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MICROSTRUCTURAL UNDERSTANDING AND CRITICAL CURRENT OPTIMIZATION OF ADVANCED HIGH FIELD SUPERCONDUCTORS

Progress Report
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NOTICE

I. Nb_3Sn

It is of great importance to improve critical current density, J_c, in A15 superconductors for high field magnet applications. Most current work to improve J_c in A15 wires concentrates on increasing the overall J_c by increasing the fraction of superconducting phase in the wire, by improving the uniformity of the superconductor cross section along the length of the wire and by adjusting the strain state of the A15 layer. The goal of the A15 work in this group was to investigate the intrinsic J_c of the A15 layer itself. To do this, a better understanding of factors controlling the intrinsic J_c of the Nb_3Sn was pursued. It is well established that A15 J_c is linked to grain size[1] and thus that grain boundaries are flux pinning sites in these superconductors.[2] Flux pinning theory suggests that grain boundary chemistry could affect the strength of flux pinning and consequently J_c. Grain boundary composition affects the impurity parameter, α, and thus the elemental pinning force (f_p) of the grain boundary.[3] Scanlan, et al,[2] found that the A15 layer J_c of bronze-processed composite wires was 20% lower than that of Nb-Sn tapes of similar grain size. Whether differences in J_c were due to differences in strain in the A15 layer or differences in layer composition produced by the presence or absence of copper is unclear. Copper is known to reside in the grain boundaries of Nb_3Sn formed in the presence of Cu,[4] as is the case for all filamentary Nb_3Sn conductors. In this work we began experiments to systematically test whether grain boundary composition does affect J_c.

The material chosen for these experiments was a binary diffusion couple of niobium and tin. Starting samples were of nominally constant grain size, bulk composition and lattice strain. Copper was electroplated onto these Nb-Sn tapes and both Cu-plated and Cu-free tapes were annealed at 600°C in order to diffuse Cu into the grain boundaries in the former case and to have a control sample of similar treatment in the latter case. Magnetization in applied magnetic fields between 0 and 12 T was measured for the untreated, as-received, tape and for the Cu-free heat treated and Cu-plated and heat treated tape. Magnetization measurements were made by vibrating sample magnetometry (VSM) with the applied field normal to the plane of the Nb_3Sn layer as shown in Figure 1. Magnetization J_c is shown in Figure 2 for the untreated tape, in Figure 3 for the Cu-treated tape and in Figure 4 for the Cu-free treated tape.

Although B_{c2} values of the treated tapes were depressed, J_c of the Cu-treated samples exceeded that of some, but not all, untreated samples and exceeded that of the Cu-free treated samples by a factor of three. Unfortunately, results for each treatment were scattered. Microstructural analysis by scanning electron microscopy (SEM) showed that the Nb_3Sn layers of these tapes were not always continuous and were not of uniform thickness. More uniform samples are needed for such experiments to be conclusive, but these results suggest that grain boundary copper enhances the J_c of Nb_3Sn. Addition of other elements to the grain boundaries of A15 compounds might further enhance J_c, but no such study is presently planned.

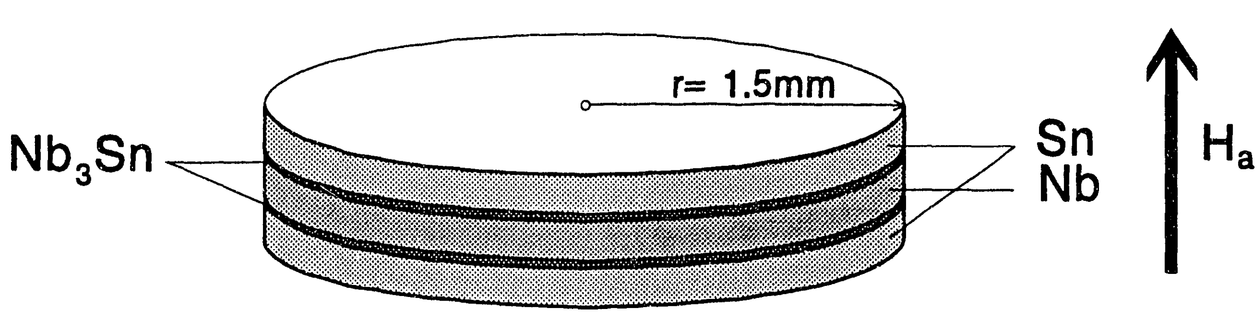

Figure 1 Sample geometry for magnetization measurements.

