

New understanding of Nb₃Sn doping for strand performance improvement

Ti and Ta don't go where you think they go

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Motivations & background

✓ Why do we need to reinvestigate doping by Ta and Ti in HEP strands?

✓ In recent years J_c in Nb_3Sn wires has been optimized at **12 T** for the HiLumi LHC upgrade that requires **balancing H_{c2} and GB density** for pinning

✓ FCC requires optimization of J_c (**16 T**) that shifts the balance toward **higher H_{c2}** and requires maximum uniformity across the whole Nb_3Sn layer

✓ Nb_3Sn is usually doped by **Ti** or **Ta** to enhance H_{c2} by disorder scattering

✓ Where do **Ti** and **Ta** go?

✓ An early experiment seemed to indicate that both dopants substitute on the Nb site

Tafto et al., Journal of Applied Physics 55, 4330 (1984)

✓ More recently the differing effectiveness of **Ti** and **Ta** in maximizing H_{c2} was interpreted as due to different doping sites (Ta on Nb, Ti on Sn)

Flükiger, R. et al. Cryogenics
48, 293–307 (2008)

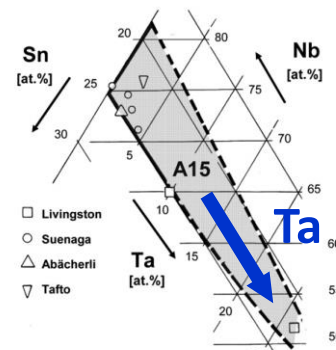


Fig. 8a. A15 phase field of the system Nb-Sn-Ta, as derived from the data of Livingston [44], Suenaga et al. [49], Tafto et al. [47] and Abächerli et al. [13], in the temperature range between 700 °C and 750 °C.

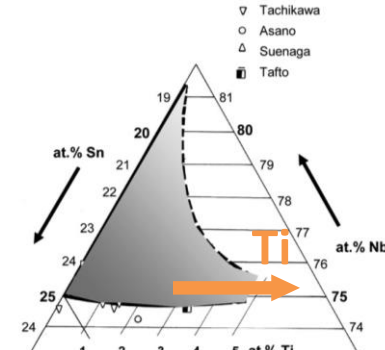


Fig. 8b. A15 phase field of the system Nb-Sn-Ti, as derived from the data of Tachikawa [46], Suenaga et al. [49], Tafto et al. [47] and Asano et al. [60], in the temperature range between 700 °C and 750 °C.

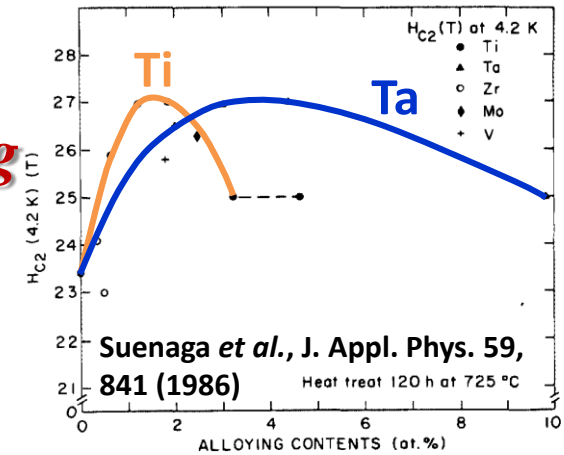


FIG. 8. Critical magnetic field H_{c2} at 4.2 K is plotted as a function of the alloying content for various transition element solutes in Nb_3Sn .

