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Phase Relationships, Basic Metallurgy and Superconducting Properties of Nb_3Sn and Related Compounds

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Phase Relationships, Basic Metallurgy And Superconducting Properties of Nb_3Sn And Related Compounds [+)]

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Abstract

The phase relationships and the superconducting properties of Nb_3Sn are compared with those of other high T_c compounds crystallizing in the A15 structure: Nb_3Al, Nb_3Ga, Nb_3Ge, V_3Si, V_3Ga ... Characteristic differences of these systems, i.e., the shape of the A15 phase field, the variation of T_c with composition or with atomic ordering, are discussed. Recent methods leading to the accurate determination of the phase relationships in these systems up to 2000 °C are reviewed. The discussion is extended to the low temperature relationships in Nb_3Sn and V_3Si with the corresponding tetragonal modifications. Methods for observing these low temperature details and recent results about their influence on T_c are presented. In the case of Nb_3Sn, the factors influencing the formation of the low temperature tetragonal phase, such as hydrostatic pressure, precompression in multifilamentary wires, or hydrogen loading, are discussed.

Zusammenfassung

Phasenbeziehungen, Metallurgie und supraleitende Eigenschaften von Nb_3Sn und anderen Verbindungen desselben Typs

Die Phasenbeziehungen und die supraleitenden Eigenschaften von Nb_3Sn werden mit denen anderer A15 Verbindungen mit hohem T_c verglichen: Nb_3Al, Nb_3Ga, Nb_3Ge, V_3Si, V_3Ga, ... Charakteristische Unterschiede in diesen Systemen betreffend das Homogenitätsgebiet der A15 Phase sowie die Änderung von T_c mit der Zusammensetzung und dem Ordnungsgrad werden diskutiert. Kürzlich entwickelte Methoden zur präzisen Bestimmung dieser Phasendiagramme bis zu 2000 °C werden beschrieben. Die Tieftemperaturphasendiagramme von Nb_3Sn und V_3Si mit der dort auftretenden tetragonalen Modifikation werden diskutiert. Die Methoden zur Untersuchung dieser Details sowie neue Resultate über deren Einfluß auf T_c werden vorgestellt. Verschiedene Faktoren wie der hydrostatische Druck, die Vorspannung in Vielkernsupraleitern oder der Wasserstoffgehalt können die Bildung der tetragonalen Phase beeinflussen und werden diskutiert.

PHASE RELATIONSHIPS, BASIC METALLURGY AND SUPERCONDUCTING PROPERTIES OF Nb_3Sn AND RELATED COMPOUNDS

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INTRODUCTION

Since the discovery of the high T_c superconductors V_3Si and Nb_3Sn in 1953[1], the A15 type superconductors have been the subject of more than a thousand publications. The main interest in the A15 materials has of course been motivated by their high T_c values, the highest known to date having been measured for Nb_3Ge: $T_c = 23K$[2]. From the known data it follows that the maximum T_c in a A15 type compound containing a nontransition element, i.e. Nb_3Sn, Nb_3Ge, Nb_3Ga, Nb_3Al, V_3Si or V_3Ga can only be reached if the following conditions are fulfilled: a) stoichiometric composition, b) perfect long-range atomic order and c) stability of the cubic A15 phase at low temperatures.

However, A15 type compounds with optimum superconducting properties tend (with one exception, V_3Ga) to be on the verge of structural instability. This empirical correlation has also been observed for materials crystallizing in other structures and seems plausible since both phenomena, superconductivity and structural stability have a common origin, the electronic structure. There are different kinds of instabilities leading to a deviation from the conditions formulated above and thus to lower T_c values:

1) at equilibrium, the compound does not form in the required A15 structure and has to be stabilized by using appropriate preparation techniques or by impurities, as $V_{\sim 3}Al$[3], $Nb_{\sim 3}Si$[4] or $Mo_{.5}Re_{.5}$[5],
2) the compounds crystallizes in the A15 structure, but the composition corresponding to the highest T_c is metastable (if at all, it is stable at high temperatures only) and must be stabilized by fast quenching or by impurities,
3) the compound crystallizes in the A15 phase at the stoichiometric composition, but undergoes a structural transformation at low

temperatures, as Nb_3Sn[6] or V_3Si[7], and

4) in Nb_3Sn multifilamentary wires, all conditions a-c) mentioned above can be fulfilled, but stress-induced structural changes are introduced through the precompression resulting from the differential contraction of bronze matrix and Nb_3Sn filaments[8,9].

