

### **Note Added 19 April 2010**

It has been some 21 years since I published this review. 2011 will see the 25th anniversary of the discovery of the copper oxide family of high temperature superconductors, and the centennial of the discovery of superconductivity itself in 1911. I will be planning a reprise of this paper early next year. However, in its present form as published, it remains remarkably prescient (forgive the immodesty). For example:

1. Although several relatively higher-than-20 K superconducting materials have been discovered the last two decades (e.g., MgB<sub>2</sub>, doped fullerenes and the iron pnictides), their T<sub>c</sub>'s come nowhere near the uppermost range (125 - 135 K, 165 K under pressure) exhibited by the layered copper oxide perovskites (sometimes referred to erroneously as cuprates).

2. Despite more than two decades of intense focus by the international condensed matter theory community, the origin of high-T<sub>c</sub> in the "cuprates" remains as mysterious as ever. There is no generally agreed upon picture, either descriptive or quantitative, as yet. About as good as it has gotten is that superconductivity in these materials is:

a: BCS-like in that pairing and an associated gap (d-wave symmetry, although that is still being questioned) exists.

b: That somehow spin is involved, giving rise to pairing through "Hubbard interactions," or "spin wave" fluctuations, and possibly electron-lattice instabilities arising from removal of the highly Jahn-Teller degenerate state of the Cu-O bond.

3. Despite impressive progress in improving the "Type II" material properties of the HTSC cuprates, none of the vast array of applications, either electronic or power, forecast during the halcyon first four years have come to pass, nor are likely to for many years to come, at least massively in the market sense, primarily due to continuing improvement in underlying "conventional" technologies. As the French might say, "Plus ça change, plus ça change."

-PMG

# High-Temperature Superconductivity: Four Years Since Bednorz and Müller\*\*

Thin Films  
Patents, Theory and  
Experiment  
1-2-3 Superconductors  
Applications  
Mechanisms

## 1. Introduction

It is now four years since *Bednorz* and *Müller* performed the work which resulted in the appearance of their historic paper,<sup>[1]</sup> published in the September, 1986 issue of that venerable German scientific journal, *Zeitschrift für Physik*, announcing the discovery of high-temperature superconductivity in copper oxide perovskites. This work presaged the most intense period of worldwide research on any subject whatsoever since modern physics began with *Galileo*, a trend which has continued and increased up to the present. It was potentially rivaled only by the recent brief, albeit intense, flurry of attention given the, what now appears to have been premature, announcement of the discovery of cold nuclear fusion.<sup>[2]</sup> Some idea of the depth of activity now being undertaken is given in Table 1. More than 1200 institutions (academic, industrial and government) worldwide are carrying out some sort of full-time program in high- $T_c$  superconductivity. These range from small companies supplying educational kits and materials to major corporations and government labs, many with no previous involvement in superconductivity.

The Government in the United States was remarkably quick to respond to the commercial possibilities offered by high-temperature superconductivity. The summer of 1987 witnessed a national conference, organized under the aegis of the Presidential Science Advisor, whose keynote speaker was none other than President *Reagan* himself. The President called for redirection of federal research funding into both basic and applied areas of high- $T_c$  work, liberalization of patent guidelines involving composition-of-matter inventions, relaxation of anti-trust restrictions on industrial coop-

eration in order to aid the rapid commercial development of the discoveries, the start-up of core technology projects (e.g., high- $T_c$  wires and films) at several national laboratories, and the formation of a committee of "Wise Men" to advise the White House and Congress on means to assure successful participation by American private enterprise in the commercial exploitation of high-temperature superconductivity. One of the first actions taken by this committee was to recommend that the private sector, academia and government take a joint, voluntary initiative in organizing "consortia" between industrial, university and national laboratories with the purpose of focusing on potential applications in the hope of shortening the development cycle preceding their manufacture and marketing. The first such consortium, just recently announced, involves an agreement between IBM, AT & T, MIT and Lincoln Laboratory for joint efforts in the development of superconducting electronic devices. In addition to these federal initiatives, several state governments, notably Texas, New York, Massachusetts and Maryland, have established centers for superconductivity research attached to their state university systems.