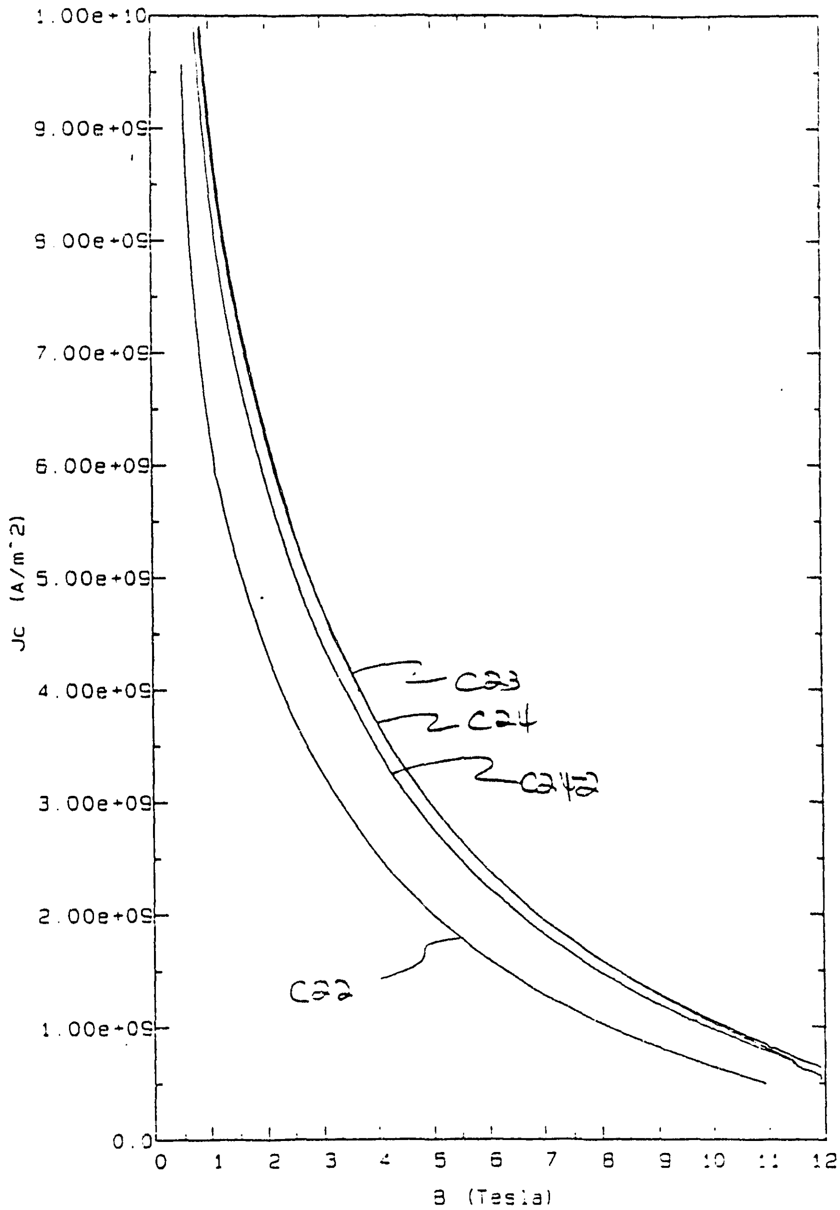

Figure 2 Repeated measurements of magnetization J_c versus applied field for the untreated Nb-Sn tape at 4.2 K

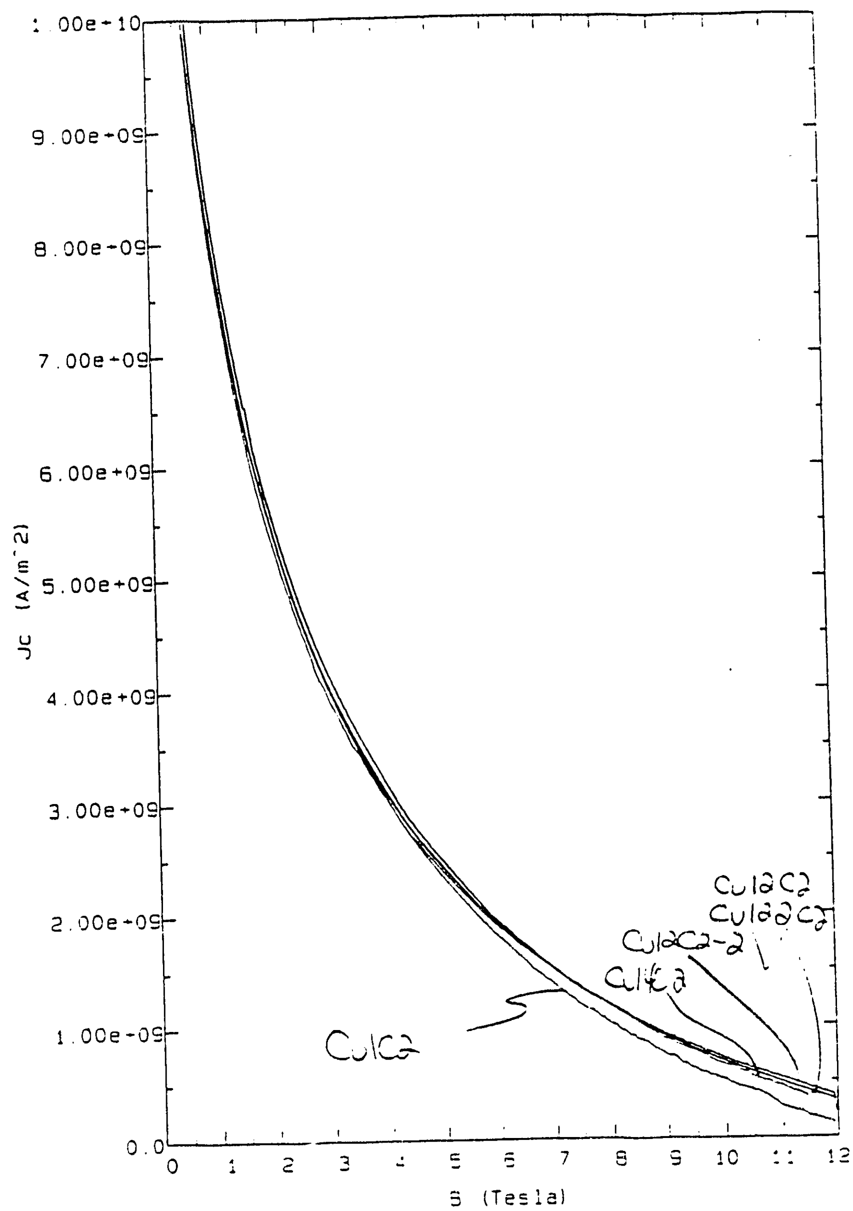

Figure 3 Repeated measurements of magnetization J_c versus applied field for the copper treated Nb-Sn tape at 4.2 K.

