently confirmed by Pan,[168] who observed $T_c = 19\,°K$ in Nb_3Si), and also the as-yet unsynthesized V_3C, Nb_3C, and Ta_3C.

8.3. *Stoichiometry*. A general property of superconducting compounds of transition metals is the high sensitivity of T_c to deviations from stoichiometry. As a rule, the highest values of T_c are reached in stoichiometric compounds with A-15 structure, in carbides and nitrides with B-1 structure, and in palladium hydride. It can be noted that the T_c obtained for Nb_3Ge
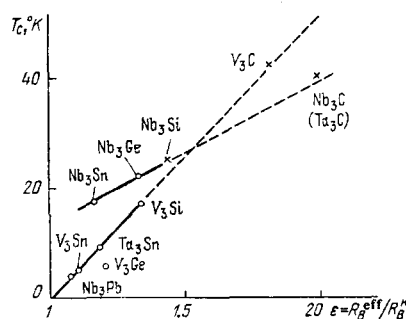

FIG. 25. Influence of the degree of crystal-chemical disequilibrium of the A-15 structure on T_c.

and NbN (23.2 and 17.3 °K, respectively), which are closest to stoichiometry, are the highest for the entire class of compounds with structure A-15 or B-1 (NaCl).

An analysis of the phase-equilibrium diagrams of A_3B compounds with A-15 structure and of AB compounds with B-1 (NaCl) structure shows[169] that the homogeneity regions are, as a rule, bounded on the one hand by the stoichiometric composition, and expand on the other as a result of the increase of the content of the A component. For A-15 compounds this means that in the case of deviation from stoichiometry the A element almost always replaces the B element, i.e., the integrity of the chain remains undisturbed. This indicates that the A−A interaction is decisive in the A-15 structure.

8.4. *Alloying*. If we consider the influence of alloying on the superconducting properties of transition-metal compounds, then we can arrive at the conclusion that this influence is different for different classes of compounds.

In compounds with A-15 and B-1 structure, alloying does not raise T_c noticeably. A much greater effect is reached here by coming closer to stoichiometric composition. This was recently demonstrated clearly with Nb_3Ge as an example, where a successive approach to stoichiometry made it possible to raise T_c from 6 to 17 and finally to 23.2 °K, i.e., to the highest T_c known at present.

On the other hand, in sesquicarbides, chalcogenides, compound of the Laves-phase type, hydrides, and deuterides of palladium, alloying produced a favorable effect. For example, whereas in palladium deuteride $T_c = 11\,°K$,[146] in the ternary system Pd−Ag−D it was possible to raise T_c to 16 °K.[147] In the binary systems Ti−S and Li−Ti, no superconductivity was observed at all, whereas in the ternary system Ti−Li−S the value of T_c reaches 17 °K.

Clear-cut criteria for the systems in which the superconducting characteristics of transition-metal compounds can be improved by alloying have not yet been established. Therefore all the extensive material accumulated in recent years on the alloying of superconductors is still empirical in character.

8.5. *Electron density*. Matthias has recently called attention to the connection between T_c and the electron density. In his plot of T_c against the electron density (the number of valence electrons per atom) for transition metals of periods I, II, and III, the values of T_c cluster about two maxima corresponding to an electron density of 5 and 7 electrons/atom.[170] When the values of T_c for transition-metal alloys are marked on the same plot as the same functions of the electron density, then it turns out that the values of T_c obtained for alloys agree well with the dependence of T_c on the electron density plotted for pure metals. The positions of the principal maxima for alloys of transition metals of periods I, II, and III (4.7 and 6.5 electrons/atom) practically coincide with one another and differ little from the positions of the corresponding maxima of pure metals (5 and 7 electrons/atom).[171]

It seemed at first that the dependence of T_c on the

electron density, plotted for transition metals and their alloys, is universal in character and is suitable for the analysis of other superconductors based on transition metals. In fact, an analysis of the superconducting properties of A_3B compounds with A-15 structure has shown that the highest values of T_c are grouped around two electron-density intervals, 4.50–4.75 and 6.25–6.60 electrons/atom, and these in fact coincide with the regions of "favorable" densities, observed for transition metals and their alloys.

In other superconducting compounds whose components are transition metals, such as σ phases, Laves phases, compounds with B-2 (CsCl) and α-Mn structure, the correlation described above also holds, i.e., high values of T_c occur in the electron-density regions 4.6–4.7 and 6.5–6.75 electrons/atom.

However, in compounds with B-1 (NaCl) structure and in sesquicarbides, high values of T_c correspond to densities of 3.6 (sesquicarbides) and 4.5 or 5.0 (carbides or nitrides with B-1 structure) electrons/atom.