In Western Europe, members of the Common Market have taken various approaches to organizing high- $T_c$  activities in their respective countries. In the UK, a national center has been established at Cambridge following extensive internal debate on site selection; however, it is still in the process of consolidation and most British high- $T_c$  research at present is coming from Birmingham and the Rutherford-Appleton Laboratory. In France, where much of the solid state chemistry underlying copper oxide perovskites, the materials later investigated by *Bednorz* and *Müller*, was laid down in the late 70's and early 80's, present high- $T_c$  research revolves around a Caen-Grenoble axis with a strong effort also at Orsay, the traditional center of French condensed matter physics. In contrast to Britain and France, and similar to the US, high- $T_c$  activity in West Germany appears more decentralized involving healthy interdisciplinary collaboration between the Max Planck Institute (MPI) in Stuttgart, Karlsruhe, Jülich and other German institutions with a history of low- $T_c$  research. Throughout Western Europe in general, each nation has its own appropriate level of ongoing high- $T_c$  program carried out within local universities; however, at least to date, there seems little evidence of a coordinated effort throughout the EEC as a whole, either presently or planned in anticipation of economic unification in 1992.

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[\*\*] This review is an extension of an invited talk delivered in January, 1989, to the 10th Low Temperature Physics Conference held in Cocoyoc, México, organized under the auspices of the Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México. I would like to thank the organizers for the opportunity to begin this review and for their hospitality during the conference, and my friends and colleagues in México, as well as those at the IBM Almaden Research Center, especially *E. M. Engler*, for numerous helpful discussions on the topics covered herein. I also want to thank *Jim Russel*, *Ellen Feinberg* and *Paul Berdahl* for providing the data contained in Table 1, and the IBM Science Center, Winchester, UK, for generating the computer graphics necessary for Figures 1-6.



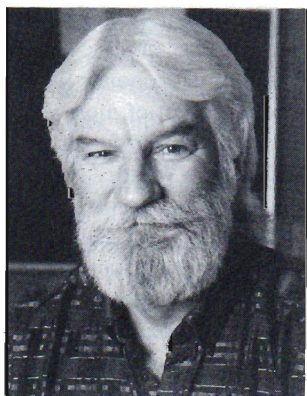
As in the West, each of the Eastern Bloc countries also has a program, with the Soviet Union possessing by far the largest. Although rather late getting started, the USSR has a long tradition in superconductivity, especially theory, to build on and is now conducting research on a large scale. As a result of perestroika and glasnost, Soviet presence and participation at recent high- $T_c$  conferences has been impressive. For those of us accustomed to past rare appearances of Soviet scientists at meetings in the US, the large number ( $>20$ ) in attendance at the recent HTSC-M<sup>2</sup> at Stanford<sup>[3]</sup> was remarkable and enjoyable. Hopefully their participation will continue at these high levels in the future.

The Japanese have had for many years a strong presence in conventional superconductivity, both in basic research and application development. Workers at the University of Tokyo were the first to independently<sup>[4]</sup> verify the findings of Bednorz and Müller. Their propensity to organize research and development programs in scientific areas at a national level is well known, and high- $T_c$  is no exception. Although Table 1 may indicate the number of Japanese institutions currently involved to be a small fraction of the total, a closer examination shows a significantly larger number of people on average at each location than is true for other countries. Also, at their industrial laboratories, the programs strongly emphasize thin film research, the technology with the greatest probability of short-term application. Partially in response to criticism that participation in Japanese research programs has in the past been closed to outsiders, a new institution dedicated entirely to superconductivity, the International Superconductivity Technology Center (ISTEC), was created as an innovative attempt to promote collaborative technologically-oriented research by otherwise extremely competitive institutions on an international scale, and is already in operation. Needless to say, it will be interesting to see how well this technical, organizational and sociological experiment proceeds.