These instabilities, together with the metallurgical difficulties encountered in preparing homogeneous, single-phased samples are the main reason why such fundamental properties as the variation of T_c, ρ, H_{c2} as a function of composition in V_3Si and Nb_3Sn are still a subject of investigation, 28 years after the discovery of these materials. In order to determine the variation of these properties for a given A15 phase, in particular at the vicinity of the stoichiometric composition, a precise knowledge of the phase diagram is needed.

In this paper, a brief review of current methods of determining phase diagrams is presented, together with the results on the most interesting A15 phases. Their superconducting properties will also be presented phenomenologically. A particular attention is given on the compound Nb_3Sn because of its actual importance for the construction of high field superconducting magnets. It is shown that the superconducting properties in the system $Nb_{1-\beta}Sn_\beta$ can only be understood on the basis of the low temperature phase diagram.

HIGH TEMPERATURE PHASE DIAGRAMS

The stoichiometric composition in most A15 phases with high T_c values is only comprised in the equilibrium phase fields at very high temperatures and has to be quenched at sufficiently high rates in order to be retained for a subsequent analysis at room temperature. However, quenching experiments depend on kinetics and thus give only an indirect image of the high temperature behavior: the retained state does not necessarily reflect equilibrium at the quenching temperature. The accurate determination of the temperature-dependent high temperature phase limits thus requires the use of direct observation methods at high temperature, in addition to the room temperature analysis of quenched alloys (indirect observation), which comprises optical and electron microscopy, X-ray and microprobe analysis and other methods, one of which being the measurement of T_c.

Direct Observation Methods

A commonly used method for detecting phase transformations at high temperature is the differential thermal analysis (DTA), which detects a signal due to the latent heat of transformation[10]. In A15 superconductors, the phase of interest always forms in the temperature range $1500 < T < 2300^\circ C$, where the contamination of the alloy by the crucible material or by impurities in the heating chamber can be a serious problem. Furthermore, the important evaporation rates of volatile components at these temperatures may render the detection of thermal arrests more difficult. In some cases, a DTA apparatus working at moderately high argon pressures (up to 20 atm.) was found to give good results[10,11]. There are, however, cases where the contamination of the analysed alloy by the crucible material induces important errors in the measurement of the solidus temperature. A technique which completely eliminates this problem is the recently developed levitation thermal analysis (LTA)[11,12]. This method is based on the fact that the shape of the melting part of the sample at the solidus temperature immediately follows the electromagnetic field gradient in the r.f. levitation coil. The consequence of the suddenly enhanced coupling is a dramatical increase in temperature, (several hundred degrees) which is detected by means of a two-color pyrometer. In order to account for the unknown spectral emissivity of each alloy and for the selective absorption of all optical components (glass window, crown glass prism, filter) the pyrometer has to be calibrated for each sample[11,12], after which the error in temperature is limited to ±10°C at 2000°C.

The occurrence of superconductivity in a given phase offers a unique possibility for determining the concentration gradient in the measured alloy. Indeed, the value of T_c depending on composition, the width of the superconducting transition as measured by low temperature calorimetry thus reflects the state of homogeneity. Prolonged homogenization heat treatments (up to 1 week) close to the solidus temperature were found to be necessary for a considerable reduction of this width to a few tenths of a degree[11]. It is obviuos that such homogenized alloys lead to sharper thermal arrests, thus improving the precision. It is a somewhat unexpected result of the research in the superconductivity field that it contributed to the development of new or improved methods for the accurate determination of high temperature phase diagrams.