A new electron density value, 3.6 electrons/atom, which deviates from the Matthias rule, comes into play, although in most compounds, just as in alloys, the surprisingly stable values, approximately 4.5 and 6.5 electrons/atom, remain favorable.

9. Types of lattice instability

The experimental data given in the preceding section show that superconducting compounds of transition metals with high T_c reveal, to one degree or another, lattice instability. The manifestations of this instability can be quite varied: in the form of a direct structural transition (of the type of weak distortion of the initial lattice), a softening of the lattice moduli, a softening of the short-wave modes of the phonon spectrum, etc. We shall consider below the types of lattice instabilities that occur in the considered compounds.

9.1. Structural transition. A low-temperature structural transition was observed in compounds with A-15 structure, in Laves phases, in compounds with B-2 (CsCl) structure, and in chalcogenides. Data on the initial structures of the foregoing compounds and on the structures after the transition are summarized in Tables 9 and 11 together with the values of T_c and T_m. In four of the eight considered compounds, the character of the transition is the same—from cubic to tetragonal. It is interesting that in three compounds of the Laves-phase type with initial C-15 structure, which undergo a transition, the low-temperature lattice distortion is different in all three cases—tetragonal, rhombohedral, and orthorhombic.

Attention is called to the fact that the temperatures of the structural transitions exceed in all cases the temperatures of the superconducting transitions. However, whereas the difference between T_m and T_c in compounds with structure A-15 (V_3Si, Nb_3Sn) and C-15 ($LaRu_2$) amount to only 6–27 °K, in the remaining compounds this quantity is much larger and reaches hundreds of degrees. It is not yet clear whether some connection exists between the proximity of the temperature regions

TABLE 11. Superconducting and structural characteristics of compounds undergoing lattice transitions.

Compound	Initial structure (cubic)	Structure after transition	T_m, °K	T_c, °K
V_3Si	A-15	Tetragonal	21—23	17
Nb_3Sn	A-15	"	43—45	18
HfV_2	C-15	Body centered orthorhombic	120	8.7
ZrV_2	C-15	Rhombohedral	90—117	8.8
$LaRu_2$	C-15	Tetragonal	30	4.45
VRu	B-2	"	110—360	5

of the superconducting and structural transitions and the value of T_c. There are still not enough experimental data for such an analysis.

9.2. "Virtual" structural transition. Ternary alloys of the Y_2C_3–Th_2C_3 system experience no structural transition whatever with changing temperature. However, by varying the synthesis conditions it is possible to obtain these alloys with bcc structure (of the Pu_2C_3 type) or body-centered tetragonal structure. This situation can be conditionally called a "virtual" structural transition. It is interesting that the T_c of a compound with cubic structure (~17 °K) is the highest in the entire class of sesquicarbides, whereas a compound with tetragonal structure is not superconducting down to 4 °K.

9.3. "Softening" of long-wave lattice moduli with decreasing temperature. An investigation of the temperature dependence of the speed of sound has shown an anomalous decrease of this parameter with decreasing temperature in compounds with A-15 structure (V_3Si, Nb_3Sn, Nb_3Al, V_3Ga), and with C-15 structure (ZrV_2, HfV_2), and significant singularities in compounds with B-2 structure (VRu). These data point to a softening of the lattice moduli in the indicated compounds, and the temperature region in which the maximum softening occurs usually coincides with T_m.

In some compounds (V_3Si, Nb_3Sn) this softening begins at room temperatures, i.e., long before the appearance of the structural transition, and is "the precursor of the phase transition." It is interesting to note that the phase transition itself may not take place (for example, it vanishes in V_3Si and Nb_3Sn at low deviations from stoichiometry or small impurity concentrations). In a number of other compounds, for example in Nb_3Al, no structural transition is observed even in stoichiometrically pure samples, but softening of the lattice moduli does take place, indicating lattice instability, and always accompanied by high T_c. For example, $T_c = 18.8$ °K in Nb_3Al.

9.4. "Softening" of short-wave phonons. In the compounds A-15, C-15, and B-2, the observed softening of the lattice moduli is proof of a developing instability of the acoustic long-wave phonons. In compounds with B-1 structure, as we have seen, the dispersion curves of the acoustic phonons have anomalies in the short-wave region. These anomalies are not sensitive to temperature, but their position and depth are determined by the parameters of the interatomic and interelectron interaction, and by varying these we might, in principle, obtain unstable phonon modes with a finite wave vector. It is said in this context that the observed anomalies

also point to a developing (with respect to the interaction parameter) lattice instability. It is interesting that these anomalies were observed only in high-temperature superconductors with B-1 structure, such as TaC.

9.5. Coexistence of different structural phases near a given composition.

In the synthesis of a number of high-temperature superconductors with A-15 and B-1 structure it was observed that different structure phases coexist near the stoichiometric compositions of the compounds Nb_3Sn, MoC, and NbN. In other words, by varying in a small range the composition, the temperature and synthesis conditions we can obtain various structural modifications of one and the same compound.

