MAGNETIZATION PROPERTIES OF A SnMo_6S_8 SINGLE CRYSTALL. Le Lay, T. C. Willis[†] and D. C. Larbalestier[†]

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Abstract

We synthesised a single crystal of the high critical field compound SnMo_6S_8 to serve as model of the superconducting behaviour of $\text{Pb}_{1-x}\text{Sn}_x\text{Mo}_6\text{S}_8$ in wires and bulk samples. Magnetization critical current densities were measured in fields up to 11 T at various temperatures from 3.1 to 7 K. We compared the behaviour of the single crystal to that of bulk and wire samples, as well as to oxide superconductors.

Introduction

Belonging to a class of materials in which many have superconducting properties, PbMo_6S_8 and SnMo_6S_8 nevertheless possess a unique feature — their upper critical fields (H_{c2}) are among the highest of the non-oxide materials — about 60 T and about 34 T at 0 K for PbMo_6S_8 and SnMo_6S_8 , respectively. Their critical temperatures (T_c) are well above the boiling point of liquid helium — usually in the range 14 to 15 K. These high values have been the motivation for the fabrication of PbMo_6S_8 and SnMo_6S_8 wires in the last decade. Indeed, over the years several teams have successfully managed to make monofilamentary wires and to increase their current carrying capabilities. The critical current densities (J_c) typically now reach 10^8 A/m^2 and higher at 20 T.¹⁻⁵

Although promising, these results are not high enough to justify widespread development efforts. If J_c could be raised by 5 to 10 times, the case would be strong. Unfortunately, at the present time there is a lack of understanding of the critical current mechanism. The J_c enhancements are mostly due to improvements in wire drawing technology and empirical tin-doping of PbMo_6S_8 . Not enough attention has been given to microstructural issues such as the intergranular connectivity, the defect structure, the grain boundary structure or the role of Sn as a doping agent. Recently the important issue of the possibly poor connectivity between $\text{Pb}_{1-x}\text{Sn}_x\text{Mo}_6\text{S}_8$ grains has been addressed in various works:

(a) Hamasaki *et al.*¹ have shown that hot isostatic pres-

sure (HIP) applied to a wire during its heat treatment can improve J_c ; this suggests that the grains are not initially well connected in the wires.

(b) Yamasaki *et al.*³ have observed the presence of lead droplets on $\text{Pb}_{1+x}\text{Mo}_6\text{S}_{7.5}$ grains, inside wires. This excess Pb phase could be one way in which poor connections exist, between the grains.

(c) A series of recent papers by the Geneva group⁶⁻⁸ shows evidence of granularity in PbMo_6S_8 bulk samples. According to careful susceptibility and specific heat measurements, they found that the limitation to J_c is the poor intergranular connections rather than the intrinsic J_c of the grains.

(d) On the other hand, it has been found that it is possible to produce bulk samples whose susceptibility is almost field-independent⁹ — this means that there are ways to make well-sintered samples whose grains are well connected such that the sample behaves as a whole, rather than as an assembly of poorly connected grains.

In addition to the connectivity-related observations, it has been shown that tin plays an important role in the improvement of the J_c for wires^{1-2,10}, ribbons¹¹, and bulk samples¹². In the case of ribbons, the improvement can be as high as an order of magnitude¹¹, and of about a factor of 5 for the wire¹⁰ and bulk samples¹². A possible explanation for this has been advanced by Capone *et al.*¹¹ They observe that PbMo_6S_8 can undergo a partial phase transformation at low temperature to a phase which is not superconducting¹³. In this scheme, SnMo_6S_8 undergoes the same kind of transformation, but to a much lesser extent. Therefore, the doping of PbMo_6S_8 by tin would yield an alloy less sensitive to this superconducting-normal transition. On the other hand, the recent specific heat data of Decroux *et al.*⁶ do not support this hypothesis.

