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Structure and properties of Nb_3SnH_x†

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The effect of alloying H with Nb_3Sn has been studied as a function of composition out to Nb_3SnH. Superconductive transition temperatures and lattice constants of the β-W phase were measured over the entire range, and the absence of the low-temperature cubic-tetragonal lattice transformation confirmed for $x > 0.1$. T_c falls to below 4.2 °K at $x \sim 1$ in a manner resembling that for Sb doping, and the rigid-band-approximation implications of this similarity are briefly discussed. Neutron diffraction reveals that the H atoms lie at the alternative Nb positions of the β-W lattice, cross linking orthogonal Nb chains. The low-temperature specific heat of lightly hydrided Nb_3Sn is strikingly different than for the same sample with the H removed, the density of states being higher, but the normal-state specific heat lower. This difference is related, through x-ray measurements of a temperature-dependent tetragonal strain near T_c in pure single-crystal Nb_3Sn, to the martensitic transformation.

INTRODUCTION

The behavior of alloys of hydrogen with β-W (*A*-15) superconductors has received little attention, even though the venerable subject of hydrogen in transition metals remains an active area of research. This is unfortunate, for, as we hope to demonstrate, the addition of small amounts of H to the Nb_3Sn lattice can provide a probe for furthering some quantitative aspects of our understanding of this important material, as well as a source of interesting phenomenological correlations such as the dependence of the superconductive transition temperature T_c on the electron/atom ratio.[1]

Sahm[2] studied the lattice constant and T_c dependence on H content in $Nb_3 SnH_x$, finding the usual lattice expansion with H content out to $x \sim 1$, followed by a two-phase region with a distorted high-H phase, and a single-phase region again about $x \sim 1.5$. T_c showed a shallow maximum near $x = 0$ and then fell monotonically to below 4.2 °K at $x \sim 1$. The region near $x = 0$ was also investigated by Ziegler,[3] who did not report a T_c maximum.

A most unusual aspect of the situation for low H concentrations in Nb_3Sn is the fact that the elastic constants have been measured on a single crystal doped with hydrogen during the growth process.[4,5] The crystal showed the extreme lattice softening of the soft shear mode responsible for the now well-studied cubic-tetragonal lattice transformation at $T \sim 50$ °K, but did not transform, as observed by x rays.[6] After removal of the hydrogen by vacuum annealing, the transformation was observed, and the elastic and other properties of the crystal remeasured.[6,7] The soft shear mode responsible for the transformation is restored below T_M to its high-temperature limit, the magnetic susceptibility drops, and a small decrease in T_c (~ 0.2 °K) is observed.[4,7] This decrease is consistent with the observation of Sahm, and is quite important in that it is not readily understood in terms of current theories of the transformation,[8,9] nor universally appreciated by experimentalists interested in the relationship between the phase transformation (lattice instability) and T_c.

Thus there is a substantial literature dealing with quantitative aspects of the effect of H on niobium-tin. In the present work, we report on the structure of the hydride as determined by neutron diffraction, and on superconductivity and specific heat in lightly doped alloys.

MATERIALS

Controlled hydriding of Nb_3Sn powders in a clean hydrogen atmosphere was not found to be possible, the amount of absorbed H being nonreproducible. Direct synthesis of Nb_3Sn by sintering of compacted Nb and Sn powders in the presence of H_2 leads to a product of good uniformity. Sintering was carried out at 1100 °C for 5 h in closed quartz ampoules. The H_2 was introduced by premixing appropriate amounts of hydrided and pure Nb powders. Heavily doped samples prepared for neutron diffraction (Nb_3SnH_1) were sintered in an autoclave. X-ray line broadening was observed in the heavily doped samples, but the principal feature of the diffraction pattern of the material used for the neutron work was an expanded Nb_3Sn (cubic) lattice, with $a_0 = 5.34$ Å.

STRUCTURE OF Nb_3SnH

Neutron diffraction data for Nb_3Sn and Nb_3SnH were collected on the RCA neutron spectrometer

TABLE I. Comparison of observed and calculated neutron diffraction intensities. Neutron scattering factors of 0.691, 0.610, and −0.378 were used for Nb, Sn, and H, respectively, and Debye-Waller factors of $B = 0.95$ Å^2 for Nb_3Sn and $B = 0.72$ Å^2 for the hydride.