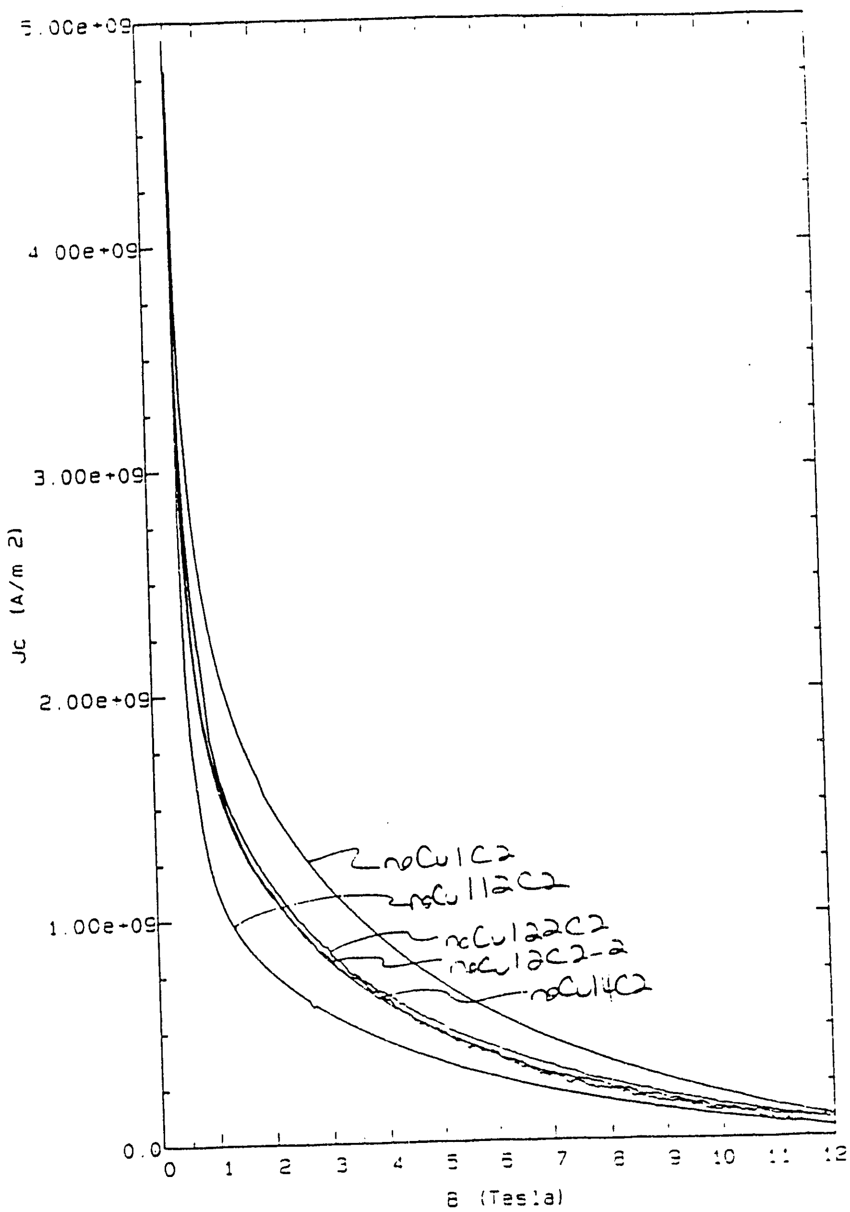

Figure 4 Repeated measurements of magnetization J_c versus field for the copper-free treated Nb-Sn tape at 4.2K.

II. CHEVREL PHASE

In September 1991 a large fraction of the Chevrel Phase research community met in Geneva in order to review the status of Chevrel Phase applications and basic science. This workshop was hosted by Øysten Fischer and Michel Decroux of the University of Geneva, and David Larbalestier was the US organizer. The central issues for high field and high current density applications are those of electromagnetic granularity at powder particle or grain boundaries and insufficient flux pinning. Both these issues were discussed extensively at the workshop and the collective opinions of the workshop participants were summarized by Larbalestier[5] in a final summary.

The Wisconsin group concentrated first on the granularity issue, since this produced the lower limit to the J_c. The principal results of this work are:

(i) Work on Mo-sheathed $PbMo_6S_8$ (PMS) wires showed that they do not densify properly unless they are hot isostatically pressed (HIP), as shown in Figure 5.[6] Without a HIP treatment, the I_c is independent of whether H is parallel to or normal to I_c, as shown in Figure 6. We interpret this as evidence that the current flows in a locally, percolative fashion, according to whatever path provides the best local connection. Only when densified by HIP'ing, does $I_c(\parallel H)$ greatly exceed $I_c(\perp H)$ (Figure 7).