Phase diagrams of high T_c materials

The Nb rich portion of the phase diagrams for the systems Nb-Ga[13], Nb-Ge[14] and Nb-Al[15] as determined by a combination of direct and indirect methods is represented in Fig.1. The particular shape of the peritectically forming A15 phase is very similar for the three systems. In Nb-Ga and Nb-Al, the stoichiometric composition represents the extremum solubility limit of the A15 phase field. In Nb-Ge the highest Ge content at equilibrium is 23 at.%, i.e. the stoichiometric composition is not comprised in the equilibrium phase field. The application of the same principles has led to the diagrams shown in Figs.2 and 3, showing the V rich portions of the V-Ga[16] and of the V-Si[17,18] systems. In contrast to the Nb based compounds, the A15 phase in both V based systems is formed congruently, in V_3Si from the melt, in V_3Ga from the bcc solid solution.

As shown recently[11], the type of formation of the A15 phase in a system $A_{1-\beta}B_\beta$ is essentially governed by the B element. If successive B elements are taken, starting from VIIB up to VA elements, the formation of the A15 phase shows the sequence: peritectoid ⟶ congruent ⟶ peritectic. The limits between two types of formation also depend on the B element (transition or nontransition ele-

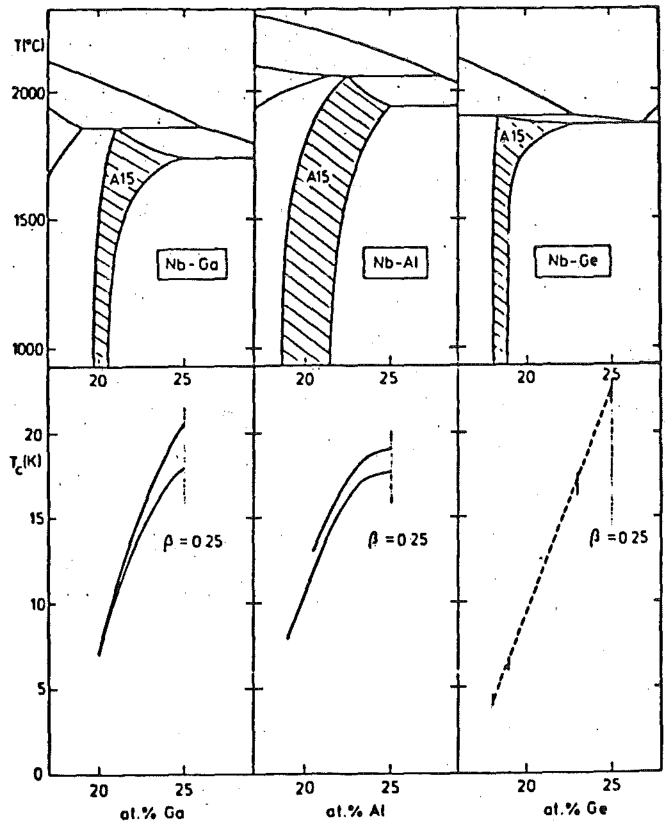
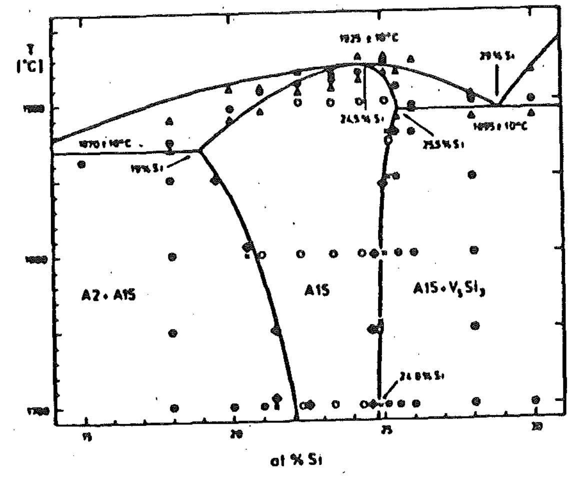


Fig.1. A15 phase fields and superconductivity in Nb_3B compounds, where B=Ga, Al, Ge (Refs. 11,12,13,14,15)