	Nb_3Sn		Nb_3SnH	
hkl	I_{obs}	I_{calc}	I_{obs}	I_{calc}
110	...	3	...	1
200	182	200	175	167
210	704	700	1003	994
211	532	514	412	430
220	...	1	...	0
310	...	1	...	0
222 320 321	758	757	774	778
400	189	189	155	150

at Industrial Reactor Laboratories, Inc., Plainsboro, N.J. The scanning speed was 0.1° per 500 sec, and in a typical run integrated intensities of about 35 000 counts above background for the strongest reflection, and 8000 counts for the weakest were recorded. The net integrated intensities, scaled down to the calculated values, are shown in Table I. The data for the hydride, which had an appreciably higher background, represent the average of three runs. Standard deviations range from 1% to 6% depending on the peak strength.

A striking feature of the data in Table I is the change in the ratio of intensities of the 210 to the 211 peaks for pure Nb_3Sn and for the hydride, from 1.32 to 2.44, respectively. This enables one to readily eliminate two structures which might be considered likely on physical grounds. In one the H positions would lie along the $\langle 111 \rangle$ directions, in the largest tetrahedral sites available. These are the 16-fold (i) positions of the space group $O_h^3 - Pm3n$, with a metal-H distance of 1.93 Å to three second-nearest-neighbor Nb atoms, and one Sn atom. A second possibility is suggested by analogy to the β form of UH_3,[10] which belongs to the same space group, with U atoms occupying both the Nb and Sn positions. In this case the H atoms lie at the 24-fold (k) positions, which in Nb_3SnH would give M-H distances of 1.87 Å. Both of these assignments, however, leave the ratio I_{210}/I_{211} virtually unchanged from that of Nb_3Sn, the values being 1.30 and 1.32 for the hydrides.

Since a maximum H scattering contribution of opposite sign to the resultant of the Nb and Sn contributions for these two reflections would be insufficient to reverse the phase angle of either, the phases are unchanged by the addition of H. Accordingly, a difference Fourier map can be computed by using as coefficients the structure amplitude observed for Nb_3SnH minus that observed for Nb_3Sn for the two reflections, with the phase angle calculated from the Nb_3Sn structure. In the whole unit cell the only negative regions (Fig. 1) were at the twofold (a) positions ($000, \frac{1}{2}\frac{1}{2}\frac{1}{2}$) already occupied by Sn atoms, and at the sixfold (d) positions ($\frac{1}{4}\frac{1}{2}0, \frac{3}{4}\frac{1}{2}0$). While the spurious negative regions at the (a) positions are attributable to the incompleteness of the Fourier series, the strongly negative regions centered at the (d) positions can only arise from the presence of the negative-scattering-cross-section H atoms. We conclude that the H atoms are randomly distributed over the sixfold (d) sites, with one third occupancy. [These sites are the alternative positions for the six Nb atoms, which have been taken as (c)–($\frac{1}{4}0\frac{1}{2}; \frac{3}{4}0\frac{1}{2}$).]

In Fig. 2 we show the structure of the hypothetical Nb_3SnH_3 in a way which emphasizes the prominent chain feature of the β-W lattice. The H atoms are seen to lie at the center of tetrahedra made up of pairs of nearest-neighbor Nb atoms lying in orthogonal chains, with a Nb-H distance of 1.89 Å.

The sixfold positions occupied in Nb_3SnH are distinguished by their relatively large distance from the Sn atoms, 2.96 Å, and the fact that they closely resemble the occupied sites in Nb metal,[11] where, for the orthorhombically distorted $NbH_{0.84}$, the Nb-H distance is found to be 1.92 Å. Assuming Vegard's law, for the hypothetical $Nb_3SnH_{2.5}$, $d_{Nb\text{-}H} = 1.91$ Å. The close resemblance of the bcc Nb and β-W cases tends to emphasize the chemical aspect of bonding in the transition metal hydrides, as opposed to the nearly-free-electron picture.[12] We note that the position of the H atoms in the β-W lattice corresponds to the point of maximum overlap of the d_π orbitals of the intersecting Nb

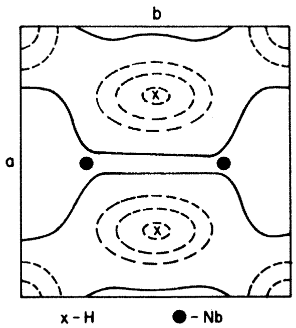

FIG. 1. Difference scattering map of the section $z = 0$, calculated with coefficients $F_{obs}(Nb_3SnH) - F_{obs}(Nb_3Sn)$ for the 210 and 211 reflections, with the phase angles calculated for Nb_3Sn attached to each amplitude. Dashed lines represent negative contours, full lines positive contours.

chains.