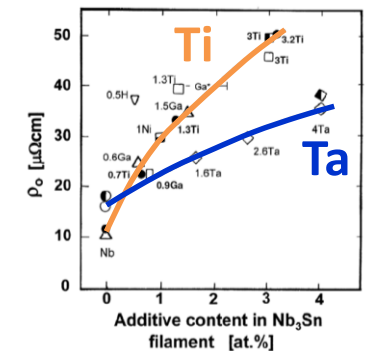
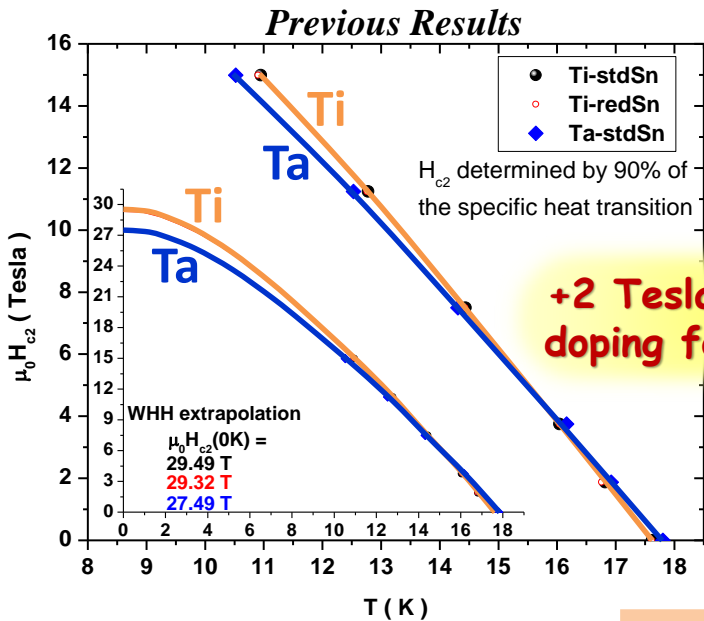
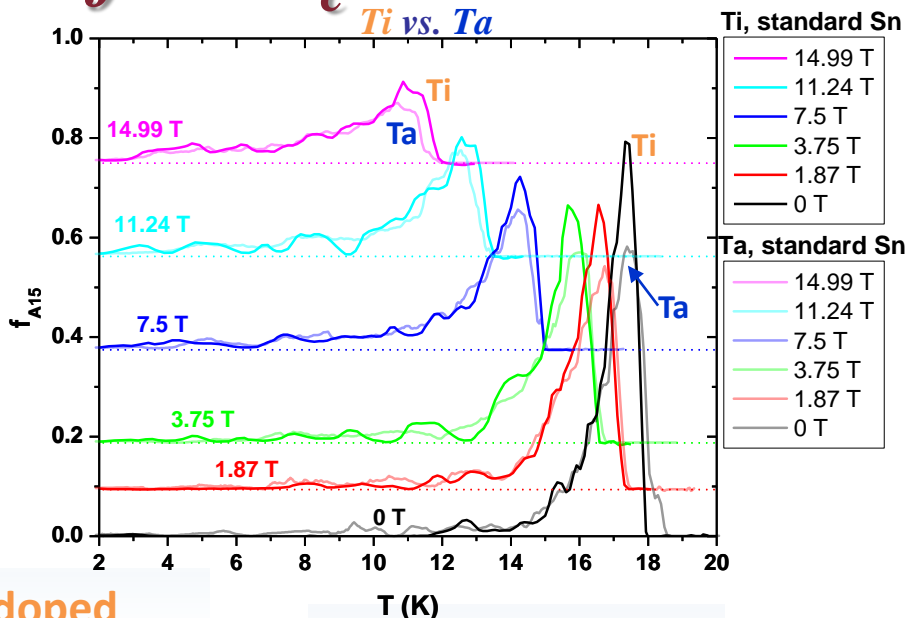


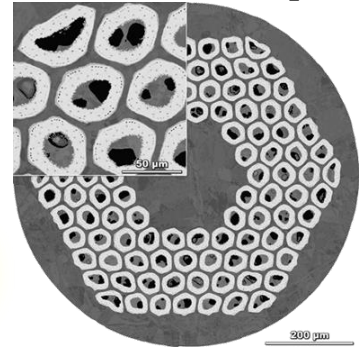
Fig. 9. Normal state electrical resistivity ρ_0 vs. additive contents: Ta [33,49], Ti [33,49], Ga [40] and Ni [41]. The slopes for Nb_3Sn alloyed with Ti, Ga and Ni coincide and are considerably steeper than for the Ta additive, reflecting a different site occupation.

The in-field T_c -distributions are higher and more homogeneous with **Ti**

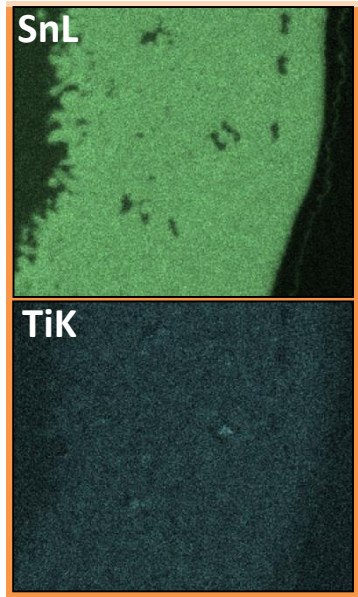
Ti vs. Ta



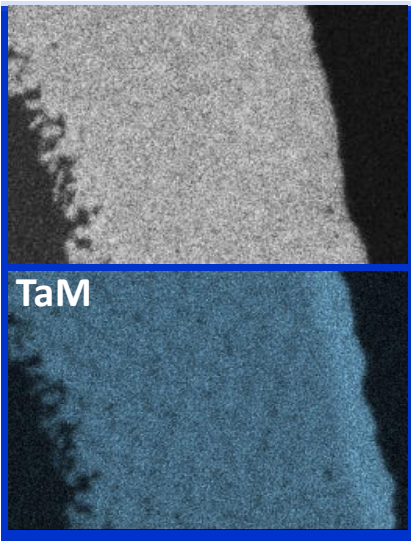
108/127 RRP samples



Ti doped



Ta doped



*Doping with **Ti** produces a more homogeneous A15 composition and a tighter distribution of T_c*

