# NEW MATERIALS FOR SUPERCONDUCTING RADIOFREQUENCY CAVITIES

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#### Abstract

According to the BCS theory, a good candidate for superconductive RF applications must not only be a good superconductor (high  $T_C$  ), but also a good metal in the normal state at low temperature. As far as residual losses are concerned,  $R_{res}$  rises with  $R_n$ , the surface resistance in normal state, according a law not weaker than proportionality between  $R_{res}$ , and the square root of  $\rho_n$ . Therefore, between two different materials with different values of  $T_C$  and  $\rho_n$ , having the same  $R_{BCS}$ , the most metallic should have the smallest  $R_{res}$ . On the basis of this criterion, NbTiN is preferable to NbTiN; V<sub>3</sub>Si, for its high RRR values, is preferable to Nb<sub>3</sub>Sn. The recently discovered intermetallic, MgB<sub>2</sub>, with a  $T_C$  of 39 K , is also taken in exam. However, although its high critical temperature and its metallic behaviour, its application to RF structures is still far. The degradation of the superconducting properties after immersion in water, the presence of a double gap, technological difficulties of preparation are only three of the many problems encountered when working with MgB<sub>2</sub>.

## **1 THE BCS SURFACE RESISTANCE**

According to the classical theory of skin effect for normal metals, in the normal regime, at a certain angular frequency  $\omega$  the surface impedance  $Z_n$  can be written as

$$Z_n = \frac{1-i}{\sigma_n \delta} = (1-i)\frac{\rho_n}{\delta}$$

where  $\sigma_n = 1/\rho_n$  is the dc conductivity at the working temperature and  $\delta$  is the classical skin depth

$$\delta = \sqrt{\frac{2}{\mu\omega\sigma_n}}$$

The results for normal metals can be promptly extended to superconductors when a complex conductivity  $\sigma_1 - i\sigma_2$ is introduced in place of the normal state conductivity  $\sigma_n$ . Hence, as derived by Nam [1], for  $T < T_C /2$  (*T* is the operational temperature, while  $T_c$  is the superconducting critical temperature),  $R_s$  can be approximated by the formula

$$\frac{R_s}{R_n} = \frac{1}{\sqrt{2}} \frac{\sigma_1 / \sigma_n}{(\sigma_2 / \sigma_n)^{3/2}} \tag{1}$$

In the framework of the BCS theory extension at finite frequencies, Mattis and Bardeen [2] found, for

h' $\omega$ <2 $\Delta$  two following integral relations for the complex conductivity of a superconductor:

$$\frac{\sigma_1}{\sigma_n} = \frac{2}{\hbar\omega} \int_{\Delta}^{\infty} [f(E) + f(E + \hbar\omega)] g^+(E) dE \qquad (2)$$

$$\frac{\sigma_2}{\sigma_n} = \frac{1}{\hbar\omega} \int_{\Delta-\hbar\omega, -\Delta}^{\Delta} \left[ 1 - 2f(E + \hbar\omega) \right] g^{-}(E) dE \quad (3)$$

where

$$f(E) = \frac{1}{1 + e^{E/K_B T}}$$

and

$$g^{\pm}(E) = \frac{E^2 + \Delta^2 + \hbar\omega E}{\sqrt{\pm \left(E^2 - \Delta^2\right)}\sqrt{\left(E + \hbar\omega\right)^2 - \Delta^2}}$$

 $\Delta$  is the superconductive energy gap, that in the relation

$$2\Delta = sK_BT_a$$

is related to the Critical Temperature by the strong coupling factor s, that equals to 3.52 for "weak coupling" superconductors, but it can reach even 4.4 for "strong coupling" superconductors.