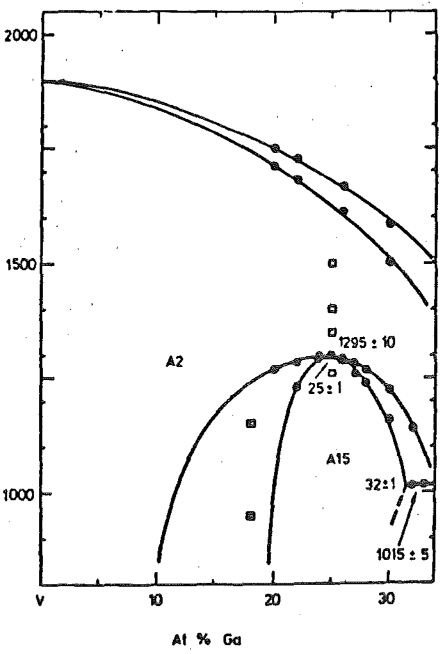


Fig.2. The A15 phase field in the system V - Si(Ref.18)

Fig.3. The A15 phase field in the system V - Ga(Ref.16)

ment. It is interesting that all known compounds containing Au form congruently, Ti_3Au and Zr_3Au from the melt, V_3Au, Nb_3Au and Ta_3Au from the bcc solid solution. It is actually not well understood how these regularities are connected to regularities in the variation of the low temperature electronic properties.

THE VARIATION OF THE ELECTRONIC PROPERTIES WITH COMPOSITION

The superconducting transition temperature

Within the homogeneity range of a superconducting phase, T_c has been found to vary considerably as a function of the chemical composition. If shielding effects[11] can be avoided, this variation can be used as a supplementary tool in determining compositions with good accuracy[11]. There is, however, an additional effect influencing T_c which so far has only been found in A15 type compounds: the degree of atomic long-range ordering[19,20]. The system V_3Ga is particularly adapted to illustrate ordering effects on T_c, the stoichiometric composition being stable at all temperatures (see Fig.3). As shown in Fig.4, a higher degree of ordering is correlated to a higher T_c value. The observed peak at 650°C is only apparent: it simply indicates the temperature at which the originally arc cast V_3Ga sample reaches its equilibrium order parameter value[21]. This illustrates the ordering kinetics: even during the very short cooling time after arc melting (initial cooling rate: 50 to 100 °C/s), the order parameter still increases. The situation is more complex if the stoichiometric composition is stable at high temperatures only. The separation of ordering and compositional changes on T_c has been stu-

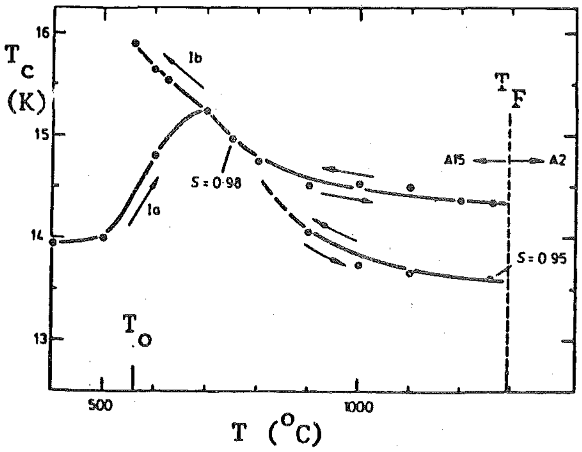


Fig.4. Variation of T_c of V_3Ga with heat treatment. Cooling rates: ● 15°C/s, o 10^3 °C/s. (Ref. 21)

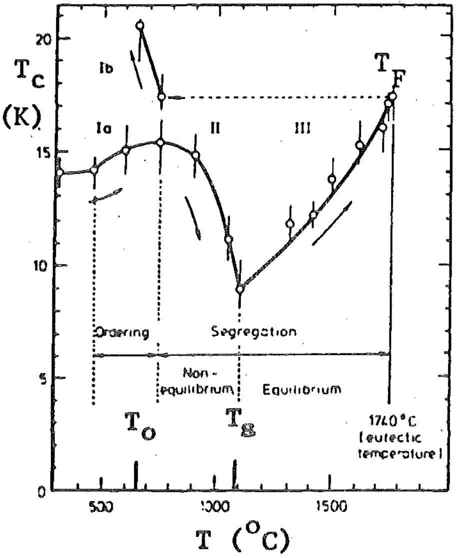


Fig.5. Variation of T_c of the Nb – Ga phase with heat treatment (Ref.21).