	Ti	Ta
Design	108/127, 0.778mm diam.	108/127, 0.778mm diam.
Heat Treatment	662°C/48h	665°C/48h
$J_c(12T, 4.2K)$, A/mm ²	3035	2950
$\mu_0 H_k(4.2K)$, T	25.45	23.84
Nb, at%	75.6	73.1
Sn, at%	23.1	23.4
Ti, Ta, at%	1.3	3.5
A15 Nb:Sn	3.27	3.12

The strong Sn deficiency in the Ti-doped sample led us to assume that Flukiger's hypothesis on the doping sites was correct

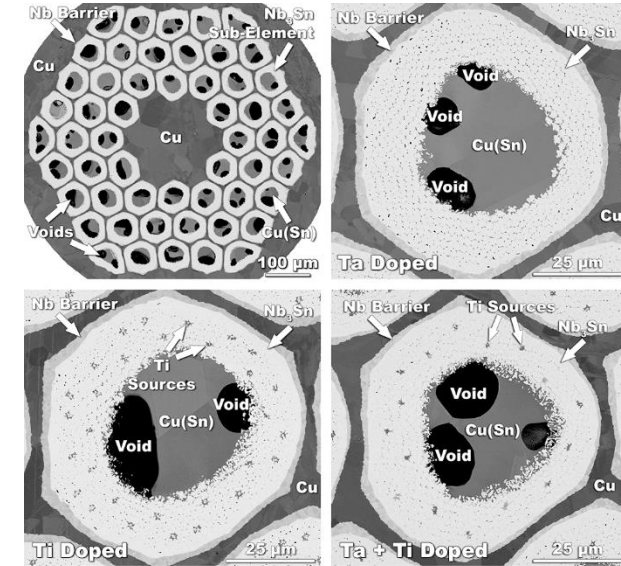
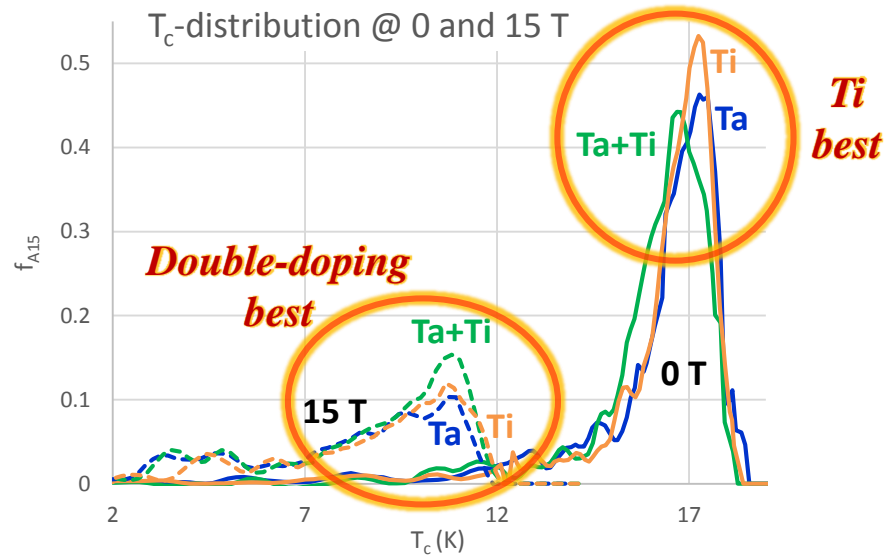
Double-doped vs. Single-doped RRP® strands

- Three 54/61 standard Sn, slightly **under-reacted** (640 °C/40h) strands with different doping:

- Only Ta (Ta#1),
- Ta+Ti,
- Only Ti (Ti#1)

In-field Ta+Ti sharper than either Ti or Ta

*Double doping \Rightarrow high H_{c2} , H_k
 \Rightarrow potential for FCC*



- Two 108/127 standard Sn , slightly **over-reacted** (662-665°C/48h) with single doping:

- Only Ti (Ti#2),
- Only Ta (Ta#2),

Sample ID	Dopant	Billet ID	Design Subs/Stack	Final HT ID	Nb at %	Sn at %	Ta at %	Ti at %	A15 Nb:Sn ratio	$T_{c, Onset}$ K	$\mu_0 H_k(4.2K)$ T	Non-Cu $J_c(12T, 4.2K)$ A/mm ²	A15 layer $J_c(12T, 4.2K)$ A/mm ²	WHH $\mu_0 H_{c2}(0K)$ T
Ta#1	4 at. %Ta	8781	54/61	640°C/40h	72.46	25.17	2.37		2.879	18.5	22.66	2712	4860	27.30
Ta+Ti	4 at. %Ta +1 at%Ti	9362-5	54/61	640°C/40h	71.41	24.64	2.60	1.37	2.898	18.1	24.59	2622	4528	28.77
Ti#1	2 at%Ti	9415-BE	54/61	640°C/40h	74.87	23.40		1.73	3.200	18.2	23.75	2872	5065	28.35

Under-reacted

EDS considerations and A15 Nb/Sn ratio:

Ti doped 54/61 is clearly **Sn deficient**.

