Evidence that the upper critical field of Nb$_3$Sn is independent of whether it is cubic or tetragonal

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Abstract:

Although 2011 marks the 50th anniversary of Nb$_3$Sn as the first high field superconductor, real understanding of its upper critical field behavior $\mu_0H_{c2}$ is incomplete. Here we show surprising $\mu_0H_{c2}$ data on highly homogeneous bulk samples examined both by small-current, transport and by volumetric-averaging specific heat and the reversible magnetization techniques, which exhibit identical upper critical field $\mu_0H_{c2}(0.3 \, K) \sim 29 \pm 0.2 \, T$ with or without undergoing the cubic to tetragonal transition, a result in strong contrast to widely used multiple-source data compilations that show a strong depression of $\mu_0H_{c2}(0K)$ from 29 T to 21.4 T in the tetragonal state.

Nb$_3$Sn is the most widely used superconductor for generating fields above ~10 T because it is easily and economically fabricated in round-wire, multifilament forms that lend themselves both to laboratory magnets and to the cabled, high-current conductors needed for accelerator and fusion uses. More than 600 tons of Nb$_3$Sn will be used in the International Tokomak Experimental Reactor (ITER). This wide and long-standing use [1] makes it all the more surprising that there is no agreed data set that shows the variation of the upper critical field $\mu_0H_{c2}$ across the variable composition of the A15 phase of Nb$_3$Sn. High Sn compositions are important for the very high critical current densities $J_c$ now achieved in commercial strands.[2] Optimizing $J_c(H)$ would be much easier with a quantitative understanding of how $\mu_0H_{c2}$ varies with Sn content since all practical Nb$_3$Sn wire forms contain the full range of A15
phase compositions (generally thought to range from ~18-25 at% Sn [3]). The integrated effect of shells of varying composition and thus $T_c$ and $H_{c2}$ has been addressed both experimentally [4] and by modeling [5]. These studies show that flattening the Sn gradient raises the effective $\mu_0H_{c2}$ and $J_c$. The modeling scheme of Cooley et al. [5] is particularly valuable, but it lacks key information, namely the composition dependence of $\mu_0H_{c2}$. To remedy this lack, we have fabricated homogeneous binary Nb$_3$Sn bulk samples to provide the compositional variation of $\mu_0H_{c2}$ with one sample set made in one, consistent fashion. Here we show whether the sample transforms to the tetragonal state or not is irrelevant to $\mu_0H_{c2}(0)$, which can equal 29.1 ± 0.2 T in both cases, values as high as any optimally Ti- or Ta-doped wire [4] [6].

Rather homogeneous bulk Nb$_3$Sn was made by Devantay et al. [7] by heating samples into the melt phase and by Goldacker et al. [8] in a Hot Isostatic Press (HIP) at 1100 °C. To further reduce inhomogeneity, we used a HIP capable of reaching up to 2200 °C. Here we report on bulk Nb$_3$Sn with nominally stoichiometric 25at% Sn and Sn-rich 27at% Sn so as to ensure the most Sn-rich composition of the A15 phase. About 45 g samples were synthesized by combining Nb (-325 mesh, 99.8%, Alfa Aesar) and Sn (-325 mesh, 99.8%, Alfa Aesar) powders in a high energy ball mill. Mixing and powder packing was performed in a dedicated glove box filled with Ar gas to minimize oxidation. After 60 minutes of ball milling, the mixed powders were pressed in a Cold Isostatic Press (CIP) to form a hard pellet, then wrapped in Ta foil and put into a steel tube with one closed end. This HIP tube was then evacuated and the open end sealed by welding. The sealed can was pressurized at 2 kbar during both a pre-anneal at 650 °C for 16 hr and during the main A15 phase reaction at 1200 °C for 72 or 160 hr. The central reacted A15 part of each of the cans was cut into 2 pieces using a precision diamond saw, one piece being then re-sealed in an evacuated Ta-lined Nb tube for a 2nd HIP homogenization and reaction-continuation anneal at 1400 °C, 1600 °C or 1800 °C for 24 hr. One piece of the 27 at% Sn
sample annealed at 1800 °C was further annealed in a Ta-lined Nb tube for 30 days at 1200 °C. In this report we describe samples by their nominal or overall atomic % Sn content, followed by the final heat treatment and time (if not specified, 24 hr). For example, 25Sn_1800 means the sample finally annealed at 1800 °C for 24 hr after pre-annealing at 650 °C for 16 hr and reaction at 1200 °C for 72 hr. However, we also report the measured compositions of the A15 grains in each sample when considering the final properties.