The two integrals  $\sigma_1 / \sigma_n$  and  $\sigma_2 / \sigma_n$  are easily numerically calculated [3]. In particular they can be approximated [4] in the normal skin effect regime for  $\hbar\omega \ll 2 \Delta$  by two analytical expressions:

$$\frac{\sigma_{1}}{\sigma_{n}} = \left[\frac{2\Delta}{\left(1+e^{-\Delta}/\kappa_{B}T\right)^{2}}\right]e^{-\Delta}/\kappa_{B}T}\ln\frac{\Delta}{\hbar\omega}$$
(4)

$$\frac{\sigma_2}{\sigma_n} = \frac{\pi \Delta}{\hbar \omega} \tanh \frac{\Delta}{2K_B T}$$
(3)

By some algebra, one arrives to the following formula, valid only if  $T < T_c / 2$ ,

$$R_{BCS} \cong \frac{R_n}{\sqrt{2}} \left(\frac{\hbar\omega}{\pi\Delta}\right)^{\frac{3}{2}} \frac{\sigma_1}{\sigma_n} = A\sqrt{\rho_n} \frac{e^{-\frac{\Delta}{K_B T_c}}}{\sqrt{sT_c} T \left(1 + e^{-\frac{\Delta}{K_B T_c}}\right)^2} \omega^2 \ln \frac{\Delta}{\hbar\omega}$$
(6)  
with  $A = 6.0 \times 10^{-21} \left[\frac{\Omega K^3}{ms^4}\right]^{\frac{1}{2}}$ 

Although limited to the dirty limit superconductors, formula (6), although approximated, clearly shows how low  $R_{BCS}$  values can be obtained, when lowering the low temperature resistivity  $\rho_n$  and increasing  $T_C$ .

In other words the BCS theory predicts that a good candidate for superconductive rf applications must be not only a good superconductor (high  $T_c$ ), but also a good metal in the normal state (low  $\rho_n$ ).

Since  $R_{BCS}$  is function of  $\rho_n$  and  $T_C$ , the nomogram [5] of fig. 1 can be constructed for materials at 4.2 K, 500 MHz and a strong coupling factor of 4. Chosen a certain value of  $R_{BCS}$ , on the corresponding curve there are all the materials with different  $T_C$  and  $\rho_n$  having the same

R<sub>BCS</sub>. From the nomogram of fig. 1 for instance, clearly appears that a Mo-Re alloy, 25 at. % Rhenium, have a  $T_C = 10$ K and  $\rho_n = 7 \mu\Omega$  cm presents at 4.2 K and 500 MHz the same BCS losses (~32 nΩ), of a Mo-Re 40, at. % Rhenium, having a  $T_C = 12$  K and  $\rho_n = 30 \mu\Omega$  cm. On the same way a NbN with  $T_C = 16.5$  K and  $\rho_n \sim 120 \mu\Omega$  cm [5], and a NbTi N with  $T_C = 15.2$  K and  $\rho_n = 35 \mu\Omega$  cm have both R<sub>BCS</sub> ~ 5 nΩ.

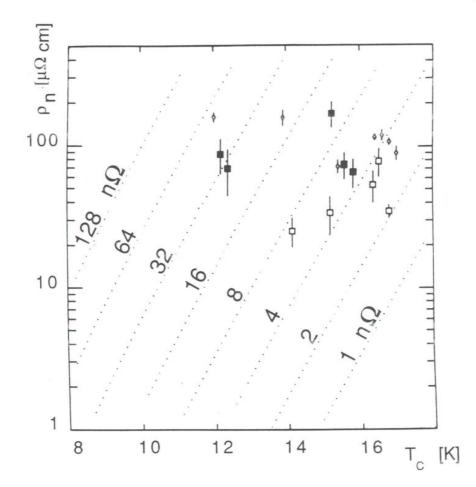


Fig. 1 - Lines of equal  $R_{BCS}$  at 4.2 K and 500 MHz in the bidimentional space ( $\rho_n, T_C$ ). Fixed the working temperature (T = 4.2 K), and the frequency (f = 500 MHz),  $R_{BCS}$  depends only on the energy gap and on the normal state resistivity. The  $T_C$  scale is draft for the case s = 4. For comparison Nb coated cavities provide  $R_{BCS} = 55 n\Omega$ . The experimental data refer to: sputtered films of (NbTi)N at 200°C (full square); (NbTi)N at 600°C(empty square); NbN at 200°C

It must be kept into account that the validity of above reported formulas is however limited to dirty limit superconductors. Niobium fails out of this limit, when mean free path becomes comparable with coherence length: in such a case even  $R_{BCS}$  increases when the Niobium purity is enhanced.