The **Ta** and **Ta+Ti 54/61** samples seems to be **Nb deficient**

Both **108/127** samples are both **Sn deficient** but again **Ti** is the most off-stoichiometric

We used EXAFS analysis to probe Ti vs. Ta site locations

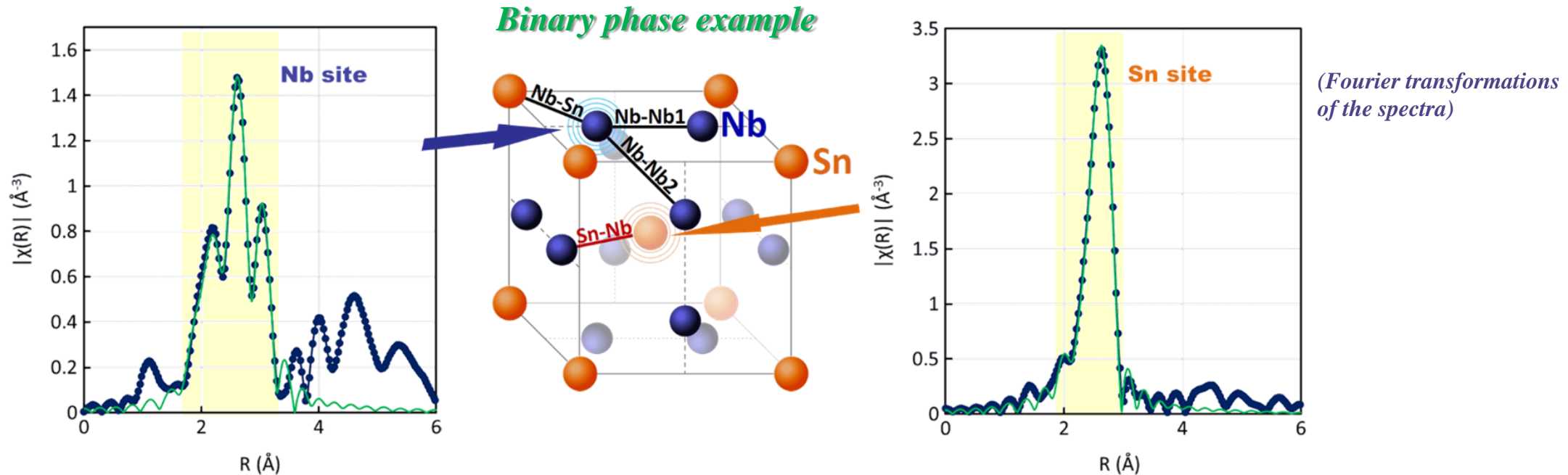
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What is EXAFS?

EXAFS is “**Extended X-ray Absorption Fine Structure**”

performed at the Advanced Photon Source –Argonne National Laboratory

- It is sensitive to the local environment of a specific element:
 - It works at **x-ray energies above the absorption edge energy** of the element under study
 - Photoelectrons** emitted by the element under study are **scattered by the neighboring atoms** revealing the local structure



