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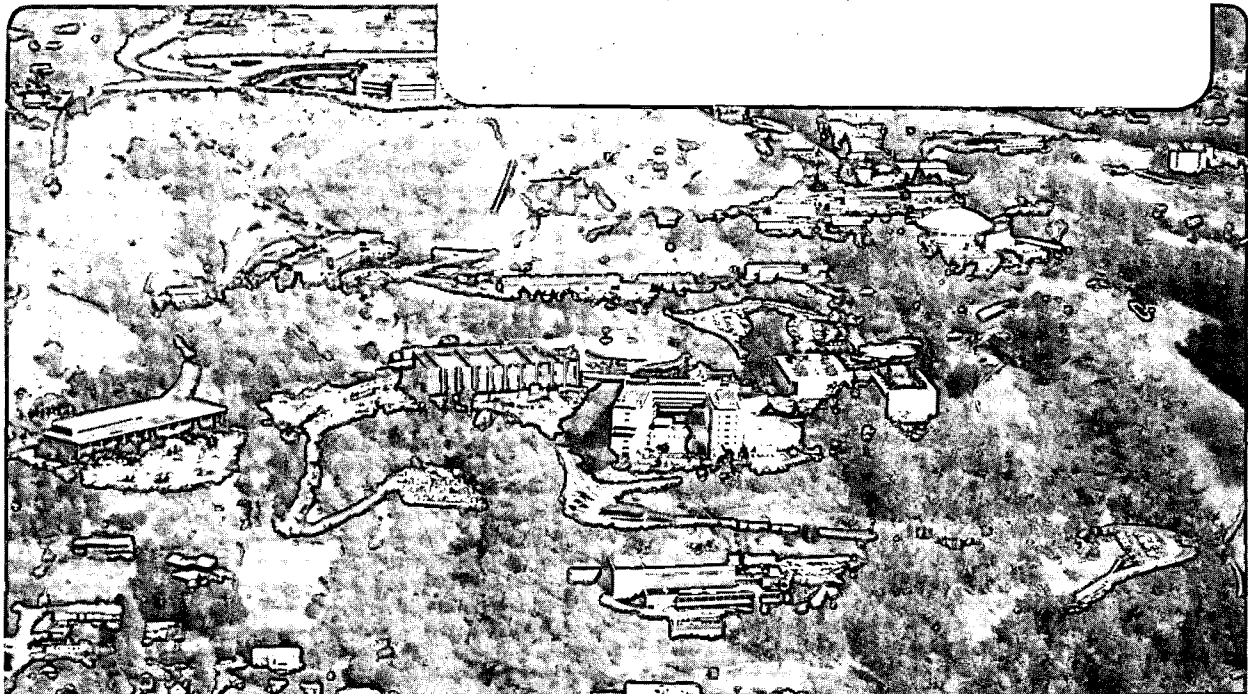
### High $T_c$ Superconductors: Will They Replace Helium Temperature Superconductors for Magnets?

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July 1988

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## HIGH $T_C$ SUPERCONDUCTORS: WILL THEY REPLACE HELIUM TEMPERATURE SUPERCONDUCTORS FOR MAGNETS?

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During the last two years,<sup>1</sup> the maximum zero resistance critical temperature for superconductors has risen from 23 K to temperatures above 120 K. This paper presents a sober view of the usefulness of the high  $T_C$  materials for generating magnetic fields in superconducting devices. The high  $T_C$  materials are compared to conventional niobium titanium superconductors in the following areas: critical current density, adiabatic and dynamic stability, normal region propagation velocity, burn out integral, energy per unit volume to quench and the maximum cryogenic stability current density. A look at the whole picture suggests that for most superconducting magnet applications, conventional conductors would be the superconductors of choice for magnets.

### THE PROPERTIES OF HIGH $T_C$ MATERIALS

The high  $T_C$  oxide superconductors are an extension of a group of superconductors known as the perovskite class of superconductors.<sup>2</sup> The discovery of a copper oxide perovskite-type superconductor with a  $T_C$  above 35 K is considered to be an important advance in solid-state physics and superconductivity. The high  $T_C$  superconductors are more complex than the true perovskite structure. The lanthanum-strontium ( $T_C = 40$  K) and the yttrium-barium ( $T_C = 93$  K) types of superconductors have a single copper oxide plane. The more recent five component superconductors have two or three copper oxide layers.<sup>3</sup> It appears that having more copper oxide layers means a higher  $T_C$  and perhaps better stability.