#### 2 RESIDUAL LOSSES

The  $R_{BCS}$  dependence on  $\rho_n$  and  $T_C$  represents an immediate criterion for selecting, among superconductors with  $T_C$  higher than the one of Niobium, those are the most favourable candidates for coated cavities. Unfortunately such a criterion is invalidated by the fact that the BCS surface resistance at T=0 in practice never vanishes, due to the presence of a temperature independent residual term of several n $\Omega$ :

# $R_s = R_{BCS}(T) + R_{res}$

In the author opinion, the term "residual" is a fictitious word, adopted for indicating all those causes that escape from the experimentalist control. Indeed even if much is reported in literature about the possible origins of the non-BCS losses, they are far from being completely understood. Both "physical phenomena" and "accidental mechanisms" (like dust, chemical residuals or surface defects on the cavity walls ) contribute to parasitic losses. In particular the following are considered to mainly affect the residual loss resistance: Losses due to a non-ideal surface quality; Metallic inclusions within  $\lambda$ ; Residual resistance due to the Niobium oxides; Residual losses on grain boundaries due to polycrystallinity; Residual resistance due to flux trapped during the cooling. Due to the variety of the phenomena involved, it is impossible to give one formula predicting the residual losses. Nevertheless it is possible to deduce some interesting information from literature analysis: <u>R<sub>res</sub> rises with R<sub>n</sub></u>, the surface resistance in normal state, by a law not weaker than proportionality. So, Rres is at least proportional to the square root of  $\rho_n$ . Therefore, among two different materials with different values of  $T_{\underline{C}}$  and  $\rho_n$ , having the same  $R_{BCS}$ , the one with lower  $\rho_n$  should have the smallest Rres. That strengthens once more the selection criteria that metallic materials are preferable to intermetallic compounds.

## **3 IDENTIFICATION OF THE MOST SUITABLE SUPERCONDUCTORS**

#### 3.1 B1 Compounds

Among B1 compounds (NaCl structure), only few Nitrides and Carbides of the IV, V and VI group Transition Metals have critical temperatures higher than that one of Niobium. Table 1 reports the B1 compounds that have been found superconductors [6].

<u>NbN</u> Because of its high critical temperature of 17.2 K, NbN is the only B1 simple compound that has widely tested for accelerating cavities. Mainly two different techniques have been investigated: Thermal diffusion of N into Nb followed by rapid quench cooling and Reactive Sputtering onto Nb cavities. Rather seldom NbN applied to superconducting cavities gives better results than those obtainable by bulk Nb or Nb sputtered Cu. The main reason for this is the anomalously high resistivity of NbN in the normal state, that, even if not always reported in the NbN cavities literature, is often higher than 100  $\mu\Omega$  cm resulting into  $R_{BCS}$  and  $R_{RES}$  values larger than the expectance.

BA	Sc	Y	La	Ti	Zr	Hf	۷	Nb	Ta	Cr	Мо	W	Re
В	Sec. 5	1.00		210	3.4	3.1							
С	<1.38	<1.38		3.42	<0.3	<1.20	0.03 3.2*	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	
Р	(16) (16)	19.2	<1.68				dia an	f e tra	12	<u>7</u> - 191			
Sb		<1.02	<1.02	14 23							2.12		
0	12	12/22	12	2.0	100		<0.3	1.39	1.1			1.00	
S	<0.33	1.9	0.87	1.3	3.3		2.11				1.1		25
Se	<0.33	2.5	1.02	1.1			120		1.1	1.2		1.10	
Te	1999	2.05	1.48	111	$1 \le 1$	1.19					- 1		No.

Table 1 - Critical Temperature of compounds with NaCl structure

NbN grains grow as columns perpendicular to the film plane, weakly bounded among each others, and separated by strong boundaries consisting of voids, normal conducting areas of Niobium and Niobium-dissolved gas composite phases like Niobium sub-Oxy-Carbo-Nitrides lumps. The denser is the grain boundary matrix, the higher is generally the normal state resistivity of NbN films. Resistivity values of the order of  $1000 \ \mu\Omega$  cm are indeed encountered by sputtered films, with small average grain size, around 100 Å wide. Such films even show a strongly negative slope of resistivity against temperature that means RRR < 1 just as for semiconductors.