died for the system Nb-Ga[21]. Fig.5 shows the variation of T_c for an arc cast alloy of the overall composition $Nb_{.74}Ga_{.26}$ which was successively annealed and quenched at increasing temperatures. In this case, the behavior of T_c as a function of the heat treatment is characterized by two activation energies for ordering and segregation, respectively. These energies correspond to the temperatures T_o and T_s in Fig.5. It is interesting that even an alloy at the metastable stoichiometric composition can in principle be ordered if $T_o < T_s$. This condition seems to be fulfilled for Nb_3Al and Nb_3Ga. However, perfect order is very rarely reached in A15 type compounds, and most order parameters are limited to values below $S_a = 0.98$[19,20,21], probably as a consequence of insufficient diffusion at the temperature T_o, which is typically of the order of 650°C. The two apparent exceptions, V_3Ga and Nb_3Sn, which will be discussed in the next paragraph.

The variation of T_c as a function of composition for a phase crystallizing in the A15 structure can be established if the annealing temperature and the cooling rate are the same for all compositions. In general, an essentially linear variation of T_c with composition is observed. In some cases, a "saturation" of T_c at compositions close to stoichiometry was reported, but was mostly due to shielding effects[11]. There is one exception, Nb_3Al: it was first reported by Muller[22] and recently confirmed by Sweedler et al.[23] and Flükiger et al.[24] that for Al contents beyond 23 at.% a further decrease of the lattice parameter was observed, while T_c remains essentially constant. In a very careful investigation which included also specific heat and order parameter measurements, it has been shown[24] that the slower increase of T_c in Nb_3Al is not connected to a decrease of the long-range order parameter. Since no low temperature structural transformation could be detected[24], the reasons for this particular behavior in this system are still unclear. A possible explanation has been furnished by Kwo et al.[25], who concluded from tunneling experiments that the phonon spectrum in Nb-Al may vary with composition.

Upper Critical Field And Electrical Resistivity

It is interesting to follow the variation of the upper critical field, H_{c2}, as a function of composition for different A15 compounds. Fig.6 shows that H_{c2} for Nb based compounds is of the order of ∿6 Tesla per at.% Ga, Ge or Sn (the latter in the cubic phase). Like T_c or the electronic specific heat, the upper critical field of A15 compounds also depends on the order parameter, as shown in Fig.7 for V_3Ga[26]. The corresponding variation of $\rho(T)$ for V_3Ga is represented in Fig.8: for a higher order parameter, a smaller resistivity value is measured. The effect of ordering on ρ has been studied on Nb_3Pt, where the order parameter was changed by quench and anneal methods[26] from $S = 1$ to $S = 0.94$: $\rho_{\gtrsim T_c}$ was found to decrease from 87 to 20 μΩcm. The electronic mean free path was determined to $\ell \approx 100$ Å in the most ordered state and decreased by a factor 10 for the state at S = 0.94. The latter corresponds to 1.5% of the Nb sites occupied by Pt atoms. From the reversibility of the resistivity curves in Fig.9, it can be deduced that the effect of the heat treatments on ρ(T) is really an order effect and is not due to microcracks, precipitations or other effects.

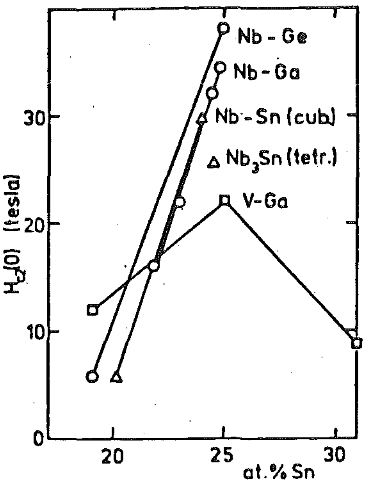


Fig.6. Variation of the upper critical field of several A15 compounds with composition

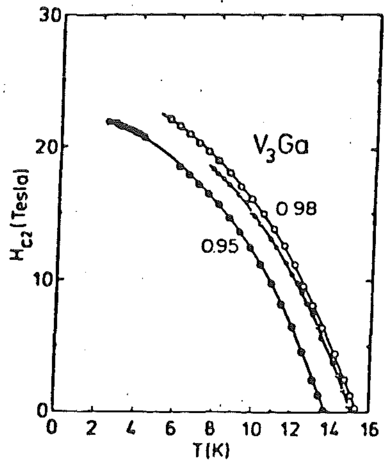


Fig.7. $H_{c2}(T)$ for V_3Ga at two different degrees of ordering, S = 0.98 and S = 0.95 (Ref.26)