The five component high  $T_C$  superconductors can have zero resistivity critical temperatures as high as 125 K.<sup>4</sup> The  $YBa_2Cu_3O_{7-x}$  superconductors have a consistent zero resistance  $T_C$  of 93 K. Studies of this conductor suggest that this type of superconductor may have granules of superconductor with a  $T_C$  above 100 K.<sup>5</sup> These granules appear to be connected by resistive regions. The production of a high  $T_C$  superconductor that has zero resistance above 90 K requires that the superconductor be oxygenated during processing.<sup>6</sup>

The claims for high  $H_{C2}$  for the high  $T_C$  superconductor should be examined carefully. Many of the claims are based on measurements where the resistance begins to change or an apparent Meisner effect is seen. The only value of  $H_{C2}$  which really counts for magnets is when the resistivity is zero. The highest values of  $H_{C2}$  are found in single crystals with the magnetic field in a direction parallel to the plane of the copper oxide planes.<sup>7</sup> The  $J_C$  superconductor is also anisotropic. The  $J_C$  is two orders of magnitude higher in the direction perpendicular to the copper oxide planes in the superconductor than in a direction parallel to the copper oxide planes. At least one type of bulk sintered Y-Ba-Cu-O superconductor makes a sharp change in  $dH_{C2}/dT$  at about 60 K.<sup>8</sup> Based on the WHH theory,<sup>9</sup> the estimated  $T = 0$  value of  $B_{C2}$  for this conductor is about 60 T ( $B_{C2} = \mu_0 H_{C2}$ ).

Table 1 compares the properties of Nb-Ti and  $YBa_2Cu_3O_{7-x}$ .<sup>10,11</sup> The  $J_C$  for the high  $T_C$  superconductors has improved considerably since their discovery.<sup>12</sup> The melted cast Y-Ba-Cu-O conductor has higher values of  $J_C$  at

77 K than do the bulk sintered samples (particularly when a magnetic field is present). The thin film superconductors show the most promise for critical current densities which approach the values of conventional superconductors.

The high  $T_c$  superconductors are brittle ceramics, whereas niobium titanium is both strong and ductile. Niobium titanium can be codrawn in copper; the high  $T_c$  superconductor cannot be drawn into fine filaments. When one compares Nb-Ti with the high  $T_c$  superconductor, one should look at Nb<sub>3</sub>Sn or V<sub>3</sub>Ga as compared to Nb-Ti. Both Nb<sub>3</sub>Sn and V<sub>3</sub>Ga have very critical current densities (as high as  $10^5$  A mm<sup>-2</sup> at 2 T for V<sub>3</sub>Ga at 4.2 K),<sup>13</sup> but they are brittle. Both Nb<sub>3</sub>Sn and V<sub>3</sub>Ga can be made in fine filament form, yet for many uses one prefers to pay more for 1.8 K refrigeration and use Nb-Ti rather than use Nb<sub>3</sub>Sn or V<sub>3</sub>Ga at 4.2 K. The conductor brittleness and the difficulty of forming multifilamentary superconductor are the high  $T_c$  superconductors biggest detriments. At this time there is no usable form of the high  $T_c$  superconductor which can be used to make useful superconducting magnets.

Table 1. Properties of Nb-Ti and Y Ba<sub>2</sub> Cu<sub>3</sub> O<sub>7-x</sub> Superconductors

	Nb-Ti <sup>a</sup> T <sub>op</sub> = 4.2 K	Y-Ba-Cu-O T <sub>op</sub> = 77 K
Type of Material	Metal Alloy	Ceramic
Critical Temperature (K)	9.4	93
Density (kg m <sup>-3</sup> )	6700	6380 <sup>b</sup>
Specific Heat at T <sub>op</sub> (J m <sup>-3</sup> K <sup>-1</sup> )	5.76 x 10 <sup>3</sup>	1.0 x 10 <sup>6</sup>
Thermal Conductivity at T <sub>op</sub> (W m <sup>-1</sup> K <sup>-1</sup> )	0.275	~13
Thermal Contraction Coefficient at 300 K	~10 <sup>-5</sup>	1.3 x 10 <sup>-5</sup>
Total Thermal Contraction Coefficient 300 K - T <sub>op</sub>	~2.0 x 10 <sup>-3</sup>	~2.3 x 10 <sup>-3</sup>
Elastic Modulus at T <sub>op</sub> (G Pa)	83	90 - 110
Ultimate Strength at T <sub>op</sub> (M Pa)	~2200	Variable
Ductility	Ductile	Brittle

a For Nb-46.5 w% Ti.

b Void-free sample, typical sintered samples are lower than this value.