In seeking to understand the ensemble of these observations, it is thus clear that multiple issues must be considered simultaneously. The granularity issue, the nature of the flux pinning defects (whether at grain boundaries or in the intra-granular region), and the important general issue of the quality of samples used for study are frequently unclear. We therefore decided to study how a small PbMo_6S_8 or SnMo_6S_8 entity, with no grain boundary involved, behaves in terms of flux pinning and critical

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Figure 1: Magnetization of SnMo_6S_8 single crystal, 4 K.

current. Such an entity is a single crystal. The next step would then be to study a bi-crystal, and finally generalize to polycrystalline sample behavior.

Since tin appears to play an important role in the improvement of the J_c values, we decided, as a first step, to grow single crystals of SnMo_6S_8 , and to study their behavior in a magnetic field. This paper reports preliminary results on the electromagnetic properties of a SnMo_6S_8 single crystal. There is much structure to the magnetization which suggests a complex internal microstructure in the crystal.

Experimental details

The single crystal was grown by a technique previously reported¹⁴. About 2 g of a mixture of SnS , MoS_2 and Mo were placed in an alumina crucible. This ensemble was then put into a Mo container which was sealed in a 250 mbar Argon atmosphere. The nominal composition of the mixture was $\text{Sn}_{0.66}\text{Mo}_6\text{S}_6$. The container was then heated in a tungsten wire resistance furnace, in a 1.3×10^{-4} mbar vacuum. The sample was heated from 20°C to 1300°C in 40 minutes, then heated to 1600°C at a 5°C/minute rate, held at 1600°C for 5 minutes, cooled from 1600°C to 600°C at 1°C/minute, and finally furnace cooled to 20°C. The crystal, grown from the molten bath, was a $270 \times 270 \times 200 \mu\text{m}$ parallelepiped.

The magnetization was measured with a Princeton Applied Research Model 155 Vibrating Sample Magnetome-

ter (VSM), in a variable temperature insert. The sample was oriented in the magnetic field (within about 10°) with the smallest dimension parallel to the magnetic field. Data were taken in a swept field at a rate of about 10 mT/s, up to 11 T, and at various fixed temperatures, from 3.1 K to 7 K. The critical current was calculated using the expression $J_{cm} = 3\Delta M/l$, where ΔM is the width of the hysteresis loop and l the dimension perpendicular to the magnetic field (*i.e.* 270 μm).

Results

Magnetization measurements were made at 3.1, 4, 5, 6 and 7 K. Typical raw data for a 4 K trace are shown in Figure 1, where background effects due to normal state properties of the sample and/or sample holder are also present. However, to calculate the J_c we need to consider the magnetization hysteresis ($\Delta M(H)$) rather than the magnetization (M), and we can thus free ourselves from this artifact. The following discussion will therefore entirely deal with J_c . J_c was derived from M by computing $3\Delta M/l$ vs B , and then fitting the curves by a 10th order polynomial. The margin of error ($\delta(J_c)/J_c$) introduced by this process increases slightly with temperature and field. For 3.1, 4 and 5 K, $\delta(J_c)/J_c \sim 10\%$ for $B < 4$ and $\sim 15\%$ for higher fields. At 6 and 7 K, $\delta(J_c)/J_c \sim 20\%$ for $B < 4$ and $\sim 25\text{--}40\%$ for higher fields.

The J_c values are shown in Figure 2 as a function of both temperature and field. The general J_c -vs-field behavior is as follows — whatever the temperature, J_c first drops sharply with increasing field, but then unexpectedly increases when the field is further increased. After reaching a maximum, J_c then decreases again.

Discussion

The magnetization curves of Figure 2 emphasize that there is flux pinning within the single crystal of SnMo_6S_8 . The most striking feature of the pinning is the marked region over which the magnetization increases with increasing field. This is strongly reminiscent of the magnetization observed by Däumling *et al.*¹⁵ in single crystals of oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

In the case of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals, the double peak structure was ascribed both to the development of field-induced pinning centres and to an apparent field-induced granularity within the crystal. This latter observation was determined from the disappearance of size scaling within the crystal. Since we did not sub-divide this crystal, we have no information on whether it exhibits granularity.