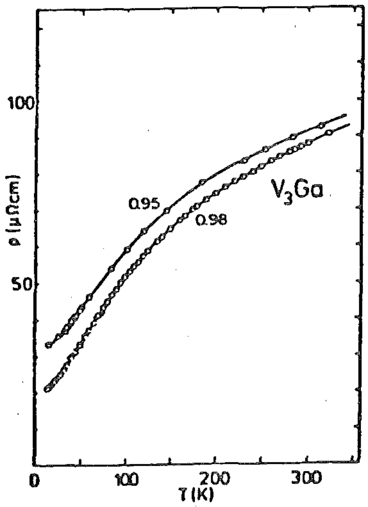


Fig.8. ρ(T) for V_3Ga at two different degrees of ordering, S = 0.98 and S = 0.95 (Ref.26)

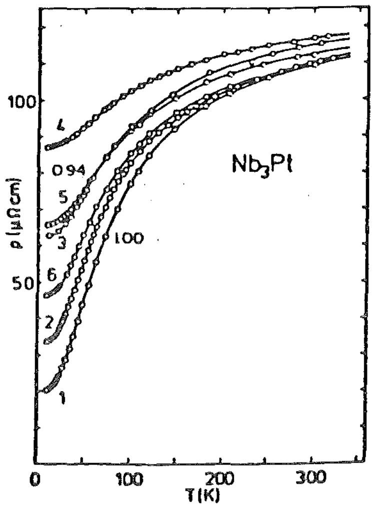


Fig.9. ρ(T) for Nb_3Pt at different degrees of ordering (Ref. 26).

THE A15 PHASE IN THE SYSTEM Nb - Sn

The cubic and the tetragonal phase fields

The high temperature phase diagram at the Nb rich portion of the Nb - Sn system according to Charlesworth et al.[27] is represented in the upper part of Fig.10. At T ≈ 1000°C,the A15 phase field varies from ∿19 to 25.5 at.% Sn, the stoichiometric composition being stable up to ∿1700°C. In the lower part of Fig.10, the phase field of the low temperature tetragonal modification has been represented. The tetragonal phase forms spontaneously at T_M = 43K and 25 at.% Sn, according to several authors[7,33,34]. This phase forms congruently from the solid A15 phase, the transformation being of the first order[34]. From a great number of observations, however, it follows that the transformation is on the verge to be of second order ("weak" first order). The tetragonal phase is stable within the limits 24.5 and 25.2 at.% Sn, the uncertainty in composition being of the order of ± 0.02%.This narrow phase field is confirmed by the specific heat data of Junod et al.[35] on Nb - Sn samples of different compositions and with different fractions of transformed phase. The calorimetrically determined superconducting transition of the tetragonal phase is indeed much narrower than that of the cubic phase present in the same sample: ∿0.5K compared to >3K[28,36].

Homogeneous Nb - Sn samples in the A15 cubic phase cannot be prepared by arc melting[36]. They have to be prepared either by a) levitation melting, followed by a homogenization heat treatment at 1800°C (both under high argon pressure)[28] or b) sintering of pressed fine Nb and Sn powders at 1300°C (1 week), followed by crushing, pressing and new sintering under the same comditions[30]. Both methods,

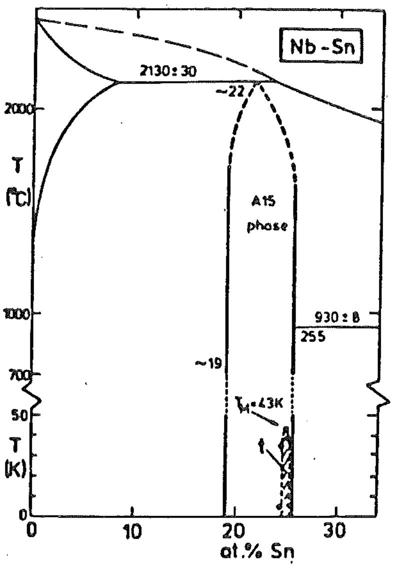


Fig.10. The A15 and the tetragonal phase fields in the system Nb - Sn.The high temperature part is taken from Ref.27.
o transformation temperature (Ref. 30)
● not transforming (Ref.28)
The point at T_M = 43K was taken from Ref. 33,34,45.

