

# Challenges of Unconventional Superconductors

J. Jeyabuvaneswari

Department of Physics

CK College of Engineering & Technology, Cuddalpre, Tamilnadu, India

**Abstract**— Since the discovery of high- $T_c$  cuprates, the quest for new superconductors has shifted toward more anisotropic, strongly correlated materials with lower carrier densities and competing magnetic and charge-density wave orders. Although these materials' features enhance superconducting correlations, they also result in serious problems for applications at liquid nitrogen (and higher) temperatures and strong magnetic fields so that such conventional characteristics as the critical temperature  $T_c$  and the upper critical field  $H_{c2}$  are no longer the main parameters of merit. This happens because of strong fluctuations of the order parameter, thermally activated hopping of pinned vortices, and electromagnetic granularity, as has been established after extensive investigations of cuprates and Fe-based superconductors (FBSs). In this paper, I give an overview of those mechanisms crucial for power and magnet applications and discuss the materials' restrictions that must be satisfied to make superconductors useful at high temperatures and magnetic fields. These restrictions become more and more essential at higher temperatures and magnetic fields, particularly for the yet-to be discovered superconductors operating at room temperatures. In this case, the performance of superconductors is limited by destructive fluctuations of the order parameter so that higher superfluid density and weaker electronic anisotropy, which reduce these fluctuations, can become far more important than higher  $T_c$ .

**Keywords:** high-temperature superconductivity, critical temperature, anisotropy, superfluid density, fluctuations, competing orders, vortices, critical current density, irreversibility field, grain boundaries

## I. INTRODUCTION

Making predictions in superconductivity, particularly for new materials or the material requirements for applications of existing or putative room-temperature superconductors (RTSs), has never been rewarding, reflecting the experimental fact that "doing the opposite" has often worked better than following the conventional wisdom and established models (1, 2). However, the important lessons of unprecedented research and development of unconventional superconductors in the past 20–30 years have changed the perception of what is important for applications at high temperatures and magnetic fields. In this paper, I discuss some of the lessons that may be helpful in the ongoing quest for new superconductors.

Incidentally, the trend of optimistic predictions was started by Kamerlingh Onnes, the discoverer of superconductivity, who was the first to recognize the advantages of superconducting magnets as the only enabling technology capable of generating the DC magnetic field of 10 tesla, which could not be achieved by resistive magnets. However, this idea had to be put aside for a long time because all type-I superconductors known before 1930–1940 went to the normal state at low magnetic fields ( $H < 0.2$  tesla) limited by the thermodynamic critical fields ( $H_c$ ) of these materials.

The fulfillment of Onnes's vision took nearly 50 years and many scientific and technological breakthroughs, including the discoveries of the Meissner effect and type-II superconductors as well as the development of the London, Ginzburg-Landau (GL), and Bardeen-Cooper-Schrieffer (BCS) theories, which showed that superconductivity is a phase-coherent condensate of Cooper pairs glued by phonons. These advances eventually led to the Abrikosov theory of a lattice of quantized vortices, which explained how type-II superconductors are able to withstand high magnetic fields up to  $H_{c2}$ . It was then realized that the upper critical field  $H_{c2}$ , above which the type-II superconductivity disappears, can be significantly increased by alloying the material with nonmagnetic impurities.