For example, according to the data of[168,173-176] the compound Nb_3Si can be obtained in three modifications: with Cu_3Au structure ($T_c = 1.5\ °K$),[173] with structure of Ti_3P type ($T_c = 5.3-9\ °K$),[7,174,176] and with A-15 structure ($T_c = 6.9,\ 9.2,\ 19\ °K$).[168,175,176]

The compound NbN can also be synthesized with a cubic structure of type B-1 (NaCl) ($T_c = 17.3\ °K$),[84,177] a tetragonally-distorted structure of the NaCl type ($T_c = 8.9\ °K$),[178] and a hexagonal structure of type TiP ($T_c < 1.94\ °K$).[98]

Molybdenum carbide MoC has two structural modifications—cubic (type B-1) with $T_c = 12.1$ to $14.3\ °K$,[71,95] and hexagonal with $T_c = 7.1\ °K$.[95]

The σ phase in the Mo-Re system at ~1250 °C borders on a phase having a crystal structure of the α-Mn type.[55] Synthesis of this compound (σ phase) by evaporation on a substrate heated to the same temperature (~1250 °C) yielded a σ phase with unit-cell dimensions that differ from those of the bulk material, and led to a doubling of T_c.[55] A similar effect was reported in[177], where it was possible to increase the lattice parameter and to raise T_c from 13.5 to 17.3 °K by evaporating NbN on a substrate heated to 700 °C.

Using the substrate temperature as an adjustable parameter, Testardi and co-workers have recently undertaken a search for new superconducting phases in compounds and alloys based on transition metals.[7] As a result they obtained a large number of new metastable phases, in which the enhancement of T_c was attained at the deposition temperature corresponding to the phase-change temperatures in these materials.

It is therefore not excluded that the proximity of a given alloy composition to the phase-equilibrium boundaries can denote one of the types of lattice instability, which is the one that leads (in one of the phases) to high T_c. Of course, to advance this hypothesis it would be necessary to verify directly the instability of some phonon modes in one of the phases of the system. A symptom of an instability of this type can also be taken to be the difficulty of obtaining stoichiometric composition. For example, strict stoichiometry could not be obtained in the synthesis of the compounds A-15 and B-1. As a rule, this took place for compounds with high T_c (Nb_3Ge, Nb_3Ga, MoC, NbN). The phase-equilibrium limit at low temperature (<200 °K) in this compound does not occur at stoichiometric composition but

is shifted towards larger contents of the transition metal. Therefore, to come closest to stoichiometry and to obtain higher T_c it is necessary to produce special synthesis conditions, using abrupt quenching from high temperatures, whereby the phase-equilibrium boundary shifts towards the stoichiometric composition.

4. THEORETICAL ANALYSIS OF STRUCTURAL TRANSITIONS

10. Phase transition in structures of class O_h, from the point of view of symmetry theory

We have seen that one of the manifestations of lattice instability, which is encountered in high-temperature superconductors, is a structure transition. Since such a transition is preceded by softening of the phonon modes with decreasing temperature, this explains, according to McMillan's formula, the increase of the superconducting transition temperature in unstable lattices. In this chapter structure transitions in a number of the previously considered compounds will be considered for their own sake, without any bearing on superconductivity, and exclusively on the basis of symmetry theory. This makes it possible, first of all, to determine the phonon-spectrum modes responsible for the transition itself, and indicate ways of further experimental study of such transitions.

Compounds of type A-15, C-15, and B-2 belong to one and the same crystal class O_h (their space groups are O_h^9, O_h^7, and O_h^1, respectively). Prior to the transition all are cubic, and below the transition temperature T_m the compounds A-15 and B-2 become tetragonal, while C-15 become (according to various data and for various compositions) either rhombic, or rhombohedral, or tetragonal.

By many of their attributes, these are second-order phase transitions, but it appears that a finite spontaneous deformation (~10^{-3}) is produced, pointing to a first-order transition that is probably close to a second-order one. The Landau theory of second-order phase transitions was used in[96,181] to predict the symmetry group of the new phase in A-15 compounds. Since the observed transitions are more readily of first order, it is necessary to review the existing results with respect to the A-15 compounds, and also obtain predictions concerning the symmetry group of the new phase for the compounds C-15 and B-2. It is desirable here not to use an expansion of the free energy in powers of the order parameter—in this case in powers of the atomic displacements—not only because of its finite value at the transition point T_m itself (the displacements are small in this case), but also because it is useful to carry out, as the first stage of the investigation, a purely group-theoretical analysis of the transition, deferring the thermodynamic treatment of the realization of the new phases and their properties to the next stage. At the same time, it is natural to employ Landau's constructive idea concerning the connection between the distorted structure and irreducible representation of the group of the initially symmetrical phase. A characteristic of all three structures is that according to the presently available experimental data the transi-

tion took place without a change in the number of atoms per unit cell. If we start from this fact, then the transition should be due to unstable modes of the cubic phase at the point Γ of the Brillouin zone (for a zero quasimomentum k).