a) and b) allow to restrict the distribution in composition within a range of ∿1 at.%[28]. The better sample homogeneity in the recent investigations[9,28,30] is probably the reason why the tetragonal phase field in Fig.10 is narrower than that previously reported by King[29], which is based on samples sintered for 3 hours at 1450°C. Indeed, a larger composition gradient always leads to a certain volume fraction with Sn contents exceeding ∿24.5 at.%. This causes a line broadening at low temperature which may be interpreted as a transformation[28].

Atomic Ordering And Superconductivity

It is well-known that V_3Si and Nb_3Sn are the only A15 compounds showing a low temperature structural transformation[6,7]. Other properties encountered exclusively in these two compounds are: a) both exhibit in single crystals residual resistivity values $\rho_{\gtrsim T_c}$ of the order of ∿3μΩcm[37], by far the lowest among all known A15 phases (see Fi.11) and b) their measured order parameter at room temperature is $S = 1$[31,32], i.e. both are perfectly ordered. It is interesting that T_c of V_3Si as well as for Nb_3Sn is not affected by conventional quenching techniques, even at $T \cong 1800$[18,32] and 1700°C[11,32], respectively. This in contrast to the behavior in all other A15 compounds with reasonably high values of T_c and of the electronic density of states, where large variations have been reported (Figs.4 and 5).On the other hand, T_c can be drastically changed by irradiation techniques, which were recently reviewed by P.Muller[38]. Recently, Pannetier et al.[39] have performed cw laser annealing on V_3Si, with quenching rates $>10^4$ °C/s, and observed a gradual decrease of T_c of several degrees from $T_Q \approx 1700$°C. This can be interpreted as the proof that the cooling rates in conventional quenching devices , $<5X10^3$, were not sufficiently high for preventing complete reordering on cooling. Thus, V_3Si seems to have a very fast ordering kinetics. If this can be extended to Nb_3Sn, it follows that the chance of obtaining disordered states in multifilamentary wires as obtained by the bronze process is small. In this case, T_c changes after different reaction heat treatments should rather depend on composition and/or on the stress state[11,32].

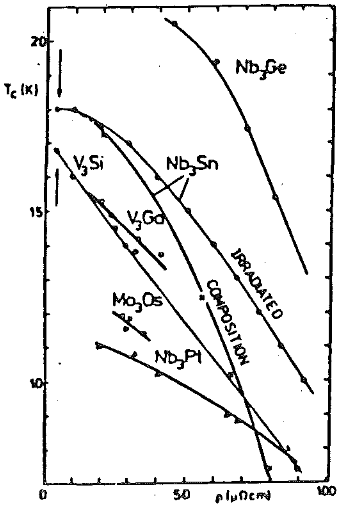


Fig.11. Superconductivity and electrical residual resistivity for various A15 compounds (Ref. 26,28,38). The arrows show the lowest values of $\rho_{\gtrsim T_c}$, measured for the compounds V_3Si and Nb_3Sn.

The electronic properties as a function of the Sn content

The variation of T_c , $\rho_{\geq T_c}$ and $(dH_{c2}/dT)_{T_c}$ as a function of the Sn content on the basis of the data of Orlando et al.[40] and Devantay et al.[28] is shown in Fig.12. The residual electrical resistivity between 24 and 25 at.% Sn decreases by a factor ~5. This strong variation reflects the perfectly ordered state in Nb_3Sn: $\rho_{>T}$ is strongly affected by small changes of both, composition and atomic ordering, the latter being obtained by irradiation methods (Fig.11). The most interesting feature is the variation of T_c(Fig.12): the reported value T_c=18K corresponds to the tetragonal phase, T_c=17.8K being measured for the cubic phase at ~24.5at.% Sn. If the cubic phase could be stabilized at stoichiometry (β = 0.25), values as high as ~18.5K would be reached[28]. The higher $\rho_{>T}$ valuefor the cubic phase, due to a lower Sn content, leads to higher values of the initial slope(Fig.12) and of H_{c2} (Fig.6). This is particularly important for the application of Nb_3Sn in high field magnets: for fields >12T, where J_c is essentially governed by H_{c2}, a stabilization of the cubic phase would be preferable.