Nb site has three closely spaced coordination shells
 ⇒ **3-peak structure**

Sn site has a single nearest neighbor shell
 ⇒ **single peak**

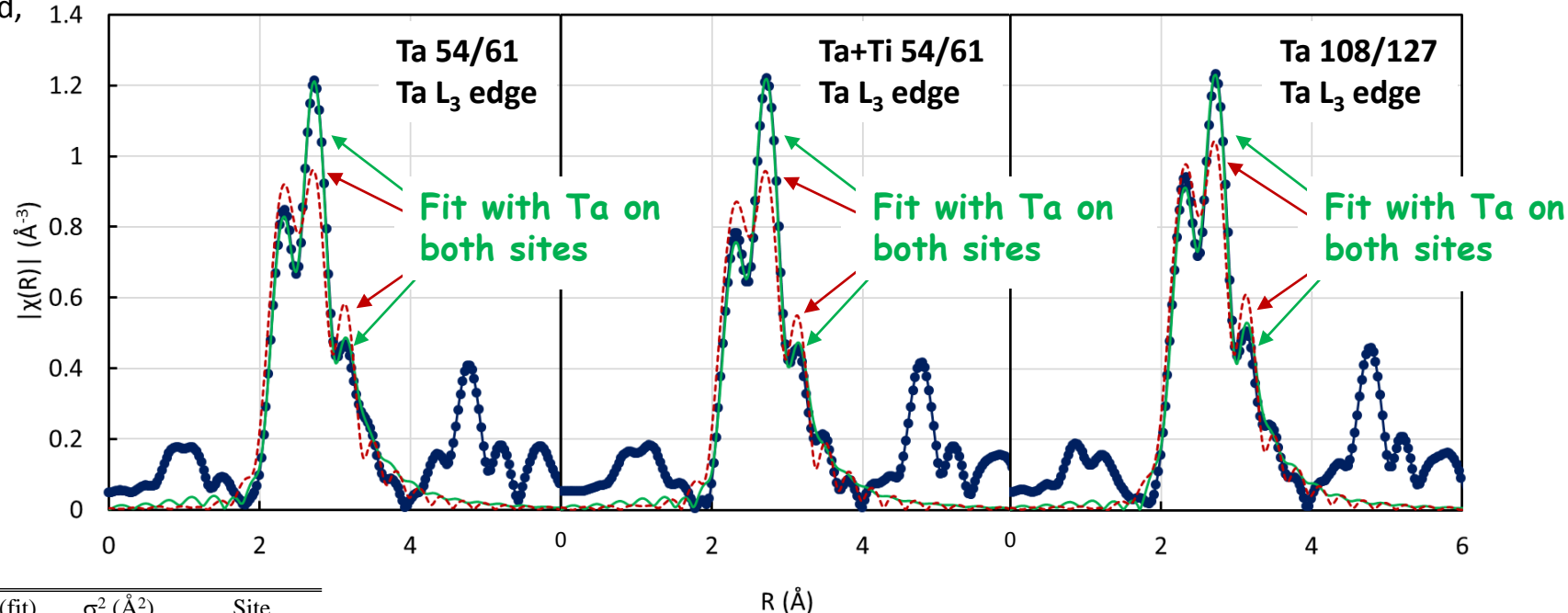
Scattering Path	N	R (Å)	R (fit)	σ^2 (Å ²)	S_0^2	E_0 (eV)
Nb – Nb1	2	2.644	2.645 (0.005)	0.0060 (0.0005)	1.06	-1.80
Nb – Sn	4	2.956	2.948	0.0044	1.06	-1.80
Nb – Nb2	8	3.238	3.241	0.0100	1.06	-1.80
Sn – Nb	12	2.956	2.951	0.0049	0.96	1.02

S_0^2 and E_0 are an overall amplitude and energy shift to match the theory to the data. σ^2 is a measure of the disorder over the distance R .

EXAFS performed by
 Steve Heald,
 Argonne National Lab.

Where is Ta?

EXAFS performed by Steve Heald,
Argonne National Lab.



Sample ID, fit type	Scattering Path	N (Fixed)	R (fit)	σ^2 (\AA^2)	Site Occupancy
Ta, 54/61 two-site fit	Ta – Nb1	2	2.68	0.0042	0.70
	Ta – Sn	4	2.96	0.0097	0.70
	Ta – Nb2	8	3.24	0.0087	0.70
	Ta – Nb	12	2.96	0.0097	0.30
Ta+Ti, 54/61 two-site fit	Ta – Nb1	2	2.64 (0.01)	0.0042 (0.002)	0.68 (0.08)
	Ta – Sn	4	2.996	0.0095	0.68
	Ta – Nb2	8	3.24	0.0084	0.68
	Ta – Nb	12	2.96	0.0095	0.32
Ta, 108/127 two-site fit	Ta – Nb1	2	2.67	0.0044	0.79
	Ta – Sn	4	2.95	0.0078	0.79
	Ta – Nb2	8	3.24	0.0091	0.79
	Ta – Nb	12	2.95	0.0078	0.21

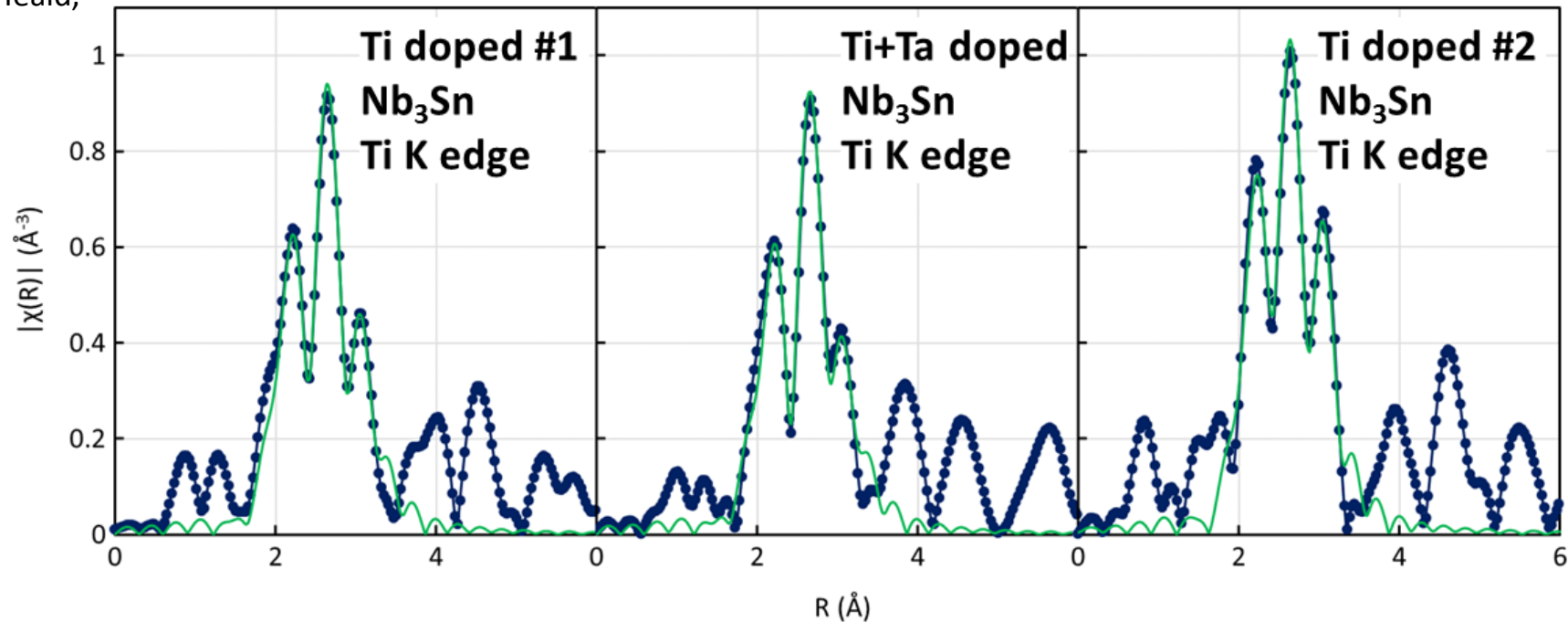
*The three-peak structure indicates that **most of the Ta is on the Nb site, however...** fitting **Ta only on Nb site generates low quality fits with unrealistic fit parameters.***