At the point Γ, the representations of the space groups reduce to representations of point groups, and therefore for all three structures A-15, C-15, and B-2 the phonon modes should be classified in accordance with 10 irreducible representations D^ν of the point group O_h. By a standard procedure, it is possible to carry out for these structures a group-theoretical analysis of the phonon spectrum (at $k = 0$), namely: 1) construct the mechanical representation, i.e., the specific set of irreducible representations D^ν of the O_h group, which characterizes the branches of the spectra of the given crystal structures; 2) find the explicit form of the basis functions φ_i^ν of these representations, i.e., the phonon modes.

Our task is to indicate the possible groups of the new phase for each of the three structures. To this end we consider the crystal density functions ρ and ρ_0 in the new initial phase respectively. Since ρ differs from ρ_0 by a certain set of atom displacements, we can write $\rho = \rho_0 + \delta\rho$, where the structure distortion $\delta\rho$ can be represented as a superposition of basis functions φ_i^ν of a certain ν-th irreducible representation (i is the number of the function), characterizing the unstable phonon mode responsible for the phase transition:

$$\delta\rho = \sum_i C_i^\nu \varphi_i^\nu. \tag{12}$$

$\delta\rho$ should be invariant with respect to the symmetry group G_1 of the new phase, which we seek by guiding ourselves by the following principles:

a) G_1 must be a subgroup of group G_0 of the initial phase.

b) The limitation of the ν-th representation of the group G_0 on the subgroup must contain a single representation (the Birman criterion[96]). This requirement follows from the fact that $\delta\rho$ must be invariant to the group G_1, and the invariant transforms in accord with a single representation.

c) The representation according to which the transition is carried out is contained in the mechanical representation of the crystal (displacive type transition).

d) The fourth principle can be called arbitrarily the principle of maximality of the group of the new phase G_1. It has in fact nothing in common with the Asher maximality principle previously encountered in the literature,[97] the inconsistency of which was illustrated many times in a number of papers. The meaning of the fourth principle is the following:

The real displacement of the atoms $\delta\rho$ in the transition in accord with the representation ν can be regarded according to (12), as a certain superposition of modes (normal displacements) with a mixing coefficient c_i; the numerical values of the modes are at present immaterial, all that matters is the type of mixing, e.g.,

$c_1(\varphi_1^\nu + \varphi_2^\nu)$, $c_1\varphi_1^\nu + c_2(\varphi_2^\nu - \varphi_1^\nu)$, $c_1(\varphi_1^\nu + \varphi_2^\nu + \varphi_3^\nu)$ etc. At the same time, each such real displacement of the atoms leads to one of the permissible groups G_1, the list of which has already been determined with the aid of the first three principles. It is clear that the set of distorted coordinates of the crystal atoms in the new phase corresponds not only to any one of the groups G_1, but also to its subgroup. When attempting to indicate the space group of the crystal in the new phase in its entirety, we must, for each type of mixing of the modes of the representation D^ν, retain only the maximal one of these groups G_1.

The foregoing requirements of group-theoretical nature limit greatly the number of possible groups of the new phase. The analysis indicated for the structures A-15, C-15, and B-2 of class O_h was carried out by Izyumov, Naish, and Syromyatnikov.[182] Taking into to account the available experimental information on the syngony of the new phase, their final results are the following:

A-15: $\underline{D_{4h}^9}$, D_{2d}^5, C_{4v}^7, C_{4h}^2

C-15: $\underline{D_{2h}^{28}}$, C_{2v}^{22}, D_2^7 or D_{3d}^5, D_3^7, C_{3v}^5 (13)

B-2: C_{4v}^1.

We note that for the A-15 the tetragonal-phase groups were investigated in[96,181] and in [96] only the groups D_{2d}^5 and C_{4v}^7 were obtained, while in[181] the group C_{4h}^2 was added to them with an indication that it was left out of[96]. The result for C-15 and B-2, on the other hand, was first obtained in[182].

The group D_{4h}^9 for A-15 is purposefully left out of[96,181] because the representation E_g corresponding to it is inactive, in accordance with the terminology[99] of the Landau theory of second-order phase transitions, since it corresponds to an invariant of third order in the expansion of the free energy in powers of the order parameter. In the summary (13) of the results we underscored the groups obtained only in transitions in accord with passive representations, and which are excluded in the theory of second-order phase transitions. They were left in the list only to make it possible to discuss both second-order transitions and transitions of first order close to second.