The suppression of the spontaneous tetragonal phase in Nb_3Sn

Dissolving hydrogen[41,42,43] or metallic additions as Al[45] or Ta[8,9,44] in Nb3Sn leads to a suppression of the tetragonal phase which forms spontaneously at T_M=43K. In both cases, the extension of the cubic phase toward higher Sn contents has led to higher T_c values, varying from 18.2 to 18.6K[30,42,44,45]. This increase in T_c confirms the above result[28] of a higher T_c value for stoichiometric, cubic

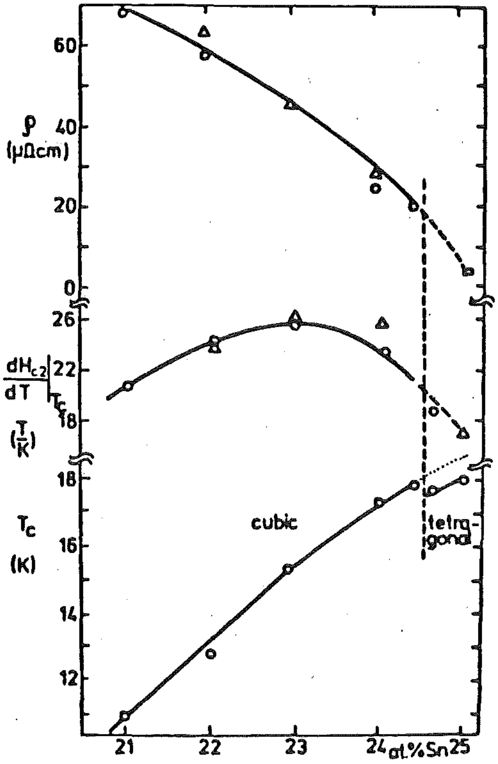
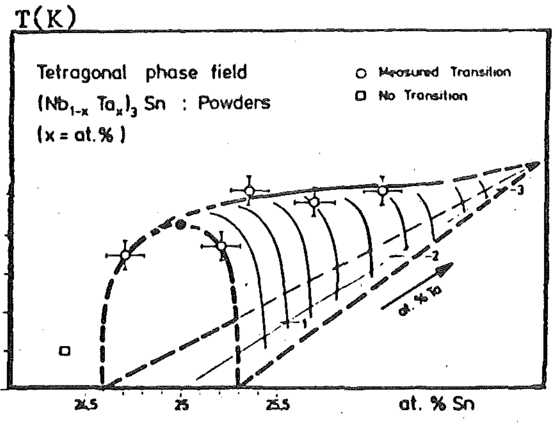


Fig.12. T_c, $(dH_{c2}/dT)_{T_c}$ and $\rho_{\geq T_c}$ in the system Nb-Sn as a function of the Sn content.
o data on bulk samples(Ref.28)
data on coevaporated films. (Ref. 40).

Fig.13. The tetragonal phase field in $(Nb_{1-x}Ta_x)_3Sn$ (Ref. 30).



Nb_3Sn. The mechanism is shown in Fig.13 for $(Nb_{1-x}Ta_x)_3Sn$ (Ref.32).

At the Ta rich limit of the tetragonal phase field in Fig.13 a maximum of T_c was observed: $T_c' = 18.3K$[30,44], which can be explained as a superposition of two opposite effects: a) with higher Ta contents, the limit of the cubic phase gets closer to the stoichiometric composition, which causes an increase in T_c, and b) the increasing amount of Ta on the chain sites causes an increasing disorder and thus to a decrease in T_c. The increase of H_{c2} as a consequence of the Ta addition is thus not only due to a shorter electronic mean free path, baut mainly to the increase of T_c of the cubic phase, in the present case close to 0.5K. The same behavior has been found for a series of other additions[30,44]

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