*The best fit requires **Ta** to be **on both sites**:*

- 32-30% Ta on the Sn site in the 54/61 samples
- 21% Ta on the Sn site in the 108/127 sample

Where is *Ti*?

EXAFS performed by Steve Heald,
Argonne National Lab.



Sample ID, fit type	Scattering g Path	N (Fixed)	R (fit)	σ^2 (Å ²)	Site Occupancy
Ti #1, two-site fit	Ti – Nb1	2	2.674 (0.01)	0.0096 (0.0005)	1.0
	Ti – Sn	4	2.914	0.0066	1.0
	Ti – Nb2	8	3.250	0.0164	1.0
Ti #2, two-site fit	Ti – Nb1	2	2.660	0.0054	1.0
	Ti – Sn	4	2.926	0.0059	1.0
	Ti – Nb2	8	3.236	0.0110	1.0
Ta+Ti, two-site fit	Ti – Nb1	2	2.660	0.0079	1.0
	Ti – Sn	4	2.917	0.0062	1.0
	Ti – Nb2	8	3.240	0.00147	1.0

Fits were performed with Ti on both sites but
the occupancy of Ti on Sn site refines to 0

Ti is on the Nb site only!

EDS+EXAFS: samples even more off-stoichiometry

Sample ID	Dopant	Billet ID	Design Subs/Stack	Final HT	Nb at %	Sn at %	Ta at %	Ti at %	EDS	x on Sn site	EDS+EXAFS	$T_{c, Onset}$ K	$\mu_0 H_k$ T	Non-Cu	A15 layer	WHH
									A15 Nb:Sn		(Nb+Ti+(1-x)Ta)/(Sn+xTa)			$J_c(12\text{ T}, 4.2\text{ K})$ A/mm ²	$J_c(12\text{ T}, 4.2\text{ K})$ A/mm ²	$\mu_0 H_{c2}(0\text{ K})$ T
Ta#1	4 at. %Ta	8781	54/61	640°C/40h	72.46	25.17	2.37		2.879	0.30	2.864	18.5	22.66	2712	4860	27.30
Ta+Ti	4 at. %Ta +1 at%Ti	9362-5	54/61	640°C/40h	71.41	24.64	2.60	1.37	2.898	0.32	2.926	18.1	24.59	2622	4528	28.77
Ti#1	2 at%Ti	9415-BE	54/61	640°C/40h	74.87	23.40		1.73	3.200		3.336	18.2	23.75	2872	5065	28.35
Ti#2	2 at%Ti	14895FE	108/127	662°C/48h	75.59	23.10		1.31	3.272		3.414	17.9	25.45	3035	4896	29.49
Ta#2	4 at. %Ta	12879	108/127	662°C/48h	73.09	23.39	3.52		3.125	0.21	3.144	18.4	23.84	2950		27.49

Ti samples are particularly off-stoichiometry

Nb:Sn stoichiometry is NOT the defining quality factor for doped Nb₃Sn

Can we use this information to explain H_{c2} (or H_k) trend?

$$H_{c2}(0) = 0.69T_c \left. \frac{dH_{c2}}{dT} \right|_{T_c}$$

$$\left. \frac{dH_{c2}}{dT} \right|_{T_c} \propto \gamma \rho_0 \propto N_F \rho_0 \quad \text{with} \quad \rho_0 \propto \frac{1}{N_F \tau}$$

$$H_{c2} \propto \frac{T_c}{\tau}$$

We can estimate τ from the long-range order (LRO) parameter but...