By 1986, many type-II superconductors, such as NbZr, NbTi, A-15 compounds (Nb<sub>3</sub>Sn, V<sub>3</sub>Si, etc.), and Chevrel phases (PbMo<sub>6</sub>S<sub>8</sub>), with  $H_{c2}$  ' 10–60 tesla and  $T_c$  ' 9–23 K had been discovered, and NbTi and Nb<sub>3</sub>Sn became the materials of choice for superconducting magnets and medical MRI machines. All these materials are conventional superconductors with the s-wave symmetry of the Cooper pairs described by the Eliashberg theory, which generalized the BCS model by taking into account strong electron-phonon interaction. At that time, the superconducting critical temperature  $T_c$  and the upper critical field  $H_{c2}$  were regarded as the main parameters of merit for magnet applications at the liquid helium temperature 4.2 K. Making superconductors useful involved incorporation of structural defects in a material to pin vortices and prevent their dissipative motion under the action of flowing current, which otherwise caused electric resistance below  $H_{c2}$  and  $T_c$ . Because stronger pinning allows a superconductor to carry larger nondissipative critical current density  $J_c(T, H)$  at high magnetic fields, materials optimization involved incorporating as many extended materials defects and impurities as possible to maximize  $J_c$  and  $H_{c2}$  without significant degradation of  $T_c$ . Finally, composite wires were produced by embedding thin superconducting filaments into a flexible metallic matrix to provide thermal quench stability, low AC losses, and good mechanical properties. This approach works for most conventional superconductors, including NbTi ( $T_c$  ¼ 9 K) and Nb<sub>3</sub>Sn ( $T_c$  ¼ 18 K). More recently, alloying the two-band BCS superconductor MgB<sub>2</sub> has increased  $H_{c2}(0)$  from 3–5 tesla to 40–70 tesla, resulting in the development of magnet conductors.

The success of this approach is based on two fundamental features of conventional superconductors in which the symmetry of the order parameter is not lower than the symmetry of the Fermi surface. First, the coherence length  $\xi_0 \approx \xi_F = 2\pi k_B T_c$ , which quantifies the size of Cooper pairs, is much greater than the mean electron spacing  $r_s$ . In a good metal with a large Fermi velocity ( $v_F$ ), it is the strong overlap of Cooper pairs that provides the superconducting phase coherence and weak sensitivity of  $T_c$  to nonmagnetic

impurities and extended crystalline defects, such as dislocations and grain boundaries (GBs). Another important feature is that fluctuations of the order parameter are negligible because of the smallness of the Ginzburg parameter  $G_i \propto \frac{1}{2} \frac{\hbar c}{k_B T_c} = \frac{\hbar c}{2k_B T_c} \propto \frac{1}{T_c}$  proportional to the squared ratio of the thermal energy  $k_B T_c$  to the condensation energy  $\frac{1}{2} \mu_0 H_c^2 = 8\pi n_s \Phi_0^2 / 4\pi \lambda^2$  in the volume occupied by the Cooper pair (24). Here,  $\lambda$  is the in-plane coherence length,  $\lambda_c$  is the coherence length along the c-axis, and the anisotropy parameter  $g = (\lambda_c/\lambda)^2$  is defined by the ratio of effective masses along the c-axis ( $m_c$ ) and in the a-b plane ( $m$ ) in a uniaxial superconductor (25, 26). In conventional superconductors,  $G_i$  varies from  $\sim 10$  for Nb ( $T_c = 9.2$  K) to  $\sim 4$  for a two-band MgB<sub>2</sub> with  $T_c = 40$  K. The materials parameters that control  $G_i$  become more transparent if  $\frac{1}{2} \mu_0 H_c^2$  is expressed in terms of the magnetic London penetration depth  $\lambda = \sqrt{m c^2 / 4\pi n_s e^2}$  in the clean, single-band limit, where  $n_s$  is the superfluid density equal to the carrier density at  $T = 0$ , and  $\Phi_0 = \frac{h c}{2e}$  is the flux quantum superconductors with small (nanoscale)  $\lambda$ , non s-wave pairing, and strong vortex fluctuations in quasi-one dimensional or layered materials. These features, first regarded as exotic and not relevant to practical conductors, were eventually recognized as being among the key issues for applications at 77 K after the groundbreaking discovery of high- $T_c$  cuprates (33). The initial enthusiasm surrounding the vision for powerful high-field magnets, motors, generators, and transmission lines working at liquid nitrogen temperatures (77 K) was based on a belief that the high  $T_c$  of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> ( $T_c = 92$  K) and (Bi,Pb)<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> ( $T_c = 110$  K) would somehow assure high field conductors.