#### FACTORS WHICH AFFECT THE HIGH USE OF HIGH $T_c$ SUPERCONDUCTORS IN SUPERCONDUCTING MAGNETS

If one wants to assess the usefulness of high  $T_c$  superconductor in magnets, one should compare the superconductor with the same value of  $J_c$  (say 4000 A mm<sup>-2</sup>, which can be achieved in Nb-Ti at a field of 5 T and 4.2 K). One should also assume that the high  $T_c$  superconductor is in fine enough filaments so that adiabatic and dynamic stability is achieved. Table 2 compares the properties of liquid helium hydrogen and nitrogen which would be used to cool high  $T_c$  superconductor. Table 3 compares niobium titanium with high  $T_c$  superconductor. In Table 3 it is assumed that niobium titanium operates at 4.2 K (in liquid helium) and Y-Ba-Cu-O operates at 20.4 K (in liquid hydrogen) and at 77 K (in liquid nitrogen). Included in Table 3 are comparisons of adiabatic stability diameter, dynamic stability diameter, normal region propagation velocity along the conductor,

**Table 2. Properties of Three Liquid Gases That Can Be Used to Cool Superconductor**

	Helium	Hydrogen	Nitrogen
1 atm Boiling Temperature (K)	4.22	20.3	77.4
Critical Temperature (K)	5.19	33.3	126.1
1 atm Liquid Density (kg m <sup>-3</sup> )	125	70.8	811
1 atm Heat of Vaporization (Jg <sup>-1</sup> )	20.8	442 <sup>a</sup>	198
Gas Specific Heat (Jg <sup>-1</sup> K <sup>-1</sup> )	5.19	14.6	1.03
Available Refrigeration Liquid to 300 K (Jg <sup>-1</sup> )	1561	4629 <sup>b</sup>	431
Design Nucleate Boiling Heat Flux <sup>c</sup> (W m <sup>-2</sup> )	2500	30000	60000
Design Nucleate Boiling $\Delta T^c$ (K)	0.5	1.7	6.8

a para hydrogen

b includes the para to ortho transition energy

c about 30 percent of the maximum nucleate boiling heat flux

**Table 3. Properties of Niobium Titanium in Liquid Helium and a 93 K High T<sub>c</sub> Superconductor in Liquid Hydrogen and Liquid Nitrogen**

	Nb-Ti in Helium	High T <sub>c</sub> in Hydrogen	High T <sub>c</sub> in Nitrogen
Operating Temperature (K)	4.22	20.3	77.4
Critical Temperature (K)	9.35	~ 93	~ 93
Adiabatic Stability Diameter (μm) <sup>a</sup>	53.7	539	2156
Dynamic Stability Diameter (μm) <sup>a</sup>	56.0	1220	328
Longitudinal Quench Velocity (ms <sup>-1</sup> ) <sup>b,c</sup>	30.5	0.13	0.16
Ratio of Transverse to Longitudinal Quench Velocity RRR = 300 Cu Matrix	0.018	0.020	0.066
Burnout Integral J <sup>2</sup> d T RRR = 300 Cu Matrix Operating Temperature to 400 K (A <sup>2</sup> m <sup>-4</sup> s)	18.6 x 10 <sup>16</sup>	18.1 x 10 <sup>16</sup>	10.1 x 10 <sup>16</sup>
Enthalpy Change per Unit Volume to Quench without Cryogen <sup>c</sup> (Jm <sup>-3</sup> )	1.26 x 10 <sup>3</sup>	1.32 x 10 <sup>6</sup>	5.17 x 10 <sup>6</sup>
Enthalpy Change per Unit Volume to Quench with 10% Cryogen by Volume <sup>c</sup> (Jm <sup>-3</sup> )	5.73 x 10 <sup>4</sup>	2.31 x 10 <sup>6</sup>	5.18 x 10 <sup>6</sup>
Cryostability Matrix Current Density RRR = 300 Copper <sup>d</sup> (A mm <sup>-2</sup> )	72.2	242	56.2 <sup>e</sup>

a J<sub>c</sub> = 4000 A mm<sup>-2</sup> at low field, copper-to-superconductor ratio = 2

b Matrix J = 500 A mm<sup>-2</sup>

c At 85% of J<sub>c</sub> along the load line

d For a typical cryostable conductor in boiling liquid

e Maximum value based on a 6.8 K boiling temperature difference

the integral of  $j^2 dt$  needed to raise the conductor plus matrix temperature from the operating temperature to 400 K, the energy per unit volume needed to initiate a quench and the matrix current density in an RRR = 300 copper matrix in boiling cryogen at one-third of peak nucleate boiling flux.

From Table 3 it is clear that the high  $T_c$  superconductor is much more stable than niobium titanium at 4.2 K. With increased superconductor stability comes reduced normal region propagation velocity. The volume rate of normal region growth is five to seven orders of magnitude smaller for the high  $T_c$  material. Not only is the volume normal region propagation rate much smaller for the high  $T_c$  superconductor, but the margin of safety during a transition is smaller. As a result, the concept of cryostability<sup>16</sup> is much more important for high  $T_c$  superconductors than it is for niobium titanium.