Is the scattering rate determined only by the dopants?

Is the scattering rate dominated also by vacancies or antisite disorder?

Antisites vs. Vacancies

Besson *et al*, Phys.Rev. B 75, 054105 (2007): “The defect structure is found to be of antisite type, with small amounts of Nb vacancies, and Sn vacancies showing a trend towards instability.”

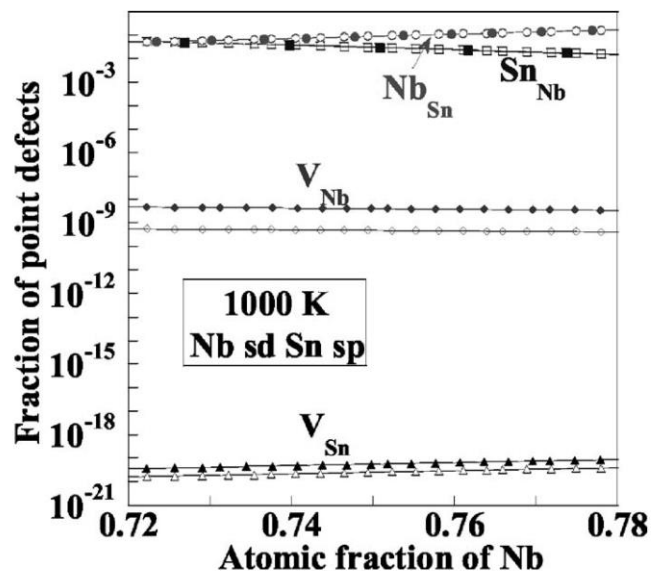


FIG. 2. Point defect structure of Nb_3Sn at $T=1000$ K, calculated with the *sd* pseudopotential for Nb (LDA and GGA: open and closed symbols, respectively).

TABLE II. Migration energies (eV) of the jumps considered (nonmagnetic LDA calculations, Nb *sd* and Sn *sp* pseudopotentials; for intersublattice jumps, ord.=ordering and dis.=disordering).

	X=Nb	X=Sn
$V_{Nb} + X_{Nb} \rightarrow V_{Nb} + X_{Nb}$ intra.	0.98	0.62
$V_{Nb} + X_{Nb} \rightarrow V_{Nb} + X_{Nb}$ inter.	2.07	1.88
$V_{Sn} + X_{Sn} \rightarrow V_{Sn} + X_{Sn}$	5.15	5.59
$V_{Sn} + X_{Nb} \rightarrow V_{Nb} + X_{Sn}$	0.15 (dis.)	0.05 (ord.)
$V_{Nb} + X_{Sn} \rightarrow V_{Sn} + X_{Nb}$	1.41 (ord.)	1.70 (dis.)

Sn site vacancies can be filled by antisite Nb with almost no energy penalty

The fraction of PD by vacancies is at least 7 orders of magnitude smaller than by antisites at 1000 K (more than 20 orders of magnitude at 300 K).

Vacancies are very rare in Nb_3Sn

\Rightarrow Off-stoichiometry occurs by antisites disorder

Estimation of disorder

Long-range order (LRO) parameters for an alloy with 2 sublattices (A_3B) are defined as:

$$\eta_A = c_A(A) - c_A(B),$$

Ruban *et al.*, Phys.Rev. B 55, 856 (1997)

$$\eta_B = c_B(B) - c_B(A)$$

with $c_\kappa(\alpha)$ being the fraction of α sites occupied by the κ element.

η ($0 \leq \eta \leq 1$) is determined by the **difference between the elements sitting on the “right” sites and the ones sitting on the “wrong” sites.**

If $\eta=1$ the system is perfectly ordered.

If $\eta=0$ the system is completely disordered (random site occupancy).

With ternary additions (X), η is always <1 (η parameters are related to other parameters like $c_X(A)$, $c_X(B)$, \bar{c}_κ the concentration of the κ element in the alloy,...)

A_3B : considering a **3:1 ratio** being **fulfilled by antisite substitution** we can write the compositions as follows and then calculate the LRO parameters η_{Nb} , η_{Sn} .

(Nb _{1-ti-taA} Ti _{ti} Ta _{taA} Sn _{snA}) ₃ (Sn _{snB} Ta _{taB} Nb _{nbB}) ₁											
Sample ID	Billet ID	Design Subs/Stack	Nb in A, nbA	Ti, ti	Ta on A, taA	Sn on A, snA	Sn on B, snB	Ta on B, taB	Nb on B, nbB	η_{Nb}	η_{Sn}
Ta#1	8781	54/61	0.966		0.022	0.012	0.972	0.028		0.966	0.960
Ta+Ti	9362-5	54/61	0.942 [0.952]	0.018 [0.018]	0.024 [0.024]	0.017 [0.006]	0.936 [0.967]	0.033 [0.033]	0.031 [0]	0.911 [0.952]	0.919 [0.960]
Ti#1	9415-BE	54/61	0.977	0.023			0.936		0.064	0.913	0.936
Ti#2	14895FE	108/127	0.983	0.017			0.924		0.076	0.907	0.924
Ta#2	12879	108/127	0.963		0.037		0.936	0.030	0.035	0.928	0.936

Disorder could still be underestimated: exchange antisites (Sn on Nb site AND Nb on Sn site) do not change the composition.