Qualitatively speaking, the behavior of Figure 2 can be explained by the presence of a distribution of phases whose T_c and H_{c2} are lower than that of SnMo_6S_8 which acts as the continuous matrix. In general outline, the situation is that the crystal is wholly superconducting in zero field and as the field is increased the weakly superconducting phases are driven normal. As they are driven normal a

Figure 2: Magnetization critical current densities of SnMo_6S_8 single crystal at several temperatures.

strong δH_c elementary core pinning interaction can occur, thus driving up J_c . When all possible regions are normal, the J_c will decline for the usual reasons (*e.g.* the core pinning interaction should decline as $(1 - H/H_{c2})$). Thus the key feature is that the magnetic field increases the density of pinning centres and, over some finite field range, also increases the elementary pinning force f_p , as regions of weak superconductivity are driven normal. This model is that already discussed for oxygen-deficient regions in 123 crystals¹⁵ and in certain low T_c materials too¹⁶.

Figure 3 plots the position of the minimum in J_c as a function of temperature. Since the minimum represents the first detectable onset of normality, this can be used as a rough guide for the T_c of the phase. A linear extrapolation of the 4–7 K data in Figure 3 would suggest a T_c lying between 9 and 10 K (specific heat measurements are presently being carried out in order to confirm this).

Although it is speculative, the above discussion is consistent with what is known about defect structures in the Chevrel phases. For instance, the SnMo_6S_8 system can be sulfur deficient. Some S sites can also be occupied by some oxygen. It has been found that partial oxygen substitution can occur and this can affect the critical superconducting parameters of the sample^{17–19}. Particularly, T_c and H_{c2} are strongly affected by even small amounts of oxygen¹⁹. In our case, the low- H_{c2} regions could be formed by either a sulfur defect or oxygen contamination.

The maximum J_c values of the sample are on the order of $1.5 \times 10^8 \text{ A/m}^2$ at 4 K. We can compare these figures

Figure 3: Field at which J_c is minimum for SnMo_6S_8 single crystal as a function of temperature.

to the *transport* current densities of ribbon, wire and bulk samples — they are about a factor of 5 lower than in the SnMo_6S_8 wire and bulk samples^{9, 20}, and about a factor of 1.5 lower than in the SnMo_6S_8 ribbons¹¹. This is an expected result, since a single crystal is believed to have fewer defects (and therefore fewer pinning centres). These figures therefore suggest the potential of flux pinning both by intragrain defects as well as grain boundaries. On the other hand, these J_c values are about 6% of those observed by Cattani *et al.*⁷ for the intragranular contribution to the J_c of their cold powder pressed bulk sample.

Cattani *et al.* also suppose that the increase in J_c with field in their bulk sample is due to some screening artifact. Our result suggests rather that it is a real effect, coming from field-induced pinning. We indeed observe such behavior also in polycrystals.²¹

We emphasize that one of the main conclusions from our study is that even a single crystal has effective pinning sites. From the viewpoint of the A15 superconductors, the tendency has been to consider grain boundaries as the important pinning centres. Thus reducing the grain size (and reducing the sintering temperature) is the conclusion of such a viewpoint. But, as noted by Yamasaki *et al.*³, the grain size of optimized PbMo_6S_8 wires lies in the range of 0.1–0.3 μm , which is very comparable to Nb_3Sn wires having J_c values an order of magnitude or more larger. From the viewpoint of the oxides and, indeed optimized Nb-Ti too, the optimum J_c comes from

coherence length (ξ) or sub-coherence length defects²². Since ξ for SnMo_6S_8 is on the order of 3 nm, the defects described above may be the appropriate pinning sites.