Experiment reveals in A-15, in the low-temperature phase, precisely the group D_{4h}^9. It can therefore be concluded that transition is either not of second order, or that the expansion of the free energy fails to include some additional thermodynamic variable. The latter consideration was developed in a paper by Anderson and Blount,[100] who have shown that actually in the structure A-15 the second-order phase transition should be characterized by at least two order parameters, one of which is the spontaneous tetragonal deformation of the unit cell as a whole, and the second is the relative displacement of the atoms inside the cell. It is precisely such a displacement which was observed in the neutron-diffraction experiment of Shirane and Axe[116] (see the review[1]).

As to C-15, experiments on HfV_2 and ZrV_2 indicate

an orthorhombic syngony of the new phase,[30,31] and x-ray structure analysis was even used in[30] to determine the space group C_{2v}^{20}. At the same time, according to the neutron-diffraction data of[32], this phase is rhombohedral, and we therefore retained in the final list (13) the groups of both syngonies. It is remarkable that it does not contain the group C_{2v}^{20}. If we trace its fate retrospectively, then it turns out that it drops out because it is not maximal in the transition with respect to the representation F_{2g} (its maximal supergroup D_{2h}^{28} is included in the list (13)). For a final determination of the symmetry of the low-temperature phase in C-15 compounds it is necessary to undertake additional diffraction experiments.

From the presently available information, it seems quite appropriate to adopt the previously assumed theoretical premises: the absence of a superstructure in the new phase ($k = 0$), displacive type transitions, and a subgroup memory of the initial phase due to the smallness of the distortions. One cannot exclude, however, violation of any one of these premises, all the more since the experimental study of transitions in C-15 were initiated only recently. The C_{2v}^{20} group may in fact turn out to be possible here.

The experimental data on the symmetry of the low-temperature phase in VRu with B-2 structure is confined so far to the indication of a tetragonal syngony,[46] and the space group has not yet been established. There is therefore as yet nothing to compare with the (unique!) result obtained in[182].

For further investigations of the new phases and their properties it may turn out to be important to reveal the possible domain structure connected with several methods of imbedding the subgroup G_1 into the initial group G_0. These domains can differ in some of the experimentally observable properties. In particular, it is of interest to note that among the admissible groups (13) of the new phase there are also polar groups of type C_{nv}, so that the domains can differ by some vector property, in analogy to ferroelectrics. In C-15, the experimentally determined group C_{2v}^{20} is also polar.

11. Electronic models of structural transitions in A-15 and C-15 compounds

The structural phase transition in the considered A-15, C-15, and B-2 compounds is preceded, as we have seen, by softening of the lattice moduli, which begins already at room temperatures. This phenomenon was investigated most fully in A-15 compounds, for which it was established that the shear modulus $C_{11}-C_{12}$ vanishes at the structural transition point T_m itself, thus leading to absolute instability of the cubic phase at $T < T_m$.

This anomalous behavior of the lattice in these compounds, accompanied by a number of anomalies of the purely electronic properties, was connected for a long time with the Weger–Labbe–Friedel hypothesis that the electronic spectrum is quasi-one-dimensional, a hypothesis based on the existence in the A-15 structure of linear chains made up of transition-metal atoms.

TABLE 12. Characters of the wave-vector group of the point X for the groups O_h^3 and O_h^7.

	O_h^3					O_h^7			
D_{4h}	X_1	X_2	X_3	X_4	D_{4h}	X_1	X_2	X_3	X_4
$\{\varepsilon\|0\}$	2	2	2	2	$\{\varepsilon\|0\}$	2	2	2	2
$\{\delta_{2x}\|0\}$	2	0	−2	0	$\{\delta_{2z}\|0\}$	2	2	−2	−2
$\{\delta_{2y}\|0\}$	−2	0	2	0	$\{\delta_{2xy}\|\tau\}$	0	0	$2i$	$2i$
$\{\delta_{2z}\|0\}$	−2	2	−2	2	$\{\delta_{2x\bar{y}}\|\tau\}$	0	0	$-2i$	$-2i$
$\{\rho_x\|0\}$	0	2	0	−2	$\{\rho_{xy}\|0\}$	2	−2	0	0
$\{\rho_y\|0\}$	0	2	0	−2	$\{\rho_{x\bar{y}}\|0\}$	2	−2	0	0

In fact, the manifestation of quasi-one-dimensionality of the d-electrons in this form is unlikely nonetheless, in view of the large relative value of the matrix element of the inter-chain transition.[134] At the same time, as shown recently by Gor'kov,[172] an entirely different explanation of the observed anomalies in the A-15 structure is possible. Its space group O_h^3 contains nontrivial transitions, and this leads to a double degeneracy of the electronic levels on the boundary of the Brillouin zone at the point X. The wave-vector group G_k for a ray oriented in the z direction ($k = 0$, 0, π/a) has four two-dimensional irreducible representations X_1, X_2, X_3, and X_4. Their characters are given in Table 12.