Exchange antisite effect might be limited for single doping, but it is likely important for the Ta+Ti (they induce antisites on opposite sites in the 54/61). For the Ta+Ti sample, the main numbers in the table include a small amount of exchange antisites proportional to the amount of antisite Ti generates in the Ti-doped samples reduced by the amount of Ta on Sn (Ta on Sn already sort of acts as exchange antisites).

Strong effect of disorder on $H_{c2}(0)$



Sample ID	Billet ID	Design Subs/Stack	η_{Nb}	η_{Sn}
Ta#1	8781	54/61	0.966	0.960
Ta+Ti	9362-5	54/61	0.911	0.919
Ti#1	9415-BE	54/61	0.913	0.936
Ti#2	14895FE	108/127	0.907	0.924
Ta#2	12879	108/127	0.928	0.936

LRO parameters show that:

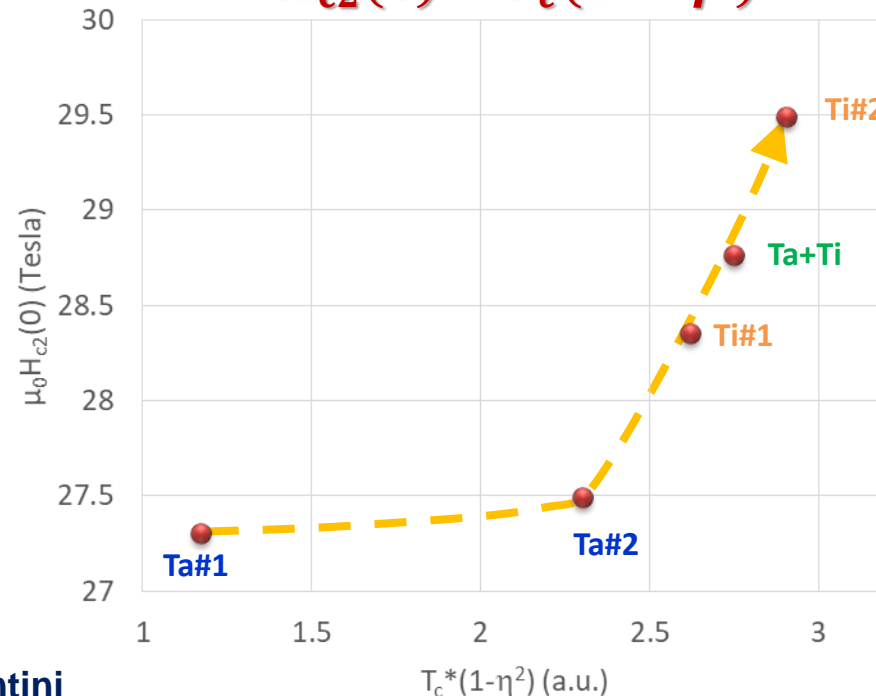
- The **Ta** samples are the most ordered (η highest values).
- The **Ti** doped samples are more disordered than **Ta**.
- The **Ta+Ti** sample is more disordered than both **Ta** and **Ti** 54/61.

Using $H_{c2} \propto \frac{T_c}{\tau}$

and $1/\tau \propto (1 - \eta^2)$


$H_{c2}(0) \propto T_c(1 - \eta^2)$

Rossiter et al., J.Phys. F:
Metal Phys. 10, 1459 (1980)



Most samples follow a linear trend despite the large number of approximations

Conclusions

- 16 T magnets demand focus on the 16-20 T properties
 - We need to **mitigate property gradients** across the layer: both the vortex pinning and the gradient of H_{c2} have to be optimized **to improve the overall 16-20 T performance**
 - Sn homogeneity is important but maybe not the only factor determining the overall H_{c2}
 - EXAFS shows quite **different site occupancy** for Ta and Ti:
 - **Ta on both sites**
 - **Ti only on Nb sites**
-  **Surprising results!!**
- Both doping and antisite disorder determine the H_{c2} behavior:
 - Nb antisite disorder induced by Ti drives up H_{c2} more efficiently than Ta.
 - Despite its lower J_c performance at 12 T, double doping (**Ta+Ti**) has better H_k and H_{c2} (in similarly HTed wires):
 - Double doping should be **re-explored for higher field applications** (16-20 T for FCC) in the latest generation of wires.
 - Is **Ta competing with Sn** for the Sn site? Is **Ti** strong preference for the Nb site **favoring the Sn diffusion** on its site?
(Ta-doped Nb_3Sn has stronger composition gradient, wider T_c -distribution down to 5-6 K than Ti-doped wire which has T_c -distribution down to only 12 K)

Acknowledgements

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