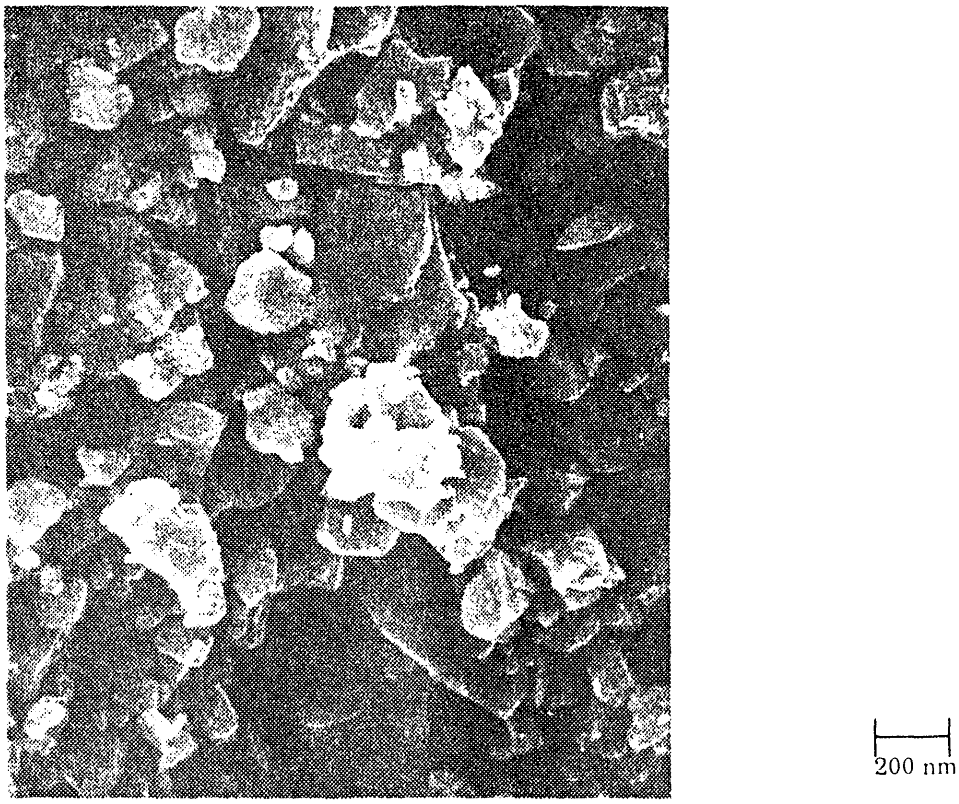

Figure 5 High-resolution scanning electron microscope micrograph of the fractured surface of conventionally sintered $Pb_{1.0}Mo_6S_{7.5}$ wire heat treated at 700 °C for 24hr.[6]

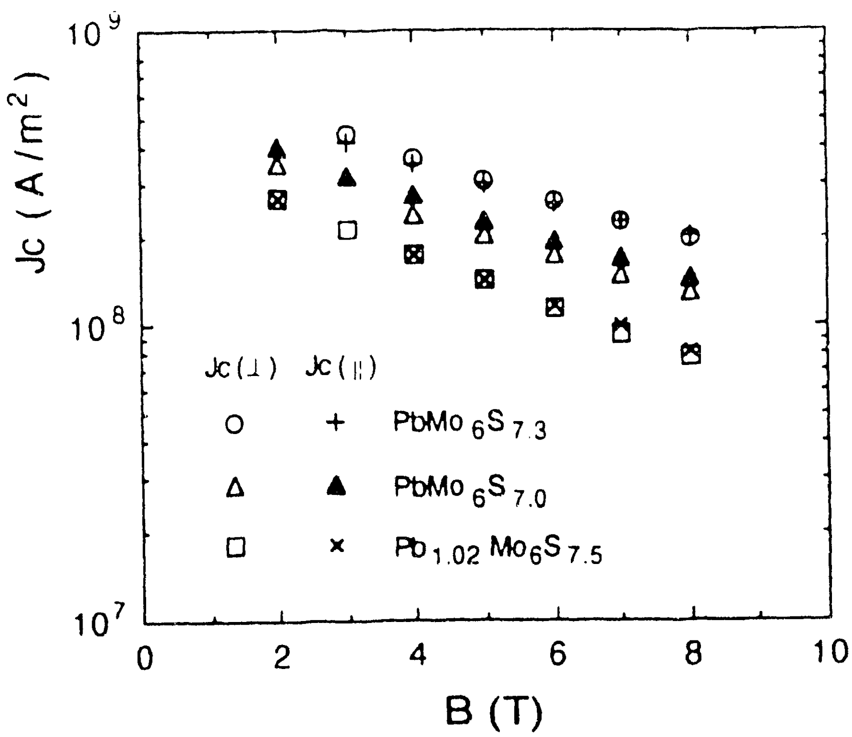

Figure 6 Comparison of $J_c(\|)$ and $J_c(\perp)$ data for conventionally sintered $PbMo_6S_{7.3}$, $PbMo_6S_{7.0}$, and $Pb_{1.02}Mo_6S_{7.5}$ wires.[6]

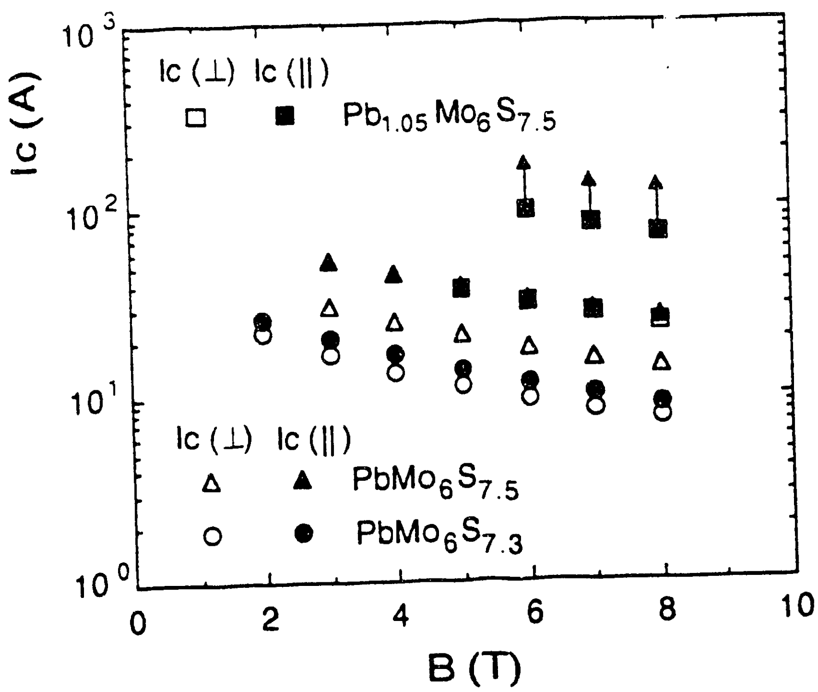

Figure 7 Typical $I_c(\parallel)/I_c(\perp)$ data for straight PMS wires HIP treated at 1200°C.[6]