On the other hand  $T_C$  's close to the maximum 17.3 K are monitored almost in correspondence of low resistivity values (100  $\mu\Omega$  cm and RRR  $\geq$  1). The right B1-NbN superconducting phase is the so- called  $\delta$ -phase corresponding to a lattice parameter of 4.388 Å and having a  $T_C$  very sensitive to Nitrogen stoichiometry. In sputtered films the  $\delta$ -phase can be found mixed to some other low  $T_C$  phases like the  $\alpha$ -Nb phase constituted by interstitial Nitrogen in bcc Nb lattice, the exagonal (W2C type)  $\beta$ -Nb<sub>2</sub>N, the face centred tetragonal (distorted NaCl type)  $\gamma$ -Nb<sub>4</sub>N<sub>3</sub> and the exagonal (TiP type)  $\epsilon$ -NbN phase.

Unfortunately even if no grain boundaries are present and a  $\delta$ -phase single crystal is considered the single grain resistivity is not so low: A minimum value of  $\rho_n = 30 \,\mu\Omega$  cm is expected, due to both metallic and gaseous vacancies in the lattice. This problem that is common to all the other B1 compounds consists in the fact that what corresponds to the equiatomic composition is not the formula Nb<sub>1.0</sub>N<sub>1.0</sub>, but Nb<sub>0.987</sub>N<sub>0.987</sub>: vacancies randomly distributed in both sublattices amounts to 1.3% respectively.

<u>*NbC*</u> It is worthwhile to consider: a  $T_C = 12$  K and  $\rho_0 > 19$  μΩ cm at 500MHz, give in the nomogram of fig. 1,  $R_{BCS} = 16$  nΩ.

Stoichiometric NbC is metastable at ambient temperature and in the stable phase only 80% of the carbon site are occupied.

A practical method to produce NbC for coating cavities is the reactive sputtering in  $CH_4$  or  $C_2H_6$  atmosphere. In literature sometimes  $C_2H_2$  is used because of the less H contamination and the lower dissociation temperature of such gas. However when grown without any external substrate heating polycrystalline films form a columnar microstructure.

<u>NbCN</u> In 1953, Matthias obtained a superconducting transition temperature of 17.8 K in the ternary alloy (NbN)<sub>0.75</sub>(NbC)<sub>0.25</sub>. In fig. 2 the transition temperature of NbN films is plotted versus the Methane partial pressure: a maximum in  $T_C$  happens increasing the Carbon content.

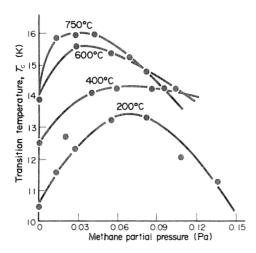


Fig. 2 -  $T_C$  of magnetron sputtered NbN films versus methane partial pressure at various substrate temperatures.

<u>NbTiN</u> It presents all the advantages of the NbN, in the meanwhile it shows electrical conduction properties as more metallic as higher the titanium percentages is. Titanium is a good Nitrogen getter and the more Titanium we have, the lower lattice vacancies will be. The Nitrogen stoichiometry hence is closer to 1 than for NbN. Moreover the critical temperature is even higher than that of NbN for Titanium content up to 40% (fig. 3). The resistivity instead decreases steeply versus the Titanium content [7-9]. This last phenomenon is the main reason under NbTiN choice.

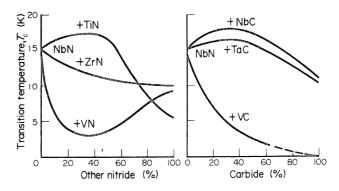


Fig. 3 - Critical temperature vs composition for nitride and carbide addition to NBN

NbTiN cavities have been sputtered at CERN and at Saclay. The  $Q_0$ , at zero field is higher than the Q-value of Niobium cavities, but the accelerating field achieved does not overcome the 10 Mv/m limit [10].

No research has been done on RF applications of NbTiNC, but from literature is well-known that this compound has a critical temperature higher than 17 K and resistivity lower than the values of all the other nitrocarbides mentioned above.

Palladium hydride, Palladium deuteride and hydride of Palladium alloys When Palladium is saturated with hydrogen or deuterium, the latter occupies the octaedral interstices and forms an NaCl structure. Superconductivity in PdH was discovered in1972 by Skowskiewicz [11] and it was found depending critically on the H/Pd ratio. Buckel and Stritzker [12] obtained a Tc around 9 K for H/Pd close to 1 using the ion implantation technique in order to obtain high hydrogen saturation in Palladium. They also discovered the reverse isotope effect due to a Tc of 11 K by saturation of Pd by Deuterium.