## II. PROBLEMS WITH STRONGLY CORRELATED LAYERED MATERIALS

The field dependence of  $J_c(T, H)$  is of major importance for magnet applications. The value  $J_c(4.2$  K, 5 T)  $\approx 0.5$  MA/cm<sup>2</sup> is characteristic of Nb<sub>47</sub>wt%Ti alloys with  $T_c = 9$  K and  $H_{c2}(4.2$  K)  $\approx 12$  tesla used in magnets (19). Many superconductors have  $H_{c2}$  much higher than  $H_{c2}(0) \approx 15$  tesla of NbTi because they have shorter  $\lambda$  and can sustain stronger fields up to  $H_{c2}(0) \approx 2\mu_0 j_0$ , at which the spacing between vortices  $(\Phi_0/H)^{1/2}$  becomes of the order of the diameter of nonsuperconducting vortex cores  $\approx 2\lambda$ . Very high values of  $H_{c2}$ s found in the cuprates and FBSs result from their small  $\lambda$   $\propto \sqrt{\hbar c / 2\mu_0 k_B T_c}$ , either because of high  $T_c = 90$ –130 K in cuprates or smaller  $\nu F$  in semimetallic FBSs. The values of  $H_{c2}(0) > 100$  tesla extrapolated from low-field measurements near  $T_c$  often exceed the BCS paramagnetic limit  $H_p$  at which the Zeeman energy equals the binding energy of Cooper pairs with antiparallel spins,  $H_p[\text{tesla}] \approx 1.84 T_c[\text{K}]$  (43, 44). Figure 1 shows  $H_{c2}(T)$  and  $H(T)$  for some low- $T_c$  superconductors, cuprates, and FBSs.

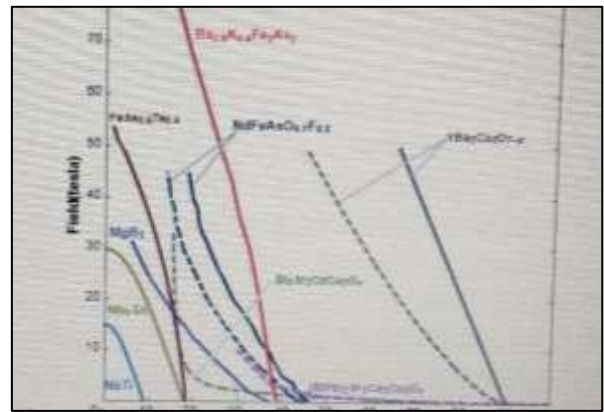


Fig. 1:

Comparative H-T phase diagram for representative cuprates, Fe-based superconductors (FBS), and conventional superconductors, where the solid and dashed lines show, respectively,  $H_{c2}(T)$  and  $H(T)$  parallel to the c-axis. In the range of fields  $5 \text{ tesla} < H < 70 \text{ tesla}$ , which can be generated by superconducting magnets, the  $H_{c2}(T)$  curves for most FBS with  $T_c > 20$  K are clustered between  $H(T)$  of the layered Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub> and  $H(T)$  for the least anisotropic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>. Here  $H(T)$  for the layered Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>x</sub> ( $T_c = 75$  K) and Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> ( $T_c = 108$  K) are much smaller than their respective  $H_{c2}(T)$ , which have slopes  $dH_{c2}/dT \approx 2 \text{ tesla/K}$  at  $T_c$  (not shown here). The difference between  $H$  and  $H_{c2}$  for NdFeAsO<sub>0.7</sub>F<sub>0.3</sub> at 20–30 K is smaller than the difference between  $H$  and  $H_{c2}$  for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> at 77 K, which reflects the diminishing role of vortex fluctuations at lower  $T$ . The less anisotropic Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub> with  $1 < g(T) < 2$  and  $T_c = 38$  K has a higher  $dH_{c2}/dT$  than NdFeAsO<sub>0.7</sub>F<sub>0.3</sub> with  $g(T) = 4.8$  and  $T_c = 42$  K (44), so the Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub> polycrystalline conductors that also exhibit a weaker grain boundary problem (93) could be superior at 20 K. The data are reproduced from Reference 70, with the addition of recent  $H_{c2}$  data for FeSe<sub>0.5</sub>Te<sub>0.5</sub> and Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub> Ni alloy sub