An intriguing and encouraging phenomenon has been the flowering of high- $T_c$  research in the Third World. Some nations, such as India, which, like France, had a firm tradition of research in the solid state chemistry of transition metal oxides, and the People's Republic of China, with a long-

standing superconductivity program at the Institute of Physics, Beijing, were participating and contributing as early as January, 1987. The more recent programs in other emerging countries have been, in part, engendered by the rather low level of materials technology required to initiate a research effort in high-temperature superconductivity, and also encouragement from respective governments hoping to reap economic benefit and development from ensuing applications. In Mexico, over one million US \$ has been appropriated to upgrade condensed matter experimental facilities at the National University, and to initiate small programs in the application of high- $T_c$  technology. Similar activities are underway in Argentina, Brazil and Venezuela. During a recent visit to Cuba, I found a vigorous program in place, co-sponsored by the University of Havana and IMRE, a government organization set up to promote technology transfer from the University to Cuban industry.<sup>[5]</sup> Although it is unlikely that the Third World will be able to compete effectively with the industrialized nations in commercializing high- $T_c$  applications, the experience obtained by experimenting with small scale technology programs will give them the wisdom to make better decisions on the eventual use of these applications within their own societies. But what is probably more important, even if the economic payoffs currently envisioned for high- $T_c$  materials do not actually accrue, not even in the First World, the modernization of their experimental plant by an investment in high- $T_c$  research will assure these countries a more effective and broader-based participation in worldwide basic condensed matter physics and materials research than was previously possible.

It is tempting to speculate on the current resource and funding allocated worldwide to high- $T_c$  research and development. US Federal funding for superconductivity is expected to reach nearly 220 million US \$ in the fiscal year 1990. At this point, it would be difficult and unrealistic to attempt any wider assessment. However, given the international focus just described, it would seem reasonable to assume that, with respect to the inorganic material sciences as a whole, high- $T_c$  science is second, albeit distantly, only to semiconductor science and technology, and is growing faster. Time will tell whether this trend will continue.



*Paul M. Grant received a B. S. degree in electrical engineering from Clarkson University in 1960 followed by a Ph. D. in physics from Harvard University in 1965. Later in the same year, he joined the IBM San Jose Research Laboratory as a Research Staff Member. Since then, Dr. Grant has conducted research primarily in the field of organic superconductors periodically holding several technical staff positions to senior management in the IBM Research Division. In late 1986 he became involved in high-temperature superconductivity and organized the team at the Almaden Research Center which identified the structure and the optimal processing conditions for the 90 K family of 1-2-3 superconductors. His current interests are the study of the relationship between structure and electronic properties of the perovskite family of high- $T_c$  compounds.*



As part of the attention given the apparent prospects for massive revenues from commercialization of high- $T_c$  technology the press, especially in the US, has focused on the "race for patents" between US and foreign, especially Japanese, institutions. Much has been made of the large number of filings entered by Japanese concerns; however, most of these do not seek broad coverage, an action consistent with their tradition of applying for many narrow patents in a given technology. The press has also reported on the current interference proceedings underway to resolve issues between AT & T, IBM, the University of Houston and the Naval Research Laboratory concerning the basic materials and processing patent covering the 90 K material "1-2-3". It was also recently reported that IBM has obtained the first high- $T_c$  materials and processing patent to be issued in the United States.<sup>[6]</sup> This patent grants rather limited coverage of the thallium-based high- $T_c$  compounds, in particular the 125 K phase. It is important to be aware of a number of factors when assessing press reports of various patent activity in high- $T_c$  work. First of all, several popular misconceptions exist about the value and use of patents. The original intention of the patent statutes in most countries was to grant the inventor a temporary monopoly in return for a public disclosure of his invention or process. This is not usually the primary purpose of large technology-based corporations in building a patent portfolio. Most high-tech firms worldwide are extensively cross-licensed with each other, and the rationale for obtaining materials and processing patents is to gain and maintain an attractive portfolio within the industry for trading purposes and also to preserve freedom of action to exploit a broad range of technologies, rather than protect just a single area. Thus, corporate patent strategies are essentially defensive in nature. Seldom these days is a successful company built on a single patent which it uses to gain market dominance. Now it is far more important for a company to be able to manufacture its products with the highest quality and greatest performance in the largest number at the lowest cost. The ability to accomplish this most often has little direct connection to the number of its patents. On the other hand, patents are frequently very valuable to universities which see them as a source of revenue. Universities naturally have no need to cross-license and tend to seek and exploit their patents in the more traditional way.