In the vicinity of the point X, the indicated degeneracy is lifted for the representations X_2 and X_4 in the structure A-15, and two branches of the spectrum appear, with nonlinear dispersion law[172]:

$$\varepsilon_i(p) = \pm vp_z \quad (i = 1.2),$$

where v is a constant with the dimension of velocity (the momentum p_z is reckoned from the point $X = \{00\pi/a\}$). If the Fermi level passes precisely through the point X, then formula (14) represents the energy of the electron and hole excitations in the vicinity of the point X. Gor'kov has proposed that in the compounds V_3Si and Nb_3Sn, where lattice anomalies are observed, the situation is precisely as follows: The Fermi surface is tangent to the boundaries of the Brillouin zone at the point X. This, as we shall show below, leads to a strong temperature dependence of the contribution to the free energy from the small electron groups localized near the points X.

The electronic spectrum near the degeneracy point is very sensitive to various perturbations that alter the symmetry of the system, particularly to lattice deformations. The use of the method of invariants makes it possible to take the influence of the deformations into account. The unperturbed spectrum can be regarded as the corresponding values of the effective Hamiltonian.

$$\mathscr{H}_0 = vp_z\tau_z, \tag{16}$$

where τ_z is a Pauli matrix. It can be shown that the interaction of the electrons with the deformations is described by an effective Hamiltonian

$$\mathscr{H}' = \Delta_z\tau_x, \quad \Delta_z = D(\varepsilon_{xx} - \varepsilon_{yy}), \tag{16a}$$

where τ_x is a corresponding Pauli matrix, $\varepsilon_{\alpha\beta}$ is a com-

ponent of the deformation tensor, and D is a certain phenomenological parameter of the electron-lattice interaction. The perturbation $\mathscr{H}'$ gives rise to transitions between bands; these transitions are described by the Hamiltonian $\mathscr{H}_0$ and cause the branches of the spectrum (14) to become entangled, so that the eigenvalues of the Hamiltonian $\mathscr{H}_0 + \mathscr{H}'$ are

$$E_i(p) = \pm \sqrt{(vp_z)^2 + \Delta_z^2}. \tag{17}$$

Thus, the tetragonal deformation leads to the appearance of a gap in the electronic spectrum at the point X, and this can lead to instability of the cubic lattice at a certain temperature. We calculate now the free energy of the electrons with the spectrum (17), corresponding to a deformed crystal:

$$\Omega = -2T \sum_{i=1,2} \int \frac{dp}{(2\pi)^3} \ln\left[1 + \exp\left(-\frac{E_i(p)}{T}\right)\right]. \tag{18}$$

We are interested only in the contribution of the electrons in a small vicinity of the point X. For a ray traveling in the z direction, the spectrum at small p depends on p_z, and therefore the corresponding contribution to the integral (18) can be written in the form

$$\Omega_z = -\frac{CT}{\pi v} \int_{-\tilde{\omega}}^{\tilde{\omega}} d\varepsilon \, [\ln(1 + e^{-\sqrt{\varepsilon^2 + \Delta_z^2}/T}) + \ln(1 + e^{\sqrt{\varepsilon^2 + \Delta_z^2}/T})], \tag{19}$$

where C is the phase "volume" of the vicinity of the point X in the transverse direction:

$$C = \int_{X(z)} \frac{dp_x dp_y}{(2\pi)^2},$$

and $\tilde{\omega}$ is the cutoff energy corresponding to the dimension of the vicinity in the z direction.

To calculate the moduli it is necessary to expand expression (19) in powers of the deformations, i.e., in terms of Δ_z^2. Summing then over all the rays of the star, we write down the deformation-dependent contribution to the free energy in the form

$$\delta\Omega = -\frac{C}{\pi v} \sum_{i=x,y,z} \Delta_i^2 \int_0^{\tilde{\omega}} \frac{d\varepsilon}{\varepsilon} \, th\frac{\varepsilon}{2T} = -\frac{C}{\pi v} \ln\left(1,14 \frac{\tilde{\omega}}{T}\right) \sum_{i=x,y,z} \Delta_i^2. \tag{20}$$

Comparing now (20) with the well known expression for the density of the elastic energy of a cubic crystal, we obtain the correction to the moduli due to the contribution from the electrons localized in the vicinity of the points X.