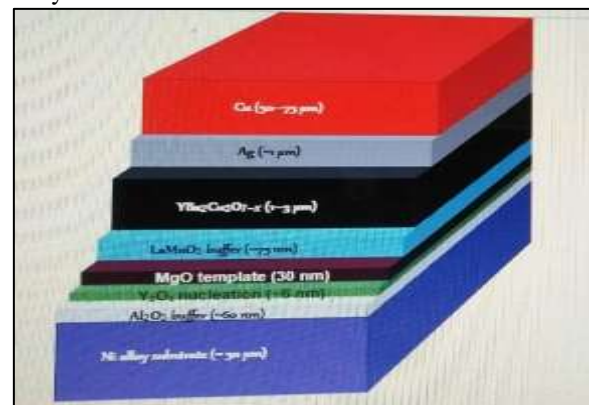


Fig. 2:

A typical architecture of a coated conductor made by ion beam-assisted deposition (53). The YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> film is grown on a textured Ni-alloyed substrate with a complex buffer layer structure, which enables replication of the low-angle grain structure of the substrate in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> film and protects that film from chemical contamination. The stabilizing layers of Ag and Cu on top of the 1–2 mm thick YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> film provide thermal quench protection

of the tape, which is usually a few millimeters wide and 0.1–0.2 mm thick. The current-carrying superconducting film takes 1%–2% of the conductor cross-section, which strongly reduces its averaged current density. Reproduced from

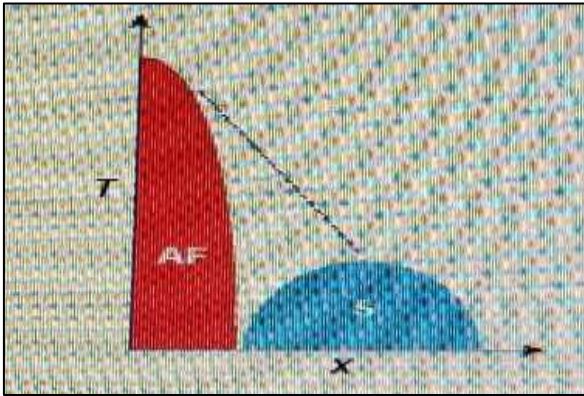


Fig. 3:

Generic phase diagram of unconventional superconductivity emerging due to doping an antiferromagnetic parent state. Here,  $T$  is temperature, and  $x$  can be proportional to either hole concentration or electron concentration, or to other external factors, such as pressure. The dashed line depicts the temperature at which a pseudogap separating Fermi-liquid from non-Fermi liquid behavior forms. AF and S refer to antiferromagnetic and superconducting states, respectively.

### III. CONCLUSION & OUTLOOK

The development of high- $T_c$  cuprates and FBSs has resulted in the evolution of parameters of merits for applications at high temperatures and magnetic fields, from the pairing-limited  $T_p$  and  $H_{c2}$  to the parameters mostly controlled by thermal fluctuations and transparency of GBs. This shift of perception reflects the recognition of the importance of thermal fluctuation of vortices at high  $T$  and  $H$  in layered, strongly correlated superconductors. Those unconventional superconductors with low Fermi energies, non-phonon pairing, and competing AF orders can have  $T_c$  up to 132 K for cuprates and up to 56 K for FBSs, and very high  $H_{c2}(0) > 100$  tesla. However, making these materials useful for power or magnet applications at 30–77 K requires a lot of innovative materials tuning and expensive technological compromises.