The  $T_C$  obtained for the ternary Pd-Ag-H, Pd-Cu-H and Pd-Au-H systems are between 13 and 17 K that are the highest among transition metal compounds. Palladium hydride is unfortunately unstable at room temperature. In the author opinion, however, it should be a good subject for further investigation, since hydrogen should not increase resistivity as it happens instead for nitrides or carbides.

### 3.2 A15 materials

Compounds with A15 structure (generally occurring close to the A<sub>3</sub>B stoichiometric ratio) were first discovered to be superconducting when Hardy and Hulm [13] found that V<sub>3</sub>Si had a transition temperature of 17.1K. In the following year Nb<sub>3</sub>Sn was also discovered with a  $T_C$  of 18.1K by Matthias [14].

Nontransition elements	<i>Т</i> <sub>с</sub> (К)	Transition elements	<i>Т</i> <sub>с</sub> (К)
Ti <sub>3</sub> Sb	6.5	Ti <sub>3</sub> Ir	4.2
Zr <sub>80</sub> Sn <sub>20</sub> <sup>a</sup>	0.92	Ti <sub>3</sub> Pt	0.5
Zr-Pb	0.76	Zr <sub>3</sub> Au	0.9
Zr~3Bib	3.4	-	8.4
V–Al <sup>e</sup>	14	V <sub>29</sub> Re <sub>71</sub> V <sub>50</sub> Os <sub>50</sub>	5.7
V <sub>3</sub> Ga	15.9	$V_{65}Rh_{35}$	~1
V <sub>3</sub> Si	17.0	$V_{63}Ir_{37}$	1.7
V <sub>~3</sub> Ge	6	$V_{\sim 3}^{\circ 3}Pd$	0.08
V <sub>~3</sub> Ge <sup>c</sup>	11	V,Pt	3.7
V~79Sn~21	3.8	V <sub>76</sub> Au <sub>24</sub>	3
V77As23	0.2	Nb <sub>75</sub> Os <sub>25</sub>	1.0
V <sub>76</sub> Sb <sub>24</sub>	0.8	$Nb_{75}Rh_{25}$	2.6
	19.1	$Nb_{72}Ir_{28}$	3.2
Nb₃Al Nb₃Ga	20.7	Nb <sub>3</sub> Pt	11
Nb <sub>~3</sub> In <sup>b</sup>	9.2	Nb <sub>~3</sub> Au	11.5
Nb <sub>82</sub> Si <sub>18</sub> <sup>a</sup>	4.4	Ta <sub>85</sub> Pt <sub>15</sub>	0.4
		Ta <sub>~80</sub> Au <sub>20</sub>	0.55
Nb-Si <sup>c</sup>	11-17		
Nb-Ge <sup>a</sup>	17	$Cr_{72}Ru_{28}$	3.4
Nb-Ge <sup>e</sup>	23	$Cr_{73}Os_{27}$	4.7 0.07
Nb₃Sn Nb–Sb	18 2	$Cr_{78}Rh_{22}$ $Cr_{82}Ir_{18}$	0.07
Nb <sub>~3</sub> Bi <sup>b</sup>	3		0.75
		$Mo_{40}Tc_{60}$	13.4
Ta <sub>~3</sub> Ge <sup>c</sup>	8	Mo <sub>~65</sub> Re <sub>~35</sub> °	$\simeq 15$
Ta <sub>~3</sub> Sn	8.3	Mo <sub>75</sub> Os <sub>25</sub>	13.1
Ta <sub>~3</sub> Sb	0.7	Mo <sub>78</sub> Ir <sub>22</sub>	8.5
Mo <sub>3</sub> Al	0.58	$Mo_{82}Pt_{18}$	4.6
Mo <sub>3</sub> Ga	0.76	$W_{\sim 60}Re_{\sim 40}c$	11
Mo <sub>77</sub> Si <sub>23</sub>	1.7		
Mo <sub>77</sub> Ge <sub>23</sub>	1.8		

a Rapid quenching b High-pressure synthesis c Film deposition techniques

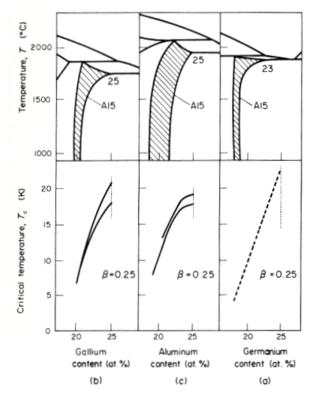
Table 2 - Critical temperature of binary A15compounds known to be superconducting