Table 1 also shows the enormous publication activity in progress as a result of this large body of work throughout the world. At least five new journals have appeared, dedicated to superconductivity, and numerous other established publications have initiated special sections on the subject, along with several commercial<sup>[7]</sup> and non-profit high- $T_c$  newsletters, an example of the latter being the excellent High- $T_c$  Update. Moreover, the proliferation of personal computers running powerful scientific text/graphics processing programs, electronic mail networks, relatively inexpensive worldwide telecommunications facilities and facsimile machines has enabled many individuals and institutions to become instant "desktop publishers," printing and distributing the results of

Table 1. Summary of worldwide high- $T_c$  institutional and publication activity as of December, 1988.

- Institutions carrying out full-time activity involving two or more people [a]
  - USA:  $\approx 400$
  - Non-USA: 800–900
  - Japan:  $\approx 100$
- Publication submission and appearance activity (all figures approximate) [b]
  - High- $T_c$  Update
    - 2700 addresses on direct mailing list, of these, 500 non-USA to more than 50 countries
    - > 300 addresses on electronic mail USA and worldwide
    - Currently receiving about 50 preprints per week, 50% from non-USA (represents a 45% increase over average rate of reception during first six months of 1988)
  - Westinghouse Bibliography of High- $T_c$  Publications
    - > 5000 publications in open literature
    - Of these,  $\approx 750$  are thin film related and their number is increasing faster than those on bulk materials.

[a] Source: Jim Russel, Superconductivity Report.

[b] Sources: Ellen Feinberg, High- $T_c$  Update; Paul Bedahl, Lawrence Berkeley Laboratory.

their research in parallel to (and sometimes in lieu of) the more traditional channels of the scientific journals. Timely access to new developments has become critical to competing and participating in high- $T_c$  research. This has always been true in science, but whereas in the past a few weeks sufficed, now it is necessary to have almost daily (and, on a few occasions, hourly) contact with colleagues worldwide. Indeed, the principal impediment at present to more effective participation in high- $T_c$  research by institutions in the Third World is generally not lack of good laboratory facilities, or qualified personnel, but rapid and efficient communication with the scientific community in the First World. Many of the scientists in these former countries find themselves handicapped more by poor and expensive government-managed mail and telecommunications systems than by limited talent and equipment resources. The tracking of preprints, publications and patent filings in high- $T_c$  has become an important and essential activity in itself. At least one government agency, the US Department of Energy, has recognized this fact and is undertaking the establishment of a national database for high- $T_c$  reports and publications. As just mentioned, the accumulation and dissemination of knowledge has always been part of the essence of science, yet it has never occurred fast enough. The advent of high- $T_c$  has served to vastly exacerbate this problem and focus attention on it. It may be that the most important short-term consequence of these discoveries, long before practical applications of economic significance are achieved, will be the development of more rapid and effective means of communication of scientific progress of all kinds to researchers throughout the world.

In a review of such an enormous and rapidly evolving field like high-temperature superconductivity, one cannot attempt to represent all aspects and opinions as to current and future directions and issues in the subject. As an active participant in high- $T_c$  research, it is not even possible for me to be totally objective... one's particular biases always creep in. However, with this caveat, I will do my best. In the Sec-



tions to follow, my purpose will be to review the past and present status of materials development and discovery, outline critical problems in both experimental and theoretical high- $T_c$  physics, touch only briefly on thin film progress, and finally critically assess the potential for commercial development of high- $T_c$  materials paying special attention to the likelihood of applications which would generate large revenues.

