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## Evidence that the upper critical field of Nb<sub>3</sub>Sn is independent of whether it is cubic or tetragonal

Jian Zhou, Younjung Jo,<sup>a)</sup> Zu Hawn Sung, Haidong Zhou, Peter J. Lee, and David C. Larbalestier<sup>b)</sup>

National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA

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Although 2011 marks the 50th anniversary of Nb<sub>3</sub>Sn as the first high field superconductor, real understanding of its upper critical field behavior  $H_{c2}$  is incomplete. Here, we show surprising  $H_{c2}$  data on highly homogeneous bulk samples that exhibit identical upper critical field  $H_{c2}(0.3\text{ K}) \sim 29 \pm 0.2$  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  $H_{c2}(0\text{ K})$  from 29 T to 21.4 T in the tetragonal state. © 2011 American Institute of Physics. [doi:10.1063/1.3643055]

Nb<sub>3</sub>Sn is the most widely used superconductor for generating fields above  $\sim 10$  T. More than 600 tons of Nb<sub>3</sub>Sn will be used in the International Tokamak Experimental Reactor (ITER). This extensive and long-standing use<sup>1</sup> makes it all the more surprising that there is no agreed data set for the variation of the upper critical field  $H_{c2}$  with composition across the A15 phase field of Nb<sub>3</sub>Sn. High Sn compositions are important for the very high critical current densities  $J_c$  now achieved in commercial strands.<sup>2</sup> Optimizing  $J_c(H)$  would be much easier with a quantitative understanding of how  $H_{c2}$  varies with Sn content since all practical Nb<sub>3</sub>Sn wires contain the full range of A15 phase compositions (generally thought to range from  $\sim 18$ -25 at. %Sn (Ref. 3)). The integrated effect of shells of varying %Sn,  $T_c$  and  $H_{c2}$  has been addressed both experimentally<sup>4</sup> and by modeling.<sup>5</sup> These studies show that flattening the Sn gradient raises the effective  $H_{c2}$  and  $J_c$ . The modeling scheme of Cooley *et al.*<sup>5</sup> is particularly valuable, but it lacks the composition dependence of  $H_{c2}$ ; To fill this need, we have fabricated homogeneous binary Nb<sub>3</sub>Sn bulk samples in one, consistent fashion to provide the compositional variation of  $H_{c2}$ . Remarkably, we find that, whether tetragonal or cubic,  $H_{c2}(0)$  is just as high and reaches the same 29.1 T value found in any optimally Ti- or Ta-doped wire.<sup>4,6</sup>

Rather homogeneous bulk Nb<sub>3</sub>Sn was made by Devantay *et al.*<sup>7</sup> by heating samples into the melt phase and by Goldacker *et al.*<sup>8</sup> using a hot isostatic press (HIP) at 1100 °C. To further reduce inhomogeneity, we used a HIP capable of reaching up to 2200 °C. We report here on nominally stoichiometric 25 at. %Sn and nominally Sn-rich 27 at. %Sn samples so as to ensure the most Sn-rich A15 compositions. 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 were performed in a dedicated glove box filled with Ar gas to minimize oxidation. After 60 min of milling, the powders were pressed into a hard pellet and

then sealed in vacuum in a Ta-lined steel tube, which was pressurized at 2 kbar in a HIP for a pre-anneal for 16 h at 650 °C and then at the main A15 phase reaction at 1200 °C for 72 or 160 h. The central reacted A15 part of each can was then cut out and re-sealed in an evacuated Ta-lined Nb tube for a 2nd HIP reaction at 1400 °C, 1600 °C or 1800 °C for 24 h. One piece of the 27 at. %Sn sample annealed at 1800 °C was further annealed in an evacuated Ta-lined Nb tube for 30 days at 1200 °C.

X-ray diffraction (XRD) using a liquid helium cryostat was used to identify the tetragonal transformation. Specific heat measurements 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  $H_{c2}$  derived from the reversible magnetization in a 14 T vibrating sample magnetometer. Due to their high uniformity, the samples showed very little magnetization hysteresis and had a linear M(H) characteristic and sharp slope change at  $H_{c2}$ . A15 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<sup>9</sup> for both nominal compositions in their various conditions. Table I summarizes the  $T_c$ , the EDS-measured Sn at. % of the A15 grains, the residual resistance ratio (RRR) [ $=\rho(300\text{ K})/\rho(20\text{ K})$ ],  $\rho(20\text{ K})$  and the resistively measured  $H_{c2}$  at 0.3 K. Raising the annealing temperature to 1800 °C reduces the A15 Sn content by about 1 at. % in each case. However, the  $T_c$  drops only slightly on raising the annealing temperature from 1400 °C to 1800 °C. All our data indicate that Sn is rejected from the A15 lattice above 1400 °C, which is consistent with the Nb<sub>3</sub>Sn phase boundary bending to Sn-poor compositions.<sup>3,10</sup> High sample homogeneity is attested by sharp resistivity transitions (except for the 27Sn\_1400 sample caused by grain boundary precipitation of NbSn<sub>2</sub>) and especially by the narrow specific heat  $T_c$  distributions in 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

<sup>a)</sup>Present address: Kyungpook National University, Daegu 702-701, South Korea.