(ii) An additional test of this hypothesis was performed in a set of experiments by Le Lay et al,[7,8] on HIP'ed and non-HIP'ed powder samples of mixed and pure Pb- and Sn-Chevrel phases (PMS and SMS). As in the Mo-sheathed wires, these samples did not densify without HIP'ing. Figure 8 compares the densified and percolative microstructures of typical of bulk Chevrel phase HIP'ed and non-HIP'ed samples, respectively.[8] In the HIP'ed samples, we found perfect size scaling of the magnetization, which indicates complete connectivity (Figure 9). This perfect size scaling, however, was absent from the non-HIP'ed samples. In addition, reduced pinning force curves ($F_p/F_{p_{max}}$ versus $b^{\dagger}$) show a $F_p/F_{p_{max}} \propto b^{1/2}(1-b)^2$ behavior typical of the grain boundary pinning mechanism found in Nb_3Sn (Figure 10).[8]

† $b = B/B^*$, where B^* is the field at which the magnetization hysteresis, ΔM, becomes zero.

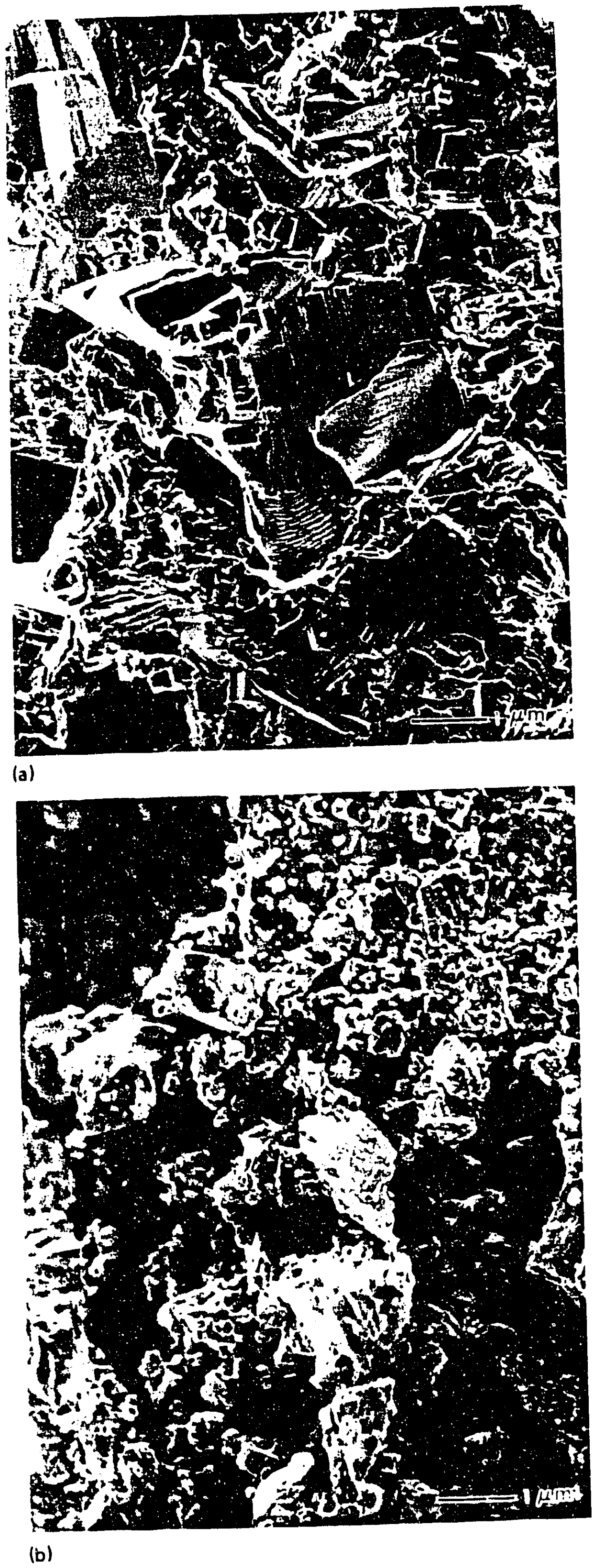

Figure 8 High-resolution SEM images of (a) $Sn_1Mo_6S_{7.6}$ HIP'ed and (b) $Pb_{0.1}Sn_{0.9}Mo_6S_{7.6}$ non-HIP'ed bulk samples made at 800°C.[8]