TRANSITION TEMPERATURE AND COMPOSITION

Figure 3 shows superconductive transition midpoints measured inductively, as a function of composition (lattice constant). Scatter in the composition (determined by chromatography) was large, and the upper abscissa represents approximate (± 25%) compositions. On the other hand, it is seen that the correlation between T_c and a_0 is quite good. Transition widths varied from ~ 0.5 °K for $x \sim 0$ to about 2 °K for $x \sim 0.5$. (The specimens differ little from typical pure Nb_3Sn prepared in this manner, i.e., T_c's are somewhat lower than for the best material, and there are substantial unreacted components.[13] The data are in good agreement with those of Sahm,[2] the specimens being more uniform in the present study, as evidenced by T_c widths.

In Fig. 4 we compare the compositional dependence of T_c for H doping and for two well-characterized substitutional dopants.[14-17] The rationale for this type of comparison is of course the rigid-band approximation, which is quite useful for many transition-metal hydride alloys (cf Refs. 18 and 19). The implications of the results for Al and Sb have been dealt with in some detail in the original references, and we wish to call attention here primarily to the role of the lattice transformation on T_c, and to the similarity between H and Sb doping.

Small additions of either H or Al inhibit the lattice transformation. This results in a clear maximum in T_c for the case of Al,[16] and as mentioned above[2,4] a possible maximum for H. Extrapolation to $x = 0$ suggests a difference in T_c between the metastable cubic phase and the tetragonal phase, of less than 2 °K. The reason for the inhibition of the transformation may be quite different for the two elements. In the case of H, a possible explanation lying outside of electronic arguments is suggested by the crystal structure. The H atoms link together orthogonal Nb chains, thereby reducing the apparent one dimensionality thought necessary to account for the elastic softness. Since the extreme softening required for the transformation is confined to $\vec{q} \approx 0$,[20] the sensitivity to small amounts of H could be quite high. The resemblance of the data of Fig. 4 for H and Al is of course confined to small x, since Nb_3Al is a high-T_c superconductor.

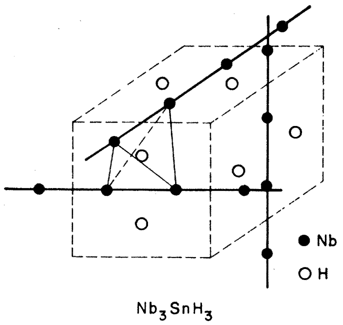

FIG. 2. Structure of Nb_3SnH_3. H and Nb atoms lie on the faces of the unit cell. Sn atoms, at bcc positions, not shown. The H sites in Nb_3SnH are randomly occupied.

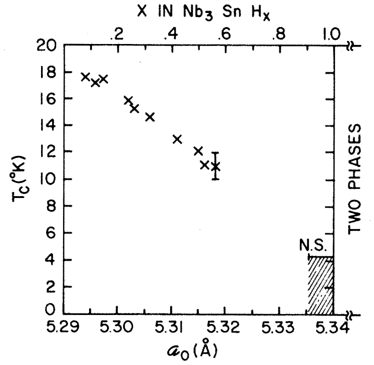

FIG. 3. Transition temperature vs lattice constant and composition for Nb_3SnH_x. Specimens in the shaded lower right corner were not superconductive above 4.2 °K. The two-phase region above $x \sim 1$ is taken from Ref. 2.

Following the idea that the inhibition of the transformation by H is not the result of an "electronic" effect, the similarity between H and Sb doping becomes clearer. The addition of Sb (electrons) does not arrest the transformation, but it does change the sign from $c/a - 1 < 0$ to $c/a - 1 > 0$.[15-17] The curve for Sb in Fig. 4 therefore represents T_c for tetragonal material throughout. (T_c and the magnetic susceptibility of the tetragonal state are found to be independent of sign.[15]) The change in sign is assumed to be an electronic effect, obscured by the arrested transformation in the case of H doping. Thus with the exception of the transformation, which has only a small effect on T_c, the behavior of the two elements is quite similar. This cannot, however, be taken as evidence for the applicability of the rigid-band approximation (RBA). In a free-electron band, the Fermi energy associated with 0.25 states/atom and a density of states (see below) of 2.5 states/(eV atom) is $> 10^3$ °K, which is too high to be consistent with a wide variety of experimental behavior. The failure of the RBA in the case of Sb is discussed in Ref. 15. For H, attention is called to the addition of bound states to the energy bands of Pd by H.[21] In both cases then, it appears that some fraction of the extra electrons introduced remain at the Fermi level.