Conclusions

In conclusion, therefore, we note that this study presented evidence for significant field-induced flux pinning within a single crystal of SnMo_6S_8 . We speculate that these pinning centres are atomic scale defects. Finally, we note that Cattani *et al.*⁷ have also observed a field-increasing intra-granular J_c in polycrystals of PbMo_6S_8 , although they suggested that the result might only be an artifact in the deconvolution process used to separate the inter- and intra-grain components of the J_c . The present results suggest that this was a real result.

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References

- [1] K. Hamasaki, Y. Shimizu, and K. Watanabe. *Adv. Cryo. Eng.*, **36A**, 335–341 (1990).
- [2] L. Le Lay, P. Rabiller, R. Chevrel, M. Sergent, T. Verhaege, J.-C. Vallier, and P. Genevey. *Adv. Cryo. Eng.*, **36A**, 329–334 (1990).
- [3] H. Yamasaki, T. C. Willis, D. C. Larbalestier, and Y. Kimura. *Adv. Cryo. Eng.*, **36A**, 343–351 (1990).
- [4] W. Goldacker, W. Specking, F. Weiss, G. Rimikis, and R. Flükiger. *Adv. Cryo. Eng.*, **36A**, 353–360 (1990).
- [5] Y. Kubo, K. Yoshizaki, F. Fujiwara, K. Noto, and K. Watanabe. *presented at MRS Symposium*, Ikebukuro, Japan, May 1988.
- [6] M. Decroux, D. Cattani, J. Cors, S. Ritter, and Ø. Fischer. *presented at LT19*, Brighton, UK, Aug. 1990.
- [7] D. Cattani, J. Cors, M. Decroux, and Ø. Fischer. *presented at LT19*, Brighton, UK, Aug. 1990.
- [8] J. Cors, D. Cattani, M. Decroux, and Ø. Fischer. *presented at LT19*, Brighton, UK, Aug. 1990.
- [9] L. Le Lay. Ph.D. thesis, Université de Rennes I, 1988.
- [10] W. Goldacker, E. Seibt, G. Rimikis, and R. Flükiger. *presented at ICMAS*, Grenoble, France, Oct. 1990.
- [11] D. W. Capone II, D. G. Hinks, and D. L. Brew. *J. Appl. Phys.*, **67**(6) (1989).
- [12] M.O. Rikel, T. Togonidze, and V. Tsebro. *Sov. Phys. Sol. State*, **28**(9), 1496–1499 (1986).
- [13] J. D. Jorgensen, D. G. Hinks, and G. Felcher. *Phys. Rev. B*, **35**(10), 5365–5368 (1988).
- [14] C. Rossel, E. Sandvold, M. Sergent, R. Chevrel, and M. Potel. *Physica C*, **165**, 233–240 (1990).
- [15] M. Däumling, J. S. Seuntjens, and D. C. Larbalestier. *Nature*, **346**, 332–335 (1990).
- [16] A. M. Campbell and J. E. Evetts. *Adv. Phys.*, **21**(90), 199–429 (1972).
- [17] D. W. Capone II, R. P. Guertin, S. Foner, D. G. Hinks, and H.-C. Li. *Phys. Rev. B*, **29**(11), 6375–6377 (1984).
- [18] D. G. Hinks, J. D. Jorgensen, and H.-C. Li. *Phys. Rev. Lett.*, **51**(20), 1911–1914 (1983).
- [19] S. Foner, E. J. McNiff Jr., and D. G. Hinks. *Phys. Rev. B*, **31**(9), 6108–6111 (1985).
- [20] M. Sergent, M. Hirrien, O. Peña, J. Padiou, R. Chevrel, M. Couach, P. Genevey, and P. Dubots. *Adv. Cryo. Eng.*, **34**, 663–668 (1988).
- [21] Crystals provided by P. Rabiller.
- [22] C. Meingast and D. C. Larbalestier. *J. Appl. Phys.*, **66**(12), 5971–5983 (1989).