## 2. High- $T_c$ Materials—Old and New

The discovery of high-temperature superconductivity by *Bednorz* and *Müller*<sup>[1]</sup> in barium-doped  $\text{La}_2\text{CuO}_4$  was preceded by a number of missed opportunities during the years of research on copper oxide materials prior to their work. By the 1970's, much work<sup>[8]</sup> had already been published on the ambient transport and magnetic properties of undoped  $\text{La}_2\text{CuO}_4$ . We now know that this parent compound to the future discoveries, although nominally insulating, also displays superconductivity itself in trace amounts when prepared under the usual conditions of solid state reaction of its constituent oxides. One can only speculate what progress might have been achieved in high- $T_c$  materials by now if only the low temperature resistivity of  $\text{La}_2\text{CuO}_4$  had then been measured! By 1979, the alkaline-earth doped  $\text{La}_2\text{CuO}_4$  compounds had been synthesized in the Soviet Union by *Shaplygin*, *Kakhan* and *Lazerev*,<sup>[9]</sup> but, once more, only the room temperature properties were investigated. The early-to-mid 1980's saw extensive research on copper oxide compounds, many of them precursors to the present high- $T_c$  materials, reported by *Raveau* and his colleagues at the University of Caen.<sup>[10]</sup> Their interest at that time seemed to center on the high-temperature properties of these systems, particularly their ability to chemically absorb and desorb oxygen and the attendant effect on electrical transport, rather than on the low-temperature regime.<sup>[11]</sup> Nonetheless, the Caen research turned out to be seminal in a number of ways. When discovered in the literature by *Bednorz*, it led the Zürich team to turn away from its disappointing search for superconductivity in nickel oxides to the copper materials. Also, the French work on oxygen processing pioneered what has turned out to be a critical aspect of almost all subsequent high- $T_c$  compounds. The preparation of these materials is largely based on straightforward methods of solid state chemistry,<sup>[12]</sup> using fairly simple equipment such as mortars and pestles, and tube and muffle furnaces capable of temperatures reaching temperatures of 1000 °C. The starting compounds themselves are readily available. It is these features which make synthesis of high- $T_c$  materials feasible in a much larger number of laboratories than otherwise might be possible for peer high-tech materials like silicon, complex polymers or thin films. In the conclusion, I will mention a particularly poignant occurrence of this kind.

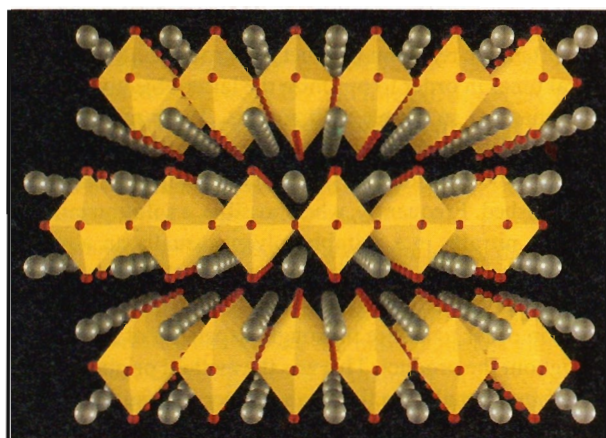
One begins by first mixing and calcining oxides or carbonates of the constituent cations at temperatures in the range

700–950 °C for times long enough to achieve complete reaction. Often, the resultant product is reground and recalcined several times in order to optimize the latter objective. This is sometimes not so simple as it sounds. These materials are ceramics with all their expected attendant granularity and hardness, and care must be taken that a complete reaction is accomplished. Frequently, when possible, a solution mixture of cation nitrates in a suitable solvent, usually an aqueous solution whose pH is adjusted to cause simultaneous co-precipitation of the cation salts, is used to seed the initial calcination in order to assure thorough dispersion of the cations throughout the product. This was the method originally used by *Bednorz* to make the first high-temperature superconductor.

In all methods, difficulties can arise, especially if one or more of the starting oxides requires very high temperature to dissociate, because the key starting ingredient, CuO, melts at around 1000 °C. On the other hand, because of its low melting point, CuO can often be used as a flux in crystal growth of copper oxide perovskites. The calcining steps are next, usually followed by either oxidation or reduction processing at temperatures appropriate to the particular compound in a particular atmosphere, most often after the calcined product has been pressed into a pellet. It has been found that the cooling rate following processing is frequently a key parameter determining whether a superconductor is eventually obtained.<sup>[13]</sup>