For instance, the coated conductor shown in Figure 2 utilizes only a few percent of the current-carrying cross-section, so  $J_c$  of the superconducting film must be pushed to the limit by incorporating dense arrays of nanoprecipitates spaced by  $\sim 10$  nm. This does increase  $J_c$  at low  $T$  and  $H$  but not necessarily  $H$  at 77 K or higher temperatures. Indeed, because of low vortex line tension  $\epsilon l(T) \sim 1$ –10 K/nm, vortex segments of length  $\sim kBTg/\epsilon_0 \sim 10$ –100 nm can hop and reconnect at neighboring pins. In turn, low energy barriers  $U_b \sim p\epsilon_0 g l \sim kBT$  for cutting and reconnection of soft vortex segments (26) between nanoprecipitates cause giant thermally activated flux creep and electrical resistance at  $J < J_c$ , no matter how strong pinning may be. Thus, the bad combination of low  $\epsilon l(T)$  and weak-linked GBs makes it hard to develop competitive conductors for high field applications

at  $T > 77$  K, using superconductors in which  $\epsilon l(T)$  is lower than  $\epsilon l$  for  $YBa_2Cu_3O_{7-x}$ .

As far as the search for new materials is concerned, mechanisms that provide high pairing temperatures may not necessarily result in RTSs that can actually be used at 300 K. In fact, it may be beneficial to explore new materials means of reducing fluctuations in cuprates or FBSs by, for example, reducing the electronic anisotropy with chemical substitutions, using contact with normal metals (130), or managing optimal inhomogeneities at the nanoscale (131). Certainly, searching for new materials with higher superfluid density and lower anisotropy than in cuprates or FBSs, even at the expense of lower  $T_c$ , could be very fruitful, as the success of MgB<sub>2</sub> has shown. Curiously, a viable RTS may have to satisfy one of the Matthias criteria (cubic symmetry is best) but not the one that requires peaks in the density of states that would increase  $m$  and  $l_0$ . The following temperature regions for applications of different materials can be identified:

### REFERENCES

- [1] Allen PB, Dynes RC. 1975. Phys. Rev. B 12:905–22
- [2] Carbotte JP. 1990. Rev. Mod. Phys. 62:1027–57
- [3] Campbell AM, Evetts JE. 1972. Adv. Phys. 21:194–428
- [4] Wilson M. 1983. Superconducting Magnets. Oxford: Clarendon
- [5] Gurevich A, Patnaik S, Braccini V, Kim KH, Mielke C, et al. 2004. Supercond. Sci. Technol. 17:278–86
- [6] Wilke RTH, Bud'ko SL, Canfield PC, Finnemore DK, Suplinskas RJ, Hannahs ST. 2004. Phys. Rev. Lett. 92:217003
- [7] Braccini V, Gurevich A, Giencke JE, Jewell MC, Eom C-B, et al. 2005. Phys. Rev. B 71:012504
- [8] Flükiger R, Kumakura H. 2012. See Ref. 134, pp. 702–10
- [9] Larkin AI, Varlamov AA. 2007. Fluctuations in Superconductors. Oxford: Clarendon Press
- [10] Blatter G, Feigelman MV, Geshkenbein VB, Larkin AI, Vinokur VV. 1994. Rev. Mod. Phys. 66:1125–388
- [11] Brandt EH. 1995. Rep. Prog. Phys. 58:1465–594
- [12] Tinkham M. 2004. Introduction to Superconductivity. New York: McGraw-Hill. 2nd ed.
- [13] Fischer O. 1978. Appl. Phys. (Berl.) 16:1–28
- [14] Stewart GR. 1984. Rev. Mod. Phys. 56:755–87
- [15] Steglich F. 2012. See Ref. 134, pp. 283–87
- [16] Jerome D, Schulz HJ. 2002. Adv. Phys. 51:293–479