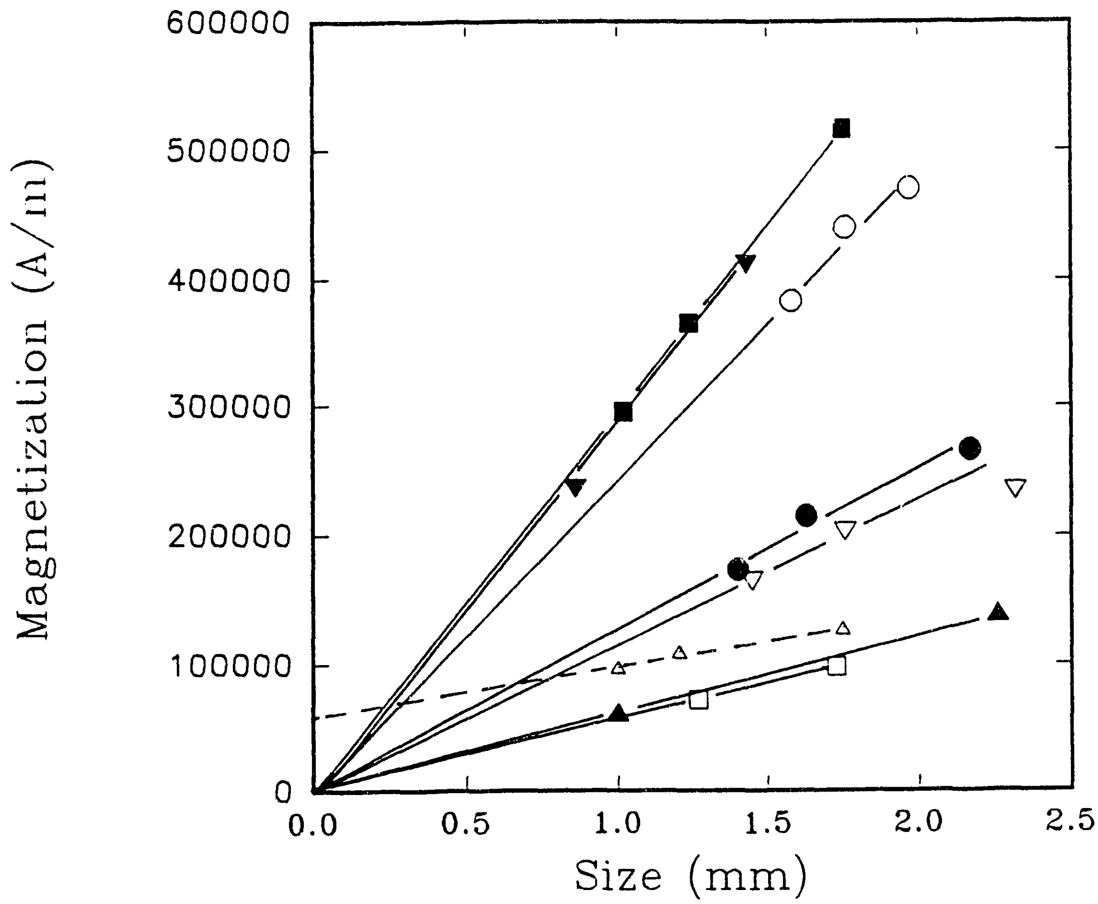

Figure 9 Magnetization as a function of sample size for various $Pb_xSn_{1-x}Mo_6S_{7.6}$ samples at 4.2K.

— HIP'ed at 800 °C : ▽ $x = 1$; □ $x = 0.5$; ■ $x = 0.1$; ▼ $x = 0$
— HIP'ed at 900 °C :○ $x = 1$; ▲ $x = 0.1$; ● $x = 0$
- - non-HIP'ed (1100 °C): △ $x = 0.5$