Table 2 shows the properties of liquid helium, hydrogen and nitrogen at their 1 atm boiling points.<sup>17</sup> Included in Table 2 is the usable design nucleate boiling heat flux and the temperature difference between the surface and the fluid when heat is being transferred at the usable nucleate boiling heat flux. The cryostable current density given in Table 3 is based on the heat transfer rates shown in Table 2 and a heat transfer area which is 100 times larger than the conductor current carrying cross-section per meter of conductor length.<sup>17</sup> The copper RRR is 300, and the copper to superconductor ratio is large. From Table 3, cryostable operation of high  $T_c$  superconductor appears to be attractive in liquid hydrogen. Cryostable current densities in liquid nitrogen appear to be attractive except that the nucleate boiling temperature difference approaches 7 K. An increase of the superconductor  $T_c$  makes cryostable operation in liquid nitrogen more attractive.

#### HIGH $T_c$ SUPERCONDUCTOR AND ITS USE IN SPACE

High  $T_c$  superconductor has been proposed for use in space because, it is said, that low temperatures are easy to get in space. Unfortunately, temperatures below 200 K are difficult to achieve on the surface of the cryostat in low earth orbit. Superconducting magnets in space are high current density devices, because the reduction of coil and cryogenic system mass is essential. The cold mass of a high current density superconducting space magnet system is directly proportional to the energy stored in the magnetic field (for quench protection and stress reasons).<sup>18</sup> From Table 2, it is clear that the best coolant for space cooling is liquid or solid hydrogen. There is over 4600 J per gram (including the para to normal hydrogen transition energy) available to cool the magnet and the shields. The available refrigeration for helium is almost 1600 J  $g^{-1}$ , while the liquid nitrogen has only 430 J  $g^{-1}$ . Hydrogen, because of extreme flammability, presents safety problems which preclude its use on devices carried by manned space shuttles or on the space station. As a result, under today's safety rules, helium is the refrigerant of choice. Helium offers some additional advantages not found with either hydrogen or nitrogen. The second liquid phase, which exists below the lambda transition temperature of 2.17 K, can be circulated through a superconducting coil using a thermal mechanical pump with no moving parts. Helium II can be phase separated from the gas using a porous plug, and direct heat transfer to helium II can be very good if the coil cryogenic system is properly designed.<sup>19</sup>

In most situations, there is very little incentive to use anything but conventional superconducting materials in space. The mechanical properties of niobium titanium make it almost ideal to withstand the accelerations and vibrations during launch as well as the magnetic forces.

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## REFERENCES

- 1) J. G. Bednorz and K. A. Muller, *Z Phys. B* 64, p. 189, 1986.
- 2) Theodore Geballe, from a talk given at the Lawrence Berkeley Laboratory, May 1987.
- 3) M.A. Subramanian et al., *Science* 239, p. 1015, 1988.
- 4) C. C. Torardi et al., *Science* 240, 631, 1988.
- 5) X. Cai et al., *Phys. Rev. Lett.*, 29 June 1987.
- 6) A. L. Robinson, *Science* 236, p. 1063, 1987.
- 7) J. W. Ekin, private communication on the behavior of single crystal high  $T_c$  superconductor.
- 8) K. Noto et al., *Advances in Cryogenic Engineering* 34, Plenum Press, p. 925, 1988.
- 9) N. R. Werthamer, E. Helfand and P. C. Hohenberg, *Phys. Rev.* 147, p. 295, 1966.
- 10) D. S. Easton and C. C. Koch, *Advances in Cryogenic Engineering* 22, Plenum Press, New York, p. 453, 1976.
- 11) H. M. Ledbetter, "Elastic Constants of Y-Ba Cu-O Superconductors", to be published in the proceedings of the MRS International Meeting on Advanced Materials (Tokyo, May-June 1988).
- 12) T. H. Geballe and J. K. Hulm, *Science* 239, p. 367, 1988.
- 13) M. N. Wilson, *Superconducting Magnets*, Clarendon Press, Oxford, UK, 1983.
- 14) M. A. Green, "High  $T_c$  Superconductor and Its Use in Superconducting Magnets", LBL-23946, February 1988.
- 15) E. W. Collings, "Flux Jump Stability and Cryogenic Stability for Superconductor for 80 K", to be published in the proceedings of the MRS International Meeting on Advanced Materials (Tokyo, May-June 1988).
- 16) Z. J. J. Steckly and Z. L. Zar, *IEEE Transactions on Nuclear Science* NS-12, No. 3, p. 367, 1965.
- 17) E. G. Birentari and R. V. Smith, *Advances in Cryogenic Engineering* 10, p. 325, Plenum Press, New York, 1964.
- 18) Interim Report of the ASTROMAG Definition Team on the Particle Astrophysics Magnet Facility, ASTROMAG, NASA-GSFC, 1986.
- 19) M. A. Green and S. Castles, *Advances in Cryogenic Engineering* 33, p. 631, Plenum Press, New York, 1987.



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