<sup>b)</sup>Author to whom correspondence should be addressed. Electronic mail: larbalestier@asc.magnet.fsu.edu.

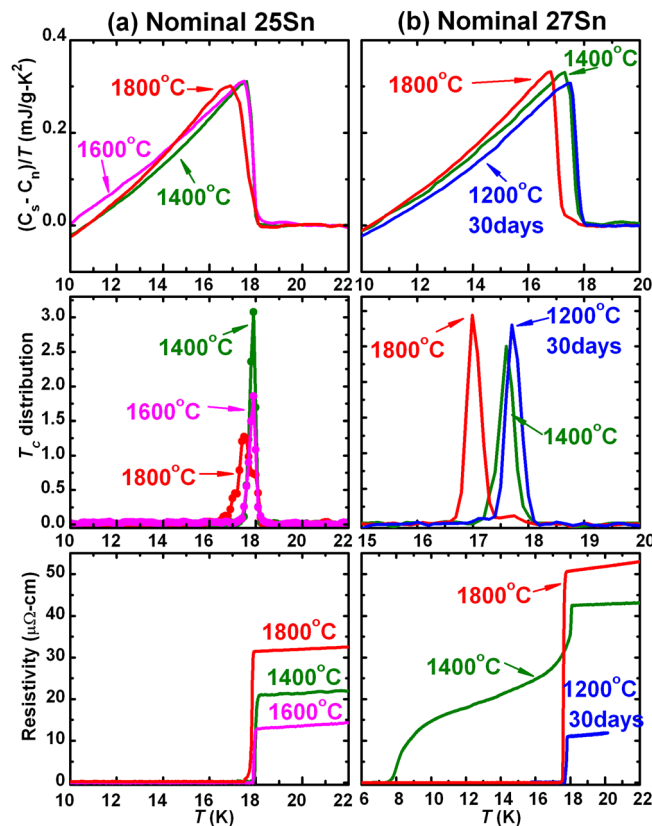


FIG. 1. (Color online)  $T_c$  plots from the resistivity and specific heat measurements for nominal 25 at. % (a) and 27 at. % Sn samples (b). The  $T_c$  distribution is obtained by deconvolution of the specific heat data in the region of the superconducting transition.

very closely with the potentially percolative, “best bit” resistivity measurements (Fig. 2). We thus have good confidence that the  $H_{c2}(T)$  values from our high-field resistivity measurements represent the entire sample (with the exception of the 27Sn\_1400 sample shown in Fig. 1).

The cubic-to-tetragonal transformation of the A15 phase has been reported to occur from 31 K to 45 K,<sup>11</sup> for example at 45 K (Ref. 7) and at 35 K,<sup>8</sup> when Sn is >24.5%. 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  $2\theta$  peak at  $71.4^\circ$  at room temperature into two peaks at 10 K is a clear evidence of the cubic-to-tetragonal transformation. The c-axis contraction distinguishes the (004) plane reflection from the {400} family and moves it to a higher angle. While the higher Sn A15 grains (25Sn\_1400 (24.6Sn), 25Sn\_1600 (24.5Sn), 27Sn\_1400 (24.6Sn), and 27Sn\_1200 30 days (24.9Sn)) display the tetragonal structure in Fig. 3, the Sn-poor samples (25Sn\_1800 (23.3Sn) and

TABLE I. Summary of physical properties of the samples.

Sample name (T)	$T_c$ (K)	Measured Sn (at. %)	RRR	$\rho$ ( $\mu\Omega$ -cm)	$H_{c2}(0.3 K)$
25Sn_1400	18.05	$24.6 \pm 0.3$	5.44	20.9	29.1
25Sn_1600	17.90	$24.5 \pm 0.4$	8.37	12.7	27.6
25Sn_1800	17.87	$23.3 \pm 0.7$	3.69	31.3	29.4
27Sn_1400	18.05	$24.6 \pm 0.2$	1.97	42.5	29.1
27Sn_1800	17.67	$23.7 \pm 0.4$	2.23	50.5	29.0
27Sn_1200 30 days	17.81	$24.9 \pm 0.2$	9.48	10.9	27.6