X-ray diffraction (XRD) was used to measure lattice parameters and search for the tetragonal transformation in an instrument equipped with a helium cryostat. Specific heat measurements of the $T_c$ distribution were performed in a 16 T Physical Property Measurement Systems (PPMS). $H_{c2}(T)$ was mostly determined by small-current resistivity measurements in fields up to 32 T down to 0.3 K but was benchmarked in several cases by measurements of $\mu_0H_{c2}$ derived from the reversible magnetization in a 14 T vibrating sample magnetometer. The samples were so well annealed that they showed very little magnetization hysteresis and clear $H_{c2}$ transitions. A15 grain compositions were determined using pure-element-standardized energy dispersive X-ray spectroscopy (EDS) in a field emission Scanning Electron Microscope (SEM).

Fig. 1 shows the resistive and specific heat superconducting transitions and the calculated $T_c$ distributions [9] [10] for both compositions in their differently heat treated conditions. Table 1 summarizes the $T_c$, lattice parameters $a_0$, the EDS-measured Sn at%, the Residual Resistance Ratio (RRR) [$=\rho(300 \text{ K})/ \rho(20 \text{ K})$], $\rho(20 \text{ K})$ and the resistively measured $\mu_0H_{c2}$ at 0.3 K. Raising the annealing temperature to 1800 °C reduces the A15 Sn content by about 1at.% in each case, but $T_c$ drops only slightly on raising the annealing temperature from 1400 °C to 1800 °C. All the data indicate that
Sn is rejected from the A15 lattice above 1400 °C, consistent with the Nb$_3$Sn phase boundary bending to Sn-poor compositions as in published Nb-Sn phase diagrams [3, 11]. High sample homogeneity is attested by narrow resistivity transitions (except for the 27Sn$_{1400}$ sample) and especially by the narrow specific heat $T_c$ distributions of Fig 1. Moreover, high homogeneity is also evidenced by the fact that the volumetric averaging measurement of the reversible magnetization yields sharp magnetization slope transitions at $H_{c2}(T)$ which overlap very closely with the potentially percolative, “best bit” resistivity measurements (Fig. 2). We thus have good confidence that the $\mu_0H_{c2}(T)$ values from our high-field resistivity measurements represent the entire sample, except in the one sample 27Sn$_{1400}$ shown in Fig. 1.

The cubic to tetragonal structural transformation of the A15 phase has been reported to occur at temperatures varying from 31 K to 45 K [12]. For example, the tetragonal transformation takes place below 45 K in the study of Devantay et al. [7] and at 35 K in the samples of Goldacker et al. [8], when Sn is >24.5% [8]. Fig. 3 shows the \{400\} XRD peaks obtained at room temperature and at 10 K for both compositions in various conditions. The split of the 20 peak around 71.4° at room temperature into two peaks at 10 K is clear evidence of the cubic to tetragonal transformation. The contraction along the c-axis distinguishes the (004) plane reflection from the \{400\} family and moves it to a higher angle. While 25Sn$_{1400}$, 25Sn$_{1600}$, 27Sn$_{1400}$, and 27Sn$_{1200}$ 30days display the tetragonal structure in Fig. 3, 25Sn$_{1800}$ and 27Sn$_{1800}$ remain cubic down to 10 K. The EDS-measured Sn contents of our tetragonal samples are 24.6% (“25Sn$_{1400}$”), 24.5% (“25Sn$_{1600}$”), 24.6% (“27Sn$_{1400}$”), and 24.7% (“27Sn$_{1200}$”), respectively, while those of the cubic samples are 23.3% (“25Sn$_{1800}$”) and 23.7% (“27Sn$_{1800}$”). This result does conform that the cubic to tetragonal transformation occurs only for Sn higher than 24.5%Sn [7] [8] [13].
Fig. 4 (a) shows $\mu_0H_{c2}(T)$ of 25Sn_1400, 25Sn_1800, 27Sn_1400, and 27Sn_1800, comparing both tetragonal (solid symbols) and cubic samples (open symbols). They have identical $\mu_0H_{c2}(T)$ behavior with $\mu_0H_{c2}(0.3K) = 29.1 \pm 0.2$ T. This result strongly contrasts with the widely reported depression of $\mu_0H_{c2}(T)$ for tetragonal Nb$_3$Sn [13] [14] [15], as is shown in the comparisons of Fig. 4(b) and (c). These new samples of known, high homogeneity show for the first time that the cubic-tetragonal transformation does not control $H_{c2}$. Also of note is that the $\mu_0H_{c2}(T)$ of our bulk Nb$_3$Sn is significantly higher than most previous reports [13][14] [15], with the exception of Foner’s [14] cubic single crystals. In fact the literature finding that tetragonal Nb$_3$Sn shows a significant depression of $\mu_0H_{c2}(T)$ comes from a sister crystal without chemical characterization [15].