For the shear modulus we obtain a logarithmic dependence on the temperature[172]:

$$\delta(C_{11} - C_{12}) = -\frac{3CD^2}{\pi v} \ln\frac{\tilde{\omega}}{T}. \tag{21}$$

When the temperature is lowered, the negative con-

tribution (21) increases and at a certain T it can cancel out the temperature-independent contribution to the modulus from the ion-ion interaction, leading to loss of stability of the cubic lattice.

This effect arises only if the Fermi level falls on the states X_2 or X_4. In the case of the states X_1 and X_3 the symmetry does not admit of the invariant (15), but instead of it of another invariant $\mathscr{H}_0 = v p_z \sigma_z \tau_z$, corresponding to the spin-orbit interaction (σ_z is the electron-spin matrix). Since $\tilde{v}$ should be much smaller than the electron velocity v on the Fermi surface, the region of the linear dispersion law becomes unusually narrow in this case, and the contribution to the free energy from the vicinity of the point X does not lead in this case to a logarithmic dependence on the temperature.

The logarithmic softening of the shear modulus with temperature was observed experimentally by Testardi[3] in V_3Si. Gor'kov's assumption that in this compound the Fermi surface passes through the point X leads also to a logarithmic increase with decreasing magnetic susceptibility, a fact again in qualitative agreement with experiment. Thus, the main group of experimental phenomena in A-15 compounds can be understood without assuming a quasi-one-dimensional motion of the d-electrons over the chains.

It is very important that the analogous structural-instability phenomena in C-15 compounds can be explained on the basis of a similar model. In fact, it has turned out[148] that the symmetry of this structure (space group O_h^7) admits, just as in A-15, double degeneracy of the electron spectrum at the point X (the reciprocal lattice is bcc) and a linear dispersion law (14) in the vicinity of this point (for the irreducible representations X_1 and X_2). The spectrum perturbation due to the deformation is described by the effective Hamiltonian

$$\mathscr{H}' = \Delta_z \tau_z, \qquad \Delta_z \equiv D\varepsilon_{xy}, \tag{22}$$

which yields the same eigenvalues (17) as for A-15, and therefore the results of the calculation of the free energy (20) remains in force also for C-15. Formula (20) together with expression (22) for Δ_z shows the logarithmic softening of the modulus C_{44} connected with sound propagation in directions of the type [001]:

$$\delta C_{44} = -\frac{CD^2}{2\pi v} \ln\frac{\tilde{\omega}}{T}. \tag{23}$$

Unfortunately, no acoustic measurements on single crystals of C-15 compounds have been made so far. An experimental check on relation (23) would be of primary significance. Were logarithmic softening of the modulus C_{44} to be observed in ZrV_2 or HfV_2, this could mean validity of the initial assumption that the Fermi surface passes through the point X. This means that in C-15 compounds, where it is impossible to separate such chains of transition-element atoms, the position of the Fermi surface can explain a number of phenomena hitherto observed in A-15 compounds. If this is so, then the Gor'kov model would turn out to be preferable to the chain model with respect to compounds of type

A-15. The final choice between them, however, can be made either by a direct experimental investigation of the Fermi surface, or by a careful experimental check on various predictions from both theories.

5. CONCLUSION

From the material presented above it follows that in each class of superconducting compounds based on transition metals there are high-temperature superconductors that exhibit some lattice instability. To ascertain whether the correlation between the high T_c and the lattice instability is universal, it would be necessary to study the lattice properties of all the compounds, using T_c within the limits of a given class. We shall now analyze how completely such experiments have been performed.

Lattice instability in the A-15 compounds V_3Si and Nb_3Sn was first observed in the form of a structural phase transition preceded by a wide temperature interval of the softening of the lattice moduli which served as a precursor of the phase transition. A similar transition was observed somewhat later in V_3Ga. What can be said concerning the other high-temperature superconductors of this class? The initial searches for a structural transition in Nb_3Al ($T_c = 18.8$ °K) were not successful, [149] but it is useful to recall that in both V_3Si and Nb_3Sn this transition was observed not in all the samples, only in chemically pure ones with stoichiometric composition. Recently searches for the transitions in Nb_3Al and in other A-15 compounds were undertaken by Kodess. [150] He carried out x-ray structure investigations at low temperatures and observed a structural transition in Nb_3Al at 80 °K and also in the alloys $Nb_3(Al_{0.75}Ge_{0.25})$ ($T_m = 105$ °K) and $Nb_{3.1}(Al_{0.7}Ge_{0.3})$ ($T_m = 130$ °K). [150] Measurements of the temperature dependence of the magnetic susceptibility of the same samples [151] have revealed anomalies in the same temperature region where a structural transition takes place (just as in V_3Si!). A similar anomaly was observed even earlier by Alekseevskiĭ for the compound $Nb_3(Al_{0.75}Ge_{0.25})$. There are also in the literature other indications that a structural transition takes place in Nb_3Al. Thus, measurements [153, 154] of the low-temperature heat capacity in Nb_3Al and V_3Ga have revealed the presence of two separate superconducting transitions, one of them ascribed to the tetragonal phase.