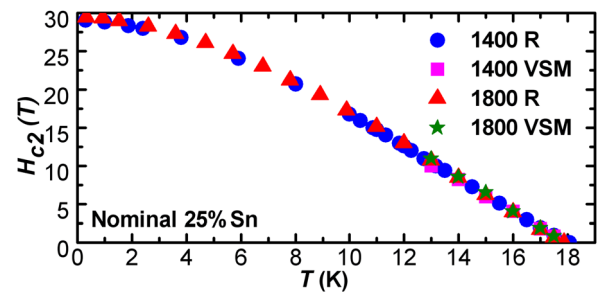


FIG. 2. (Color online) High sample homogeneity is evidenced by overlap of the percolative  $H_{c2}$  deduced from the 90% point on the resistivity curves and the volumetric average  $H_{c2}$  deduced from reversible magnetization measurements up to 14 T in a VSM.

27Sn\_1800 (23.7Sn)) remain cubic down to 10 K, consistent with earlier reports that the transformation occurs only for Sn higher than 24.5% Sn.<sup>7,8,12</sup>

Fig. 4(a) compares  $H_{c2}(T)$  of both tetragonal and cubic samples. They have identical  $H_{c2}(T)$  behavior with  $H_{c2}(0.3 K) = 29.1 \pm 0.2$  T. This result strongly contrasts with the widely reported depression of  $H_{c2}(T)$  for tetragonal  $Nb_3Sn$ ,<sup>12–15</sup> as is shown in the comparisons of Figs. 4(b) and 4(c). The previous study and reviews have directly tied the  $H_{c2}$  suppression to the onset of the tetragonal transformation.<sup>12–15</sup> However, our samples of known high homogeneity show that the cubic-tetragonal transformation does not shift the  $H_{c2}$ . Also of note is that the  $H_{c2}(T)$  of our bulk  $Nb_3Sn$  is significantly higher than most previous reports,<sup>12–14</sup> with the exception of Foner’s<sup>13</sup> cubic single crystals.

There remains the issue of the normal state resistivity and RRR dependence of  $H_{c2}$ . Orlando *et al.*<sup>16</sup> noticed a crossover on going from a “clean” film with  $\rho = 8.8 \mu\Omega$ -cm (RRR  $\sim 9.5$ ) to a rather “dirty” sample with  $\rho = 36 \mu\Omega$ -cm,  $H_{c2}(0)$  rising from  $\sim 26.5$  to 29 T. Table I similarly divides our samples into a “cleaner” group with resistivities around  $\rho \sim 10 \mu\Omega$ -cm and RRR  $> 8$ , and a “dirtier” group with  $\rho > 20 \mu\Omega$ -cm and RRR  $< 5.5$ . Fig. 5(a) shows that the “cleaner” samples have a lower  $H_{c2}(0.3 K) \sim 27.6$  T, while Fig. 5(b) shows that  $H_{c2}$  and A15 phase Sn% are much less well correlated, since samples with Sn contents of 23.3 and 24.6 at. % Sn both have  $H_{c2}(0.3 K) > 29$  T. As a conclusion, the dominant control variable for  $H_{c2}$  is not Sn composition

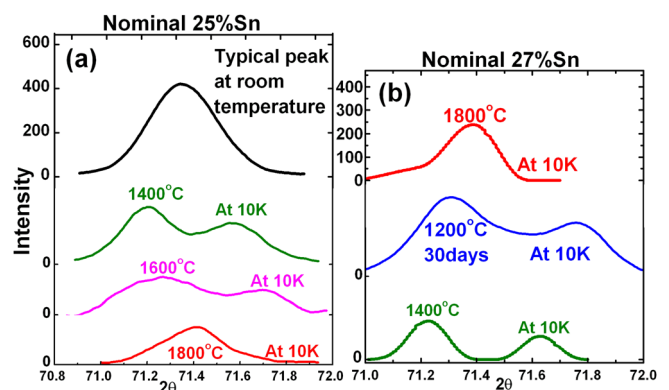


FIG. 3. (Color online) Samples with and without tetragonal transformation shown by their low temperature XRD traces for the nominal 25% Sn (a) and 27% Sn (b) sample sets. Note that the transformation does not occur for samples annealed at 1800 °C when the A15 Sn content falls below 24 at. %. The instrument resolution is about  $0.005^\circ$ , well below the changes seen.