The  $T_C$  of most A15 compounds is strongly influenced by the degree of Long-Range crystallographic Order (LRO). For compounds in which the B atom is not a transition metal,  $T_C$  is maximized when all the atoms are on the A sites, all the B atoms are on B sites and the LRO parameter *S* approaches 1. When instead the B atom is a transition element, the compounds do not have the same sensitivity to order[15].

The critical temperatures of all the known A15 superconductors are reported in Table 2, displayed in two

columns: non-transition elements at the B site and transition elements at the B site.

Among some fifty A15 compounds, however, only a few could have a practical interest for RF applications, Nb<sub>3</sub>Sn, Nb<sub>3</sub>Al, Nb<sub>3</sub>Ge, Nb<sub>3</sub>Ga, V<sub>3</sub>Ga, V<sub>3</sub>Ga, V<sub>3</sub>Si and V-Al for instance. Of these, V<sub>3</sub>Si, V<sub>3</sub>Ga, and Nb<sub>3</sub>Sn have a range of homogeneity that includes the A<sub>3</sub>B composition and maximum  $T_C$  is readily obtainable in bulk samples of these compounds. Nb<sub>3</sub>Al and Nb<sub>3</sub>Ga include the ideal composition only at temperatures so high that thermal disorder is excessive. Nb<sub>3</sub>Ge does not exist in equilibrium at the stoichiometric ratio. Phase diagrams of the most interesting Nb-based A15 are displayed in fig. 4.



*Fig.* 4 - A15 phase fields and superconductivity in a) Nb-Ge, b) Nb-Ga and c) Nb-Al Systems

The three compounds Nb<sub>3</sub>Ge, Nb<sub>3</sub>Ga and Nb<sub>3</sub>Al exhibit the highest values of  $T_C$  in A15. The A15 phase field in these three systems has common features which can be characterised as follows:

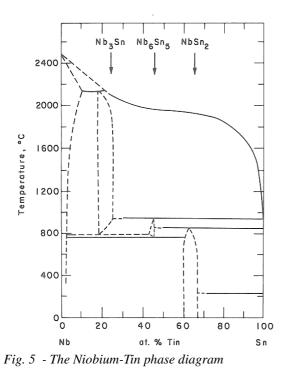
- peritectic formation
- tetragonal and bcc neighbouring phases,
- strongly temperature dependent low niobium phase limit,
- the stoichiometric composition is only stable at high temperature close to the next lower peritectic or eutectic line.

<u> $Nb_3Al$ </u> This compound is formed by a peritectoid reaction from the bcc solid solution and sigma (Nb<sub>2</sub>Al) phase at 1730°C, and contains 26 at. % Al. The stoichiometric composition is metastable at room

temperature and is only stable at 1940 C. The aluminium content of the A15 phase decreases with decreasing temperature; the homogeneity range at 1000°C is  $19\div22$  at.% Al.

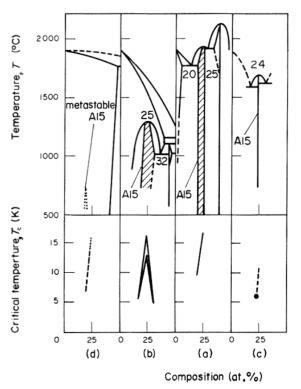
<u>Nb<sub>3</sub>Ge</u> The most striking feature of Nb<sub>3</sub>Ge phase field is that the stoichiometric composition is not included at equilibrium, the highest solubility of Germanium being 23 at.%. At 1000°C, the homogeneity range of the A15 phase is very narrow and is centred at 18 at.% with total width of 1 at.%. It has not been possible to rise  $T_c$  above 17÷18 K in bulk sample either by quenching or other means. Metastable stoichiometric, or near stoichiometric, Nb<sub>3</sub>Ge can be prepared as thin films with critical temperature of 23 K.