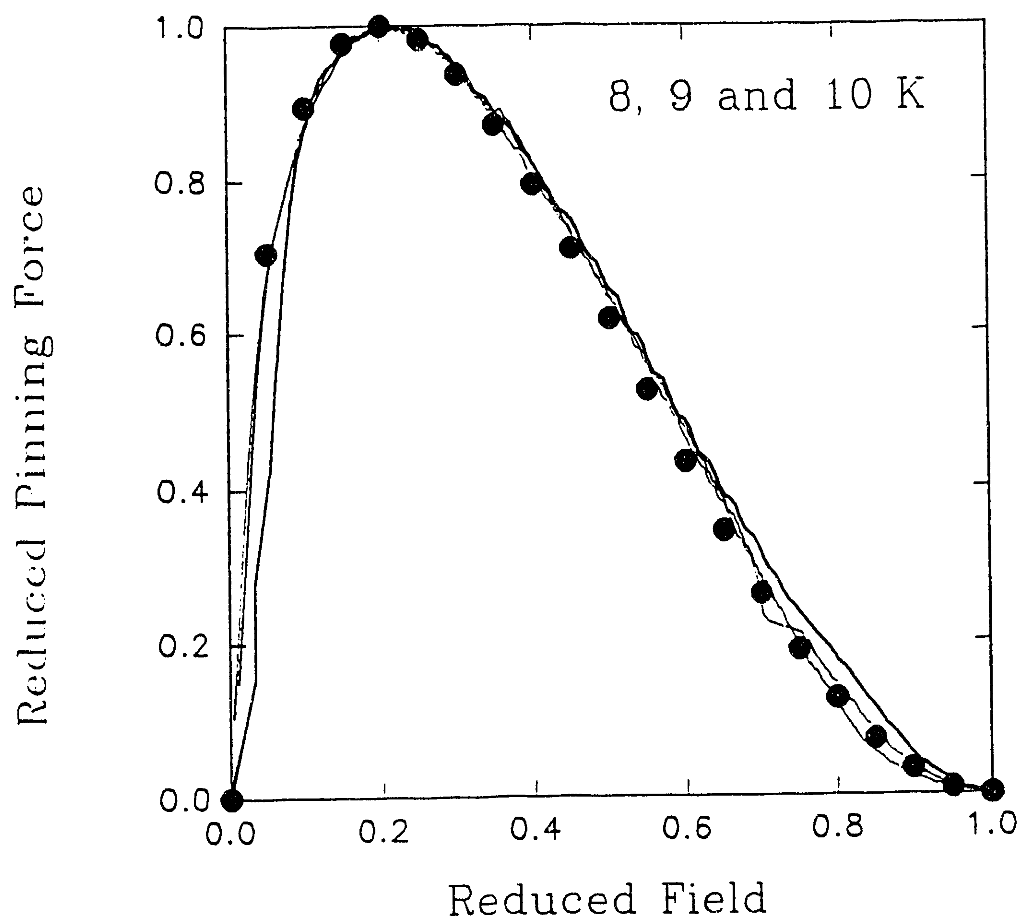

Figure 10 Reduced pinning force as a function of reduced critical field for a $Pb_{0.1}Sn_{0.9}Mo_6S_{7.6}$ bulk sample (800 °C HIP). ● = points calculated using $F_p/F_{p_{max}} = C[b^{1/2}(1-b)^2]$.[8]

These results are conceptually important because they make it clear that there is no *intrinsic* granularity to Chevrel Phases.[††] The problem is rather one of grain-to-grain connectivity, which is a problem that can be solved by appropriate processing, in particular by the use of the HIP. Thus, the next step was to tackle the second important issue which is that of flux pinning. To address this problem Le Lay grew some single crystals of $SnMo_6S_8$ and measured their magnetization.[9] The most-studied crystal was tin-deficient and had a composition of $Sn_{0.854}Mo_6S_8$.[10] The principal results of this study are:

[††] This point was persuasively argued by Deutscher at the Geneva workshop.

(a) Single crystals, which contained defects that could act as pinning sites, do have measurable flux pinning. Despite the high defect density, however, the flux pinning in these single crystals is about a factor of 5 less than observed in polycrystalline SMS (~ 150A/mm^2 versus 750A/mm^2 at 10T)(Figure 11).[9]

(b) The implication of these results is that the way to high J_c is to refine the grain size thus ensuring a high density of grain boundary flux pinning sites and to fully densify the material so that there is no connectivity problem.

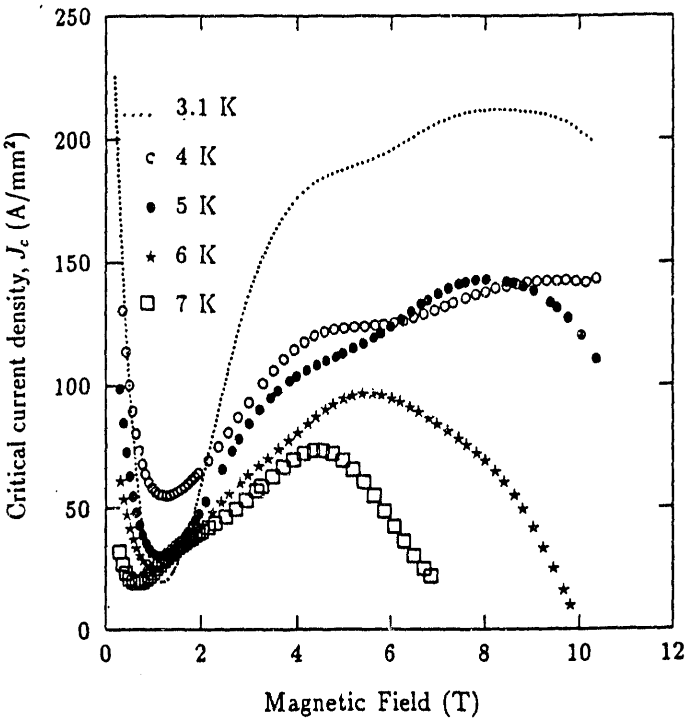

Figure 11 Magnetization critical current densities of $SnMo_6S_8$ single crystal at several temperatures.[7]

To test whether grain size refinement is the key to higher J_c in Chevrel Phase materials, Bonney has been performing experiments which compare grain size and J_c in $SnMo_6S_8$.[11] Results indicate that J_c is proportional to grain boundary length per unit area at lower fields (Figure 12). Thus, microstructure refinement is important to J_c enhancement. Bonney has begun experiments to characterize high field J_c dependencies in $SnMo_6S_8$. J_c has been measured by vibrating sample magnetometry (VSM) up to 30 Tesla at MIT's Bitter Magnet Laboratory. Further microstructural analysis by transmission electron microscopy is being performed.