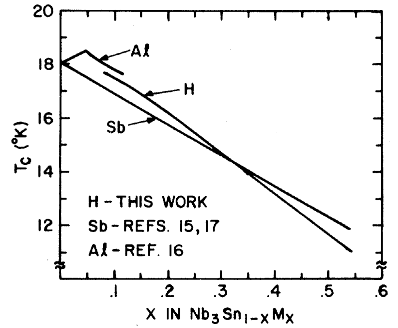

FIG. 4. Transition temperature as a function of composition for H, Sb, and Al dopants.

SPECIFIC HEAT OF CUBIC $Nb_3SnH_{0.08}$

The normal-state specific heat of Nb_3Sn in the vicinity of T_c (18 °K) is known to be anomalous, in the sense that an extrapolation of normal-state data to 0 °K according to the usual assumptions does not satisfy the requirements that the entropy of the normal and superconducting states be equal at T_c.[22] The very high (> 200 kG) fields necessary to quench superconductivity make direct determination of the normal-state properties below T_c difficult. We have therefore attempted to capitalize on the arrest of the lattice transformation by small amounts of H by measuring the specific heat in the cubic state of lightly doped Nb_3Sn, in an attempt to differentiate anomalies associated with the lattice transformation from other peculiarities of this material.

A specimen doped to a lattice constant $a_0 = 5.2948$ ($x \sim 0.08$) was prepared, and a small piece removed for x-ray measurement. After observing that the transformation did not take place (by x-ray diffractometry), the specific heat was measured. The H was then removed by pumping at dull red heat until no further gas evolution could be detected, and the test piece was again subjected to x-ray analysis, demonstrating that the lattice constant had returned to normal (5.290 Å) and the lattice transformation was present. The sample was then remeasured.

Heat-pulse calorimetry was used, with a sample weight of 16 g and a calibrated addendum whose specific heat was about 10% of the total. In order to facilitate comparison with previous results obtained with more perfect material, a number of corrections were necessary, particularly for what appeared to be about (15–20)% unreacted Nb as observed metallographically. These corrections do not affect the direct comparison of the data for the specimen before and after H removal, except in the uncertainty arising from a lack of information about the degree of hydriding and/or specific heat of hydrided Nb. The error introduced is expected to be small.

The specific heat is shown in Fig. 5, plotted in the usual way to emphasize the ordinary lattice and electronic terms. It is apparent that the arrest of the transformation drops the normal-state term in a way consistent with removing the entropy anomaly. In order to proceed further, it is necessary to idealize the transition curves. This was done by replotting the data in the form C/T vs T, and assuming a sharp transition at a T_c determined by the conservation of entropy (i.e., the entropy of the normal state is unchanged). Extrapolation of the normal-state data into the transition region is straightforward. The superconducting state was extrapolated to the peak by comparison with the date of Ref. 22. The results are given in Table II.

Although the width of the transition for the hydrided specimen makes the determination of the specific-heat jump more uncertain than for the tetragonal phase, the jump is found to be larger. Scaling γ to $\Delta C/T_c$ for the two specimens, with a value of γ_t from Ref. 22, we find $\gamma_c = 15$ mJ/(g atom °K^2). The inferred 11% decrease in density of states attributable to the transition is in reasonable agreement with susceptibility measurements[7] which give $[(\chi_c - \chi_t)/(\chi_c - \chi_{\text{orb}})]_{0\,°\text{K}} = 0.19$, where $\chi_{c,t}$ is the extrapolated susceptibility, and γ_{orb} is the temperature-independent orbital (+ s band) term. The agreement is further improved by reasoning that the addition of H probably decreases the susceptibility, by analogy to H in Nb,[23] or to Nb_3Sb.[24] Assuming that the d-band susceptibility decreases linearly to near zero at $x = 1$, a 12% reduction in $N(0)$ is attributable to the H. With this correction, we get $(\gamma_c^m - \gamma_t)/\gamma_c^m \approx 0.18$, where m signifies the metastable $x = 0$ cubic state.

The question remains as to why the specific heat

TABLE II. Idealized specific-heat data for Nb_3Sn in which the lattice transformation was arrested by the addition of H. Numbers in parentheses are taken from Ref. 22, and the value of γ_c is scaled from the specific-heat jumps.