<u>Nb<sub>3</sub>Sn</u> Nb<sub>3</sub>Sn is the only A15 material that has given promising results when applied to the construction of a real cavity [16]: Tin was reactively diffused into a Nb bulk cavity and the Q-factor was in the order of  $10^{11}$ , the accelerating field being limited to about 12 MV/m. In the author opinion, this work was excellent and it should be pursued further.



According the phase diagram of fig. 5, the A15 phase is unstable below 775°C. From the same diagram, it is seen that several spurious phases are also possible, and this can represent a limitation for the fabrication of superconducting cavities. Besides  $T_C$ , however for Nb-Sn system there is another quantity undergoing a much stronger variation in the narrow composition range between 24.5 at. % and 25 at.% Sn: the resistivity in normal state just before transition. Resistivity indeed changes from 20  $\mu\Omega$  cm at 24.4 at. % tin to less than 4  $\mu\Omega$ cm at 25 at.% tin; this sharp change being a direct consequence of the perfectly ordered state of Nb3Sn. In the author opinion and according to all written up to now in this paper, this consideration is absolutely critical: for everybody wishing to carry on further investigation on Nb<sub>3</sub>Sn, it is mandatory to look for low resistivity.

The A15 phase fields and the superconducting Critical Temperature of the systems Vanadium-Silicon, Vanadium Gallium and Vanadium-Aluminium are reported in fig. 6.



*Fig.* 6 - A15 phase fields and superconductivity in a) V-*Si*, b) V-Ga, c) V-Ge and d) V-Al Systems

<u>V<sub>3</sub>Ga</u> The A15 phase forms by a congruent reaction from the bcc solid solution at 1295°C and is stable from 20 at. % to 32 at. % gallium. The  $T_C$  shows a marked maximum of 15.9K at stoichiometry and decreases almost linearly on both sizes. V<sub>3</sub>Ga has the highest electronic density of states of all known A15 compounds. In contrast to the latter, however, it does not exhibit a low temperature phase transformation, which is explained by the fact that perfect ordering in this compound cannot be reached, the highest order parameter being S = 0.98.

<u>The V-Al system</u> It shows a  $T_C$  up to 14K, but it is a metastable compound, superconducting only under thin film form. In principle metastability would be not a problem for RF applications construction, if V-Al is sputtered into a resonator, moreover one has the advantage of a relatively low temperature of deposition. It should deserve further investigation, being a relatively little studied compound. The real problem indeed is that, because of metastability, this compound is not applicable

to superconducting magnet construction, then it has been generally neglected in A15 treatises.

<u> $V_3Si$ </u> This material is one of the few examples of an A15 compound that form congruently from the melt. The A15 phase in the Vanadium-Silicon system is stable between 19 and 25 at. % Silicon. Large single crystals can be grown in the whole range either by zone melting or by recrystallization at 1870°C. There is a linear increase in  $T_C$  from 19 at. % to 25 at. % silicon, where a maximum  $T_C$  of 17.1K is achieved. For this compound, the variation of resistivity in normal state before transition has been studied in detail. Fig. 7 reports the RRR value versus the Silicon content.

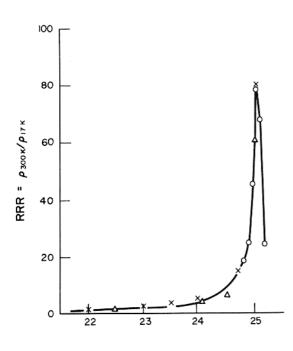




Fig. 7. - RRR values in V<sub>3</sub>Si versus Silicon content

So, now, one question to the reader! Do you know any other binary superconductor with RRR up to 80? The problem of adopting materials other than Niobium for superconducting cavities is just disorder, and disorder means entropy, i.e. resistivity. Residual Resistance will never approach the low values needed for being competitive with Niobium if the system is not ordered. Referring to Fig. 7, at the stoichiometric composition V<sub>3</sub>Si is perfectly ordered. The author and his co-workers have explored the possibility to deposit thin films into a resonator, proposing an original technique for preparing V3Si thin films with good superconducting properties: Vanadium is reactively sputtered in Silane atmosphere, then the film is post-annealed in situ still in Silane atmosphere [17]. This latter operation enables a kind of phase-lock mechanism that corrects the stoichiometric non-homogeneity, unavoidably happening when coating a complex shape substrate. Fig. 8 reports the critical