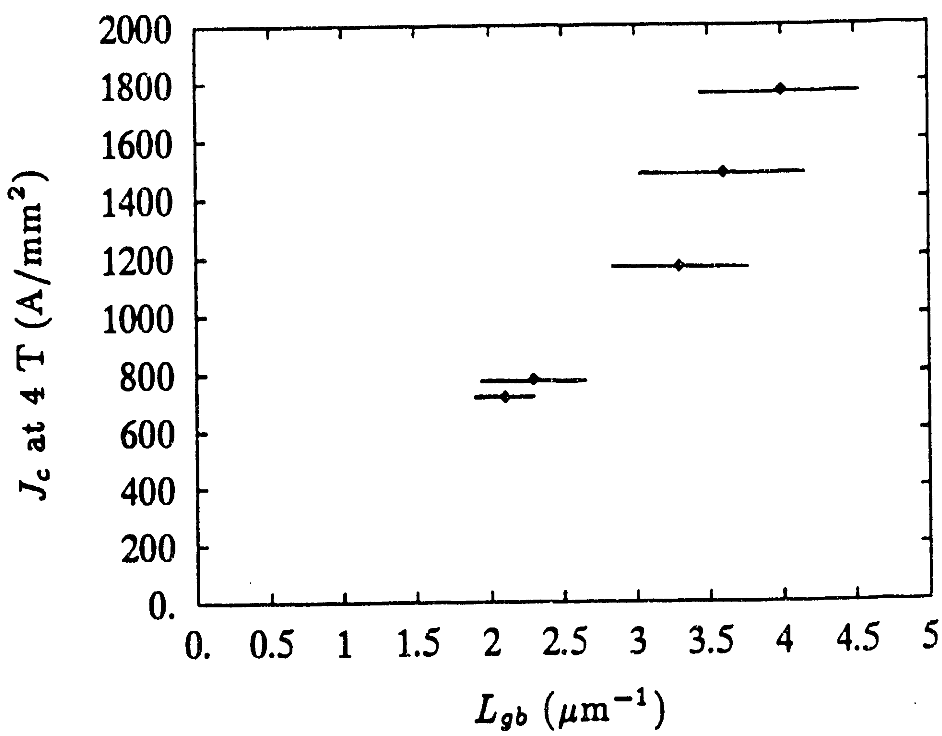

Figure 12 J_c dependence on grain boundary line length per unit area, L_{gb}.

These results have therefore clearly indicated the future direction of Chevrel phase superconductor development. A benefit of the Geneva Workshop was that we were able to learn how to make oxygen-free materials from Dave Hinks. Bonney and Willis have replicated this process and in their latest samples (which were reported in Willis' talk at the 1992 Berkeley Low Temperature Materials Workshop) they have achieved J_c and T_c values equivalent to the best yet reported (Figure 13).

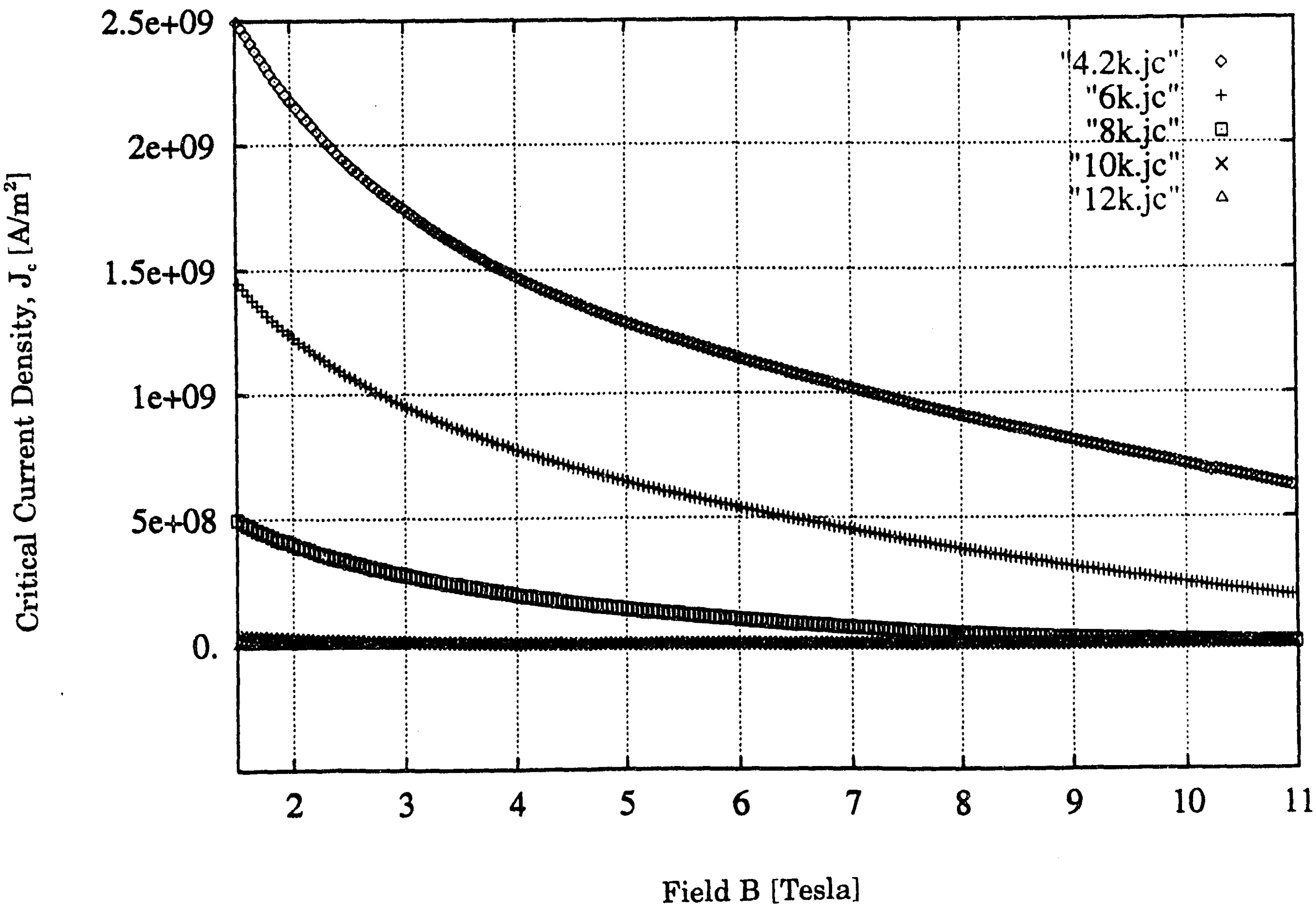

Figure 13 Critical current densities of HIPped $Pb_{0.8}Sn_{0.2}Mo_6S_8$ sample prepared at UW, measured at temperatures of 4.2, 6, 8, 10, and 12K.

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