It must be indicated at the same time that in Nb_3Ge no structural transition was revealed by measurements of the elastic properties, and no search for it was made to date in other A-15 compounds with high T_c: Nb_3Ga, Nb_3Si, Nb_3Au, Nb_3Pt, Ta_3Au, V_3Al. It goes without saying that further research is needed in this direction, but there is no doubt even now that structural transitions can be observed not only in V_3Si and Nb_3Sn, but also in other high-temperature superconductors with A-15 structure.

Investigations of superconductors with NaCl structure have shown softening of the longitudinal acoustic modes in NbC and TaC ($T_c = 10-12$ °K) and the absence of this softening in HfC and ZrC ($T_c < 1$ °K). Unfortunately, no

such measurements were undertaken on other compounds of this class with relatively high T_c (ZrN, NbN, MoC) and it is difficult to say anything concerning the universality of the noted correlation. There exist, how however, other experimental facts evidencing that the lattice-property anomalies observed in NbC and TaC are not accidental. An anomalously large change of the thermal expansion was observed in [155] for Nb and TaC in the temperature region 60-70 °K. This indicates an abrupt increase of the atom-displacement amplitudes in the indicated temperature region. If these data are compared with the analogous investigations performed on V_3Si, [156] then it can be verified that for a V_3Si sample undergoing a structural transition an anomaly in the temperature dependence of the thermal-expansion coefficient was also observed.

Now a word on the other classes of compounds. We have already noted that a structural transition was observed in the ternary sulfides of modybdenum $CuMo_4S_5$ ($T_c \approx 11$ °K) and $CoMo_3S_4$ (T_c was not measured). [138] In the same study, however, a search was made for structural transitions in other compounds of this class, namely $SnMo_5S_6$ ($T_c = 11.3$ °K), $AgMo_4S_5$ ($T_c = 8.9$ °K) and $NiMo_3S_4$ (no measurement of T_c), but no transition was observed. A final clarification of this question is of great interest.

For compounds such as σ phases and α-Mn, sesquicarbides, and palladium hydrides there are only isolated indirect indications of lattice instability. An extensive study of the acoustic properties and x-ray investigations are needed here.

Summarizing this discussion, we can note that in spite of the limited amount of experimental data, [3] the considered material allows us to posit the existence of a correlation between the lattice instability and high-temperature superconductivity in transition-metal compounds. However, it is still too early to speak of universality of this correlation, since the experimental data on the lattice properties of many of these compounds are far from complete.

As to the theoretical aspect of this correlation, the situation here is much worse. The lattice instability by itself can contribute to an increase of T_c, for example via the mechanism of softening the phonon spectrum, but the temperature T_m of the structural transitions is higher (and as a rule much higher) than T_c. Thus, the restructuring of the unstable lattice occurs much sooner when the temperature is lowered, and superconductivity appears already in the new phase, in

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[3] We have considered the most thoroughly investigated types of compounds. Recently, values $T_c > 10$ °K were reported for a number of other compounds. Thus, for example, in the class of superconductors with C-16 structure, $T_c = 11.1$ °K was observed in $RhZr_2$ [184,185] and $T_c = 10.6-10.8$ °K in alloys of the Rh-Ru-Zr system. [184,185] We note also that in Pd hydrides and in alloys on their basis, values $T_c > 15$ °K were obtained, namely $T_c = 16.6$ °K in the Pd-Cu-H system. [179] We have left out of this review the discussion of hydride systems, since a special article on this topic was published recently in the present journal. [186]

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which the lattice becomes more rigid. On the other hand in those cases (NbC, TaC) where the lattice instability manifests itself in anomalies of the short-wave phonons and is not connected with the temperature, the corresponding softening of the short-wave region of the spectrum cannot as we have seen above, yield a sufficiently large increase of T_c according to the existing theories (McMillan's formula). In general, the theoretical treatment of the experimentally obtained correlation between the high T_c and the lattice instability is at present a great problem. Nor can we exclude a future solution for it in the following form: the lattice instability is not by itself the cause of the high T_c, but these two phenomena—high T_c and lattice instability—are manifestations of the effect of the strong electron-lattice binding in metallic compounds based on transition metals. In this case, the solution of the problem of the discussed correlation must be preceded by the development of a theory of electron-phonon interaction in these metallic compounds.

Note added in proof. L. P. Gor'kov has proposed a new electronic model[188] of compounds with A-15 structure. Unlike the earlier model,[172] in which the non-interacting-chain approximation was in fact employed, in the new model this interaction is taken into account. The model explains the temperature dependence of the lattice moduli and of the magnetic susceptibility above the structural-transition temperature.

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