temperature of  $V_3Si$  films reactively sputtered after a 800 C annealing in Silane atmosphere. The highest RRR value got at the moment was 17, but this result could be easily improved by increasing the annealing temperature. One problem must be solved before to apply this method to cavities: a proper substrate should be chosen. Niobium is not the right choice, because of the large diffusion coefficient of Vanadium into Niobium at high temperatures. The choice of Vanadium itself, as a substrate, should be more deeply considered, due to the drawback of lower thermal conductivity than Niobium, and this is a problem for the achievement of high gradients.

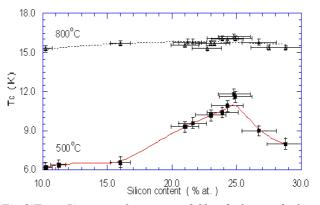


Fig.8 Tc vs Si content for sputtered films before and after in situ post-annealing in SiH<sub>4</sub> atmosphere.

<u>Mo-Re</u> Metastable Mo-Re has the highest Critical Temperature value of even 15 K out of the  $A_3B$  stoichiometry, if grown under thin film form. It has been already applied for cavity prototyping [18], and in the author opinion it would be worthwhile to reconsider. The peculiarities of Mo-Re can be resumed in the following.

The superconducting Critical temperature  $T_C$  in bulk bcc Mo<sub>1-x</sub>Re<sub>x</sub> rises from 0.92K for pure molybdenum up to 12 K at x = 0.40.

The solubility of interstitial elements, particularly oxygen, is low in Mo-Re alloys. Moreover, there is indication that such contamination does not depress superconductivity.

If compared with other alloys, Mo-Re shows low values of the GL parameter, k, and consequently rather high values of  $H_{C1}$  and coherence length. This contributes to decrease the effect of small inhomogeneities by proximity effect.

The highest values of  $T_C$  were observed for sputtered films onto substrates held at 1000°C in the composition  $Mo_{60}Re_{40}$  and 1200°C in the composition  $Mo_{60}Re_{62}$ . An attempt to sputter from a single  $Mo_{60}Re_{40}$  target at low temperatures (300°C) has brought to  $T_C$  values of 11K [19]. Resistivity decreases steadily when increasing the substrate temperature, leading to the conclusion that maybe it would be convenient to try the sputtering at high temperature on a suitable substrate.

# 4 FUTURE: THE RECENTLY DISCOVERED MgB<sub>2</sub>

The discovery of superconductivity in exagonal MgB<sub>2</sub>, by Nagamatzu and Akimitsu [20] in 2001, is remarkable for its unusually high transition temperature of 39K for an sp-bonded. A  $T_C$  of 39K has lead to the general interest in this material, since it opens the way to a new class of simple and low-cost binary intermetallic superconductors with a record HTCs for non-oxide and non C-60 based compounds. Most experimental works, as Raman Spectroscopy, Boron-isotope effect, Spin lattice relaxation time, tunneling measurements and optical conductivity data, are all consistent with the existence of a phonon mediated superconductivity. However an unusual superconducting gap behavior has been observed indicating the existence of a double gap [21] and the presence of a smaller gap is a serious drawback for RF applications. On the other side the material appears promising for RF, since it is rather insensitive to impurity content; it is highly metallic and has strong linked grain boundaries.

Although  $MgB_2$  should be theoretically convenient for radiofrequency and microwave applications even if cooled already at 10K, all results collected up to now [22-24] are limited by high losses even at lower temperature. Nevertheless samples prepared all over the world are of better and better quality better and better results are found.

It is without doubt that in a few years,  $MgB_2$  will be completely mastered by the technology and by sure it will be adopted in even shorter time in the superconducting magnet field. As far as superconducting cavities are concerned, still many problems must be solved: the degradation of superconducting properties of  $MgB_2$  after the immersion in water; the difficulty in sputtering thin films due to the fact that the phase formation temperature is higher than the sublimation temperature.

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