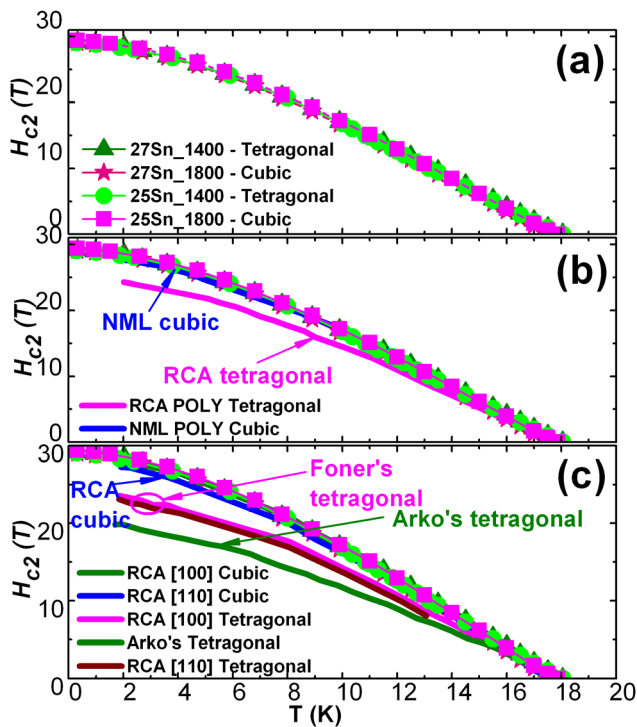


FIG. 4. (Color online) (a) Representative  $H_{c2}$  plot of our bulk  $\text{Nb}_3\text{Sn}$  samples. (b) Comparison to Foner's polycrystalline  $\text{Nb}_3\text{Sn}$  sample. (c) Comparison to Foner's and Arko's single crystal  $\text{Nb}_3\text{Sn}$  samples (See Refs. 12 and 13, and 14).

or structure but the carrier scattering quantified by RRR and the  $\rho$ . Moreover, the fact that the “dirtier” 25Sn\_1400 and 27Sn\_1400 become tetragonal at low temperature indicates that the structural transformation can happen in materials with significant scattering.

In summary, these results overturn the broadly accepted view that  $H_{c2}$  is suppressed in the tetragonal state and speculations that this may explain some of the strong reversible strain sensitivity of the superconducting properties<sup>12,15</sup> of  $\text{Nb}_3\text{Sn}$ . This previously unchallenged conclusion may have resulted from making compilations of limited  $H_{c2}$  data taken on a wide variety of samples fabricated in different ways in diverse material forms (thin films, single crystals, and polycrystals). In contrast, we have varied the A15Sn% while maintaining the same sample quality, form and fabrication method. Multiple measurement types (electrical, chemical, and crystallographic) have directly addressed the sample homogeneity issue, leading us to conclude that all except one sample (27Sn\_1400) are indeed very homogeneous. We also found that our highest  $H_{c2}$  (0.3 K) values of  $29.1 \pm 0.2$  T agree well with the highest previous measured  $H_{c2}$  values.<sup>12,15,17</sup> Finally we note that Cooley *et al.*<sup>18</sup> have shown that ball milling followed by low temperature reactions ( $\sim 650^\circ\text{C}$ ) can strongly increase the  $H_{c2}(T)$  slope at  $T_c$ . Based on standard Werthamer, Helfand, and Hohenberg (WHH) fitting to  $H_{c2}$  of data up to 9 T, they deduced that  $H_{c2}(0)$  could reach 35 T. However, to make our ball-milled samples homogeneous, we had to take our samples to tem-

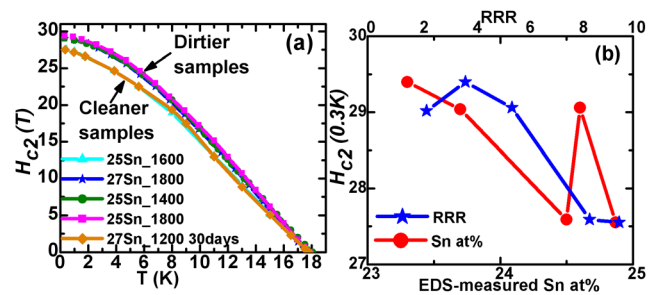


FIG. 5. (Color online) (a) shows the depressed  $H_{c2}(T)$  of the “cleaner” samples and (b) demonstrates that  $H_{c2}(T)$  correlates to lower resistivity and higher RRR value rather than the EDS-measured Sn content for Sn-rich (23.3 ~ 24.7% Sn) samples.

peratures well above  $1200^\circ\text{C}$  where this valuable milling disorder anneals away. In search of the maximum critical field, we may note the surprising result of the present binary samples that  $H_{c2}(0) = 29$  T is as high as any optimized Ta- or Ti-doped wire,<sup>4,6</sup> suggesting that wires do not yet have the optimum  $H_{c2}$  possible in the system.

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