There remains the issue of the normal state resistivity dependence of $\mu_0H_{c2}$. Orlando et al [15] noticed a crossover in on going from a “clean” film with $\rho = 8.8 \mu\Omega\cdot$cm (RRR~9.5) to a rather “dirty” sample with $\rho = 36 \mu\Omega\cdot$cm), $\mu_0H_{c2}(0)$ rising from ~26.5 to 29 T. Table I similarly divides our samples into a “cleaner” group with resistivities around $\rho \sim 10 \mu\Omega\cdot$cm and “dirtier” samples with $\rho > 20 \mu\Omega\cdot$cm. Fig. 5(a) shows that the “cleaner” samples have a lower $\mu_0H_{c2}(0.3K) \sim 27$ T. Fig. 5(b) shows that $\mu_0H_{c2}$ and A15 phase Sn content % are much less well correlated, since samples with Sn contents of 23.3 and 24.6at.%Sn both have $\mu_0H_{c2}(0.3K) > 29$T. This result is in agreement with the expectations of standard GLAG expressions for $H_{c2}$ as shown in Orlando et al. [16].

The conventional view that $\mu_0H_{c2}$ is suppressed in the tetragonal state and speculations that this may explain some of the strong reversible strain sensitivity of the superconducting properties [17,18] has been derived from compilations of limited $\mu_0H_{c2}$ data taken on a wide variety of samples fabricated in
different ways and of various material forms (thin films, single crystals and polycrystals). By contrast here we have varied the Sn% while maintaining the same sample quality, form and fabrication method. Multiple measurement types have directly addressed our sample homogeneity issue, leading us to conclude that all except one sample (27Sn_1400 – see Fig. 1) are indeed very homogeneous. We also found that our highest $\mu_0H_{c2}(0.3 \text{ K})$ values of $29.1 \pm 0.2 \text{ T}$ agree well with the highest previous measured $\mu_0H_{c2}$ values [16, 18]. We conclude that the previously reported low values of $\mu_0H_{c2}(0) \sim 21.4 \text{ T}$ for tetragonal Nb$_3$Sn [13] [14] [15] are not determined by whether they undergo the cubic to tetragonal transformation or not. Finally we note that Cooley et al. [20] have shown that ball milling followed by low temperature reactions (~650°C) can strongly increase the $\mu_0H_{c2}(T)$ slope at $T_c$. Based on standard Werthamer, Helfand and Hohenberg (WHH) fitting to $\mu_0H_{c2}$ of data up to 9 T, they deduced that $\mu_0H_{c2}(0)$ could reach 35 T. However, to make our ball-milled samples homogeneous, we had to take our samples to temperatures well above 1200°C where this valuable milling disorder anneals away. But in search of the maximum critical field, we may note the surprising result from the present binary samples is that $\mu_0H_{c2}(0) = 29 \text{ T}$ is as high as any optimized Ta- or Ti-doped wire, suggesting that wires do not yet have the optimum $\mu_0H_{c2}$ possible in the system.

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References:
1 Kunzler, E. Buehler, F. Hsu and J. Wernick, Phys. Rev. Lett, 6, 89(1961)

2 P. J. Lee and D. C. Larbalestier, "Microstructure, Microchemistry and the Development of Very High Nb3Sn Layer Critical Current Density," IEEE Trans. Applied Superconductivity, 15(2), pp. 3474-3477, 2005