Composition	Structure at T_c	T_c (°K)	$\frac{\Delta C}{T_c}\left(\frac{\text{mJ}}{\text{g atom °K}^2}\right)$	$\gamma\left(\frac{\text{mJ}}{\text{g atom °K}^2}\right)$	$(\gamma_c - \gamma_t)/\gamma_c$
Nb_3Sn	Tetragonal	17.25(18.05)	33(32.5)	(13)	···
$Nb_3SnH_{0.08}$	Cubic	16.9	37	15	+0.11

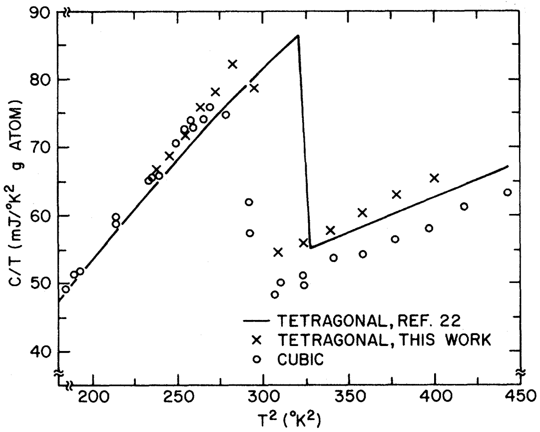

FIG. 5. Specific heat of cubic Nb_3Sn doped to $Nb_3SnH_{0.08}$ (○) and same sample with H removed (tetragonal, *x*). The reference (solid) curve also pertains to tetragonal material.

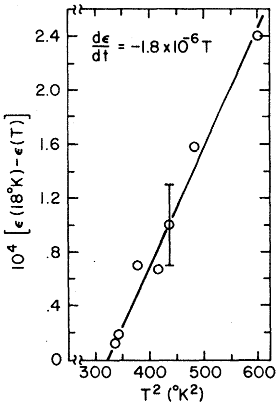

FIG. 6. Temperature dependence of the tetragonal strain near T_c determined from the position of back-reflection peaks ($2\theta > 150°$) on single-crystal Nb_3Sn.

above T_c of the tetragonal crystal is substantially higher than that of the cubic phase. We have therefore investigated the contribution arising from the temperature dependence of the tetragonal strain ϵ. This gives rise to an excess specific heat analogous to $C_p - C_v$, which is readily shown to be $C_\tau - C_\epsilon = \frac{3}{2}\,(C_{11} - C_{12}) \times (d\epsilon/dt)^2$, where τ is the appropriate stress tensor associated with the tetragonal strain. While the elastic constant is well known, the temperature dependence of ϵ near T_c is very small, and difficult to determine. In Fig. 6 we show data obtained from a study of the displacement of the 0014 Mo $K\alpha$ and 036 Cu $K\alpha$ x-ray peaks with temperature above 18 °K for single-crystal Nb_3Sn. The data for ϵ are plotted as a function of T^2 since this is physically not unreasonable and appears to give the best smoothed fit with higher-T data obtained earlier.[25] (We emphasize that these data are only obtainable on single crystal, and therefore do not represent actual experimental evidence on the sintered material under discussion.) From the slope of Fig. 6 and elastic-constant data from Ref. 7, we calculate the excess specific heat C/T to be 3.4 and 4.0 mJ/(g atom °K²) at 18 and 20 °K, respectively. Subtracting out the increase in γ as observed for the cubic state, values of 7.0 and 8.2 mJ/(g atom °K²), attributable to the T dependence of ϵ, are required to fully account for the data. Such values would require an increase in slope $d\epsilon/dT$ of 40%, which is somewhat outside experimental error for this crystal.

We therefore conclude that most, but perhaps not all, of the anomalous specific heat of Nb_3Sn is a consequence of the lattice transformation, and that the specific heat at constant strain is largely explicable in terms of the ordinary electron and phonon contributions. From the data of Ref. 22 and an electron-phonon interaction λ calculated from McMillan's formula[26] we get, for tetragonal Nb_3Sn, $N(0) = 2.5$ states/(eV atom), where $N(0)$ is the bare density of states, with $T_c = 18.05$ °K. Using $\delta\chi/\chi$ from Ref. 7 and extrapolating the data of Fig. 4, we deduce, for *metastable* cubic Nb_3Sn, $N(0) = 3.1$ states/(eV atom), with $T_c < 20$ °K.

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