3 J. P. Charlesworth, I. Macphail, and P. E. Madsen, J. Mat. Sci. 5, 580 (1970)

4 A. Godeke, M. Jewell, C. Fischer, A. Squitieri, P. Lee and D. Larbalestier, J. Appl. Phys. 97, 093909 (2005)

5 L. Cooley, C. Fischer, P. Lee and D. Larbalestier, J. Appl. Phys., 96, 4(2004)

6 M. Suenaga, D. Welch, R. Sabatini, O. Kammerer and S. Okuda, J. App. Phys. 59 (1986)

7 H. Devantay, J.L. Jorda, M. Decroux, and J. Muller, J. Mat. Sci. 16, 2145 (1981)

8 W. Goldacker, R. Ahrens, M. Nindel, B. Obst, and C. Meingast, IEEE Trans. Appl. Supercon. 3, 1322 (1993)

9 Y. Wang et al., Supercond. Sci. Technol. 19, 263 (2006)

10 C. Senatore et al., IEEE Trans. Appl. Supercond. 17, 2611 (2007)

11 Mei Li, Z. Du, C. Guo, and C. Li, J. of Alloys and Compounds, 477 104-117(2009)

12 Y. Watanabe, N. Toyota, T. Inoue, H. Komatsu, and H. Iwasaki, Jpn.J. Appl.Phys. 27, 2218 (1988)

13 A. Godeke, Supercond. Sci. Technol. 19 No 8, R68-R80 (2006)

14 S. Foner and E. McNiff, Solid State Communications, Vol. 39, pp. 959 (1981).

15 A. Arko, D. Lowndes, F. A. Muller, L. W. Roeland, J. Wolfrat, A.T. van Kessel, H. W. Myron, and F. M. Muller, Phys. Rev. Lett Vol 40 (24), (1978)

16 T. Orlando, E. McNiff, Jr. and S. Foner, and M. Beasley, Phys. Rev. B, vol 19, No 9, (1979)

17 A. Godeke, Supercond. Sci. Technol. 19, R60-R80, (2006)

18 R. Flukiger, D. Uglietti, C. Senatore and F. Buta, Cryogenics 48 (2008) 293-247
19 M. Jewell, Godeke A, Lee P and Larbalestier D Adv. Cryog. Eng. (Mater.) B 50 474, (2004)

20 L. Cooley, Y, Hu and A. Moodenbaugh, Appl. Phys.Lett. 88 142506 (2006)
**Fig. 1** The $T_c$ plots from the resistivity and specific heat measurements for overall 25 at% (a) and 27 at% Sn samples (b). The $T_c$ distribution is obtained by deconvolution of the specific heat data in the region of the superconducting transition.
Fig. 2 High sample homogeneity is evidenced by overlap of the percolative \( H_{c2} \) deduced from the 90\% point on the resistivity curves and the volumetric average \( H_{c2} \) deduced from reversible magnetization measurements up to 14 T in a VSM.
Fig. 3 Samples with and without the signature of the low temperature tetragonal transformation shown by their low temperature XRD traces for the nominal 25%Sn (a) and 27%Sn (b) samples in all annealing conditions. Note that the transformation does not occur for samples annealed at 1800°C when the A15 Sn content falls below 24at.%. 

Nominal 25% Sn
Typical peak at room temperature

Nominal 27% Sn

1400°C At 10K
1600°C At 10K
1800°C At 10K

1200°C 30 days At 10K
1400°C At 10K
Fig. 4 (a) Representative $\mu_0H_{c2}$ plot of our bulk Nb$_3$Sn samples. (b) Comparison to Foner’s polycrystalline Nb$_3$Sn sample. (c) Comparison to Foner’s and Arko’s single crystal Nb$_3$Sn samples. [12] [13] [14].
Fig. 5 Dividing our samples into “cleaner” and “dirtier” samples following the work of Orlando et al. [15] we show that the “cleaner” samples lower $\mu_0H_c(T)$. (a) shows the depressed $\mu_0H_c(T)$ of the cleaner samples and (b) demonstrates that the $\mu_0H_c(T)$ relates to the cleaner samples (lower normal resistivity and higher RRR values) rather than the EDS-measured Sn content for the Sn-rich (23.3–24.7% Sn) samples.
Table 1 Summary of physical properties of the samples

| Sample Name | $T_c$ (K) | $a_0$ by XRD (Å) | EDS-measured Sn (at%) | RRR | $\rho$ (μΩ-cm) | $\mu_0H_c2(0.3\ K)$ (T) |
|-------------|-----------|------------------|-----------------------|-----|----------------|--------------------------|
| 25Sn_1400   | 18.05     | 5.2882±2E-4      | 24.6±0.3              | 5.44| 20.9          | 29.1                     |
| 25Sn_1600   | 17.90     | 5.2872±6E-4      | 24.5±0.4              | 8.37| 12.7          | 27.6                     |
| 25Sn_1800   | 17.87     | 5.2871±3E-4      | 23.3±0.7              | 3.69| 31.3          | 29.4                     |
| 27Sn_1400   | 18.05     | 5.2871±3E-4      | 24.6±0.2              | 1.97| 42.5          | 29.1                     |
| 27Sn_1800   | 17.67     | 5.2873±2E-4      | 23.7±0.4              | 2.23| 24.9          | 29.0                     |
| 27Sn_1200   | 17.81     | 5.2871±1E-4      | 24.9±0.2              | 9.48| 9.48          | 27.6                     |
| 30days      |           |                  |                       |     |               |                          |