The materials developments in late 1986 and early 1987 following on *Bednorz* and *Müller* are by now well known. The discovery of the 90 K “1-2-3” (so-named after the stoichiometric ratio of its cations, Y, Ba and Cu) structure stressed that the essential ingredient in high-temperature superconductivity was sheets of planar coordinated copper oxide. This point is emphasized further in the family of high- $T_c$  structures given in Figures 1–6. Figure 1 contains the atomic arrangements of the substituted  $\text{La}_2\text{CuO}_4$  compound in which *Bednorz* and *Müller* discovered high- $T_c$  superconductivity. The most apparent feature is the bipyramidal arrangement of oxygens surrounding the copper atoms. It is the copper-oxygen plane formed by the base of these bipyramids which is the key structural aspect of high-temperature superconductivity. This plane is more readily seen in Figure 2, which contains the structure of the closely related material  $\text{Nd}_2\text{CuO}_4$  in which the apical oxygens are missing and the CuO sheets clearly visible. I will say more about this particular compound later. Both compounds are insulating antiferromagnets in their pure stoichiometric form, with nominal ionic states on the lanthanide, copper and oxygen ions of +3, +2 and –2, respectively. In order to introduce carriers, and hence obtain superconductivity, it is necessary to partially substitute lanthanum in  $\text{La}_2\text{CuO}_4$  with a divalent alkaline earth element thus inducing excess positive charge (holes) over and above those in the parent material. Exactly where this charge resides and how it is delocalized is a current topic of active investigation and debate, but it has become a common convention for counting purposes to con-





Figs. 1-6. Crystal structures of the generic copper oxide perovskite high- $T_c$  compounds. Unless otherwise noted, the colors of the various spheres, whose size reflects scaled ionic radii, designate the following elements: red = oxygen, blue = copper, grey = lanthanide (La, Y, Gd, Eu, etc.). The yellow polyhedra indicate the copper coordination in the presence of an apical oxygen. Square-planar coordinated copper is shown by the light blue plaquets. Fig. 1.  $\text{La}_2\text{CuO}_4$ ; alkaline earth substitution occurs on a lanthanum site. The copper sites are at the body centers of the bipyramids.

sider it to be on the copper and I will often refer to it this way. At one time, it was thought that the differing Jahn-Teller states between  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  were important in producing an enhanced electron-phonon coupling and thus a high- $T_c$ , but this is no longer the majority theoretical view.

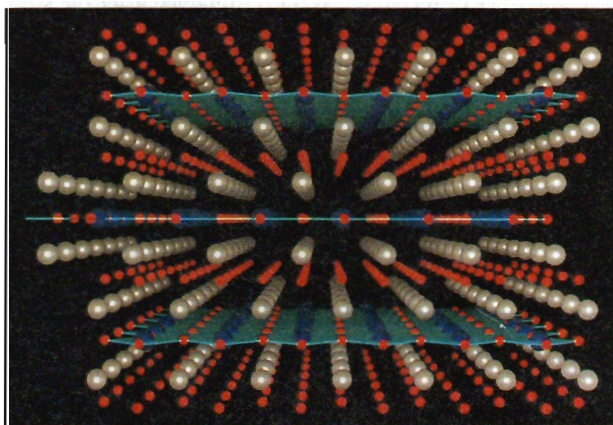


Fig. 2.  $\text{Nd}_2\text{CuO}_4$ ; cerium or thulium substitution occurs on a neodymium site, fluorine on an oxygen site coordinated to neodymium. For color coding see Figure 1.

$\text{YBa}_2\text{Cu}_3\text{O}_7$  ("1-2-3"), shown in Figure 3, is an example of how this necessary excess charge can be created in an alternative way to cationic substitution.  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is an oxygen-deficient perovskite; that is, not all possible oxygen sites (nine per unit cell) in the structure are occupied. To have oxygen at each would require impossible values of cationic charge. It turns out that the number of sites normally occupied, the seven shown, yields an average positive copper

ionicity of 2.33. It is seen that, in addition to a planar  $\text{CuO}$  network (evident in Figure 3 as the basal plane of the five-fold coordinated copper-oxygen pyramids on each side of the central yttrium cation) there exists a set of four-fold coordinated  $\text{CuO}$  chains, thus complicating the task of excess charge location. It turns out to be possible to lower the oxygen occupation below seven to 6.5 or even six, as shown in Figure 4, by annealing the sample in an inert environment such as argon or nitrogen. As Figure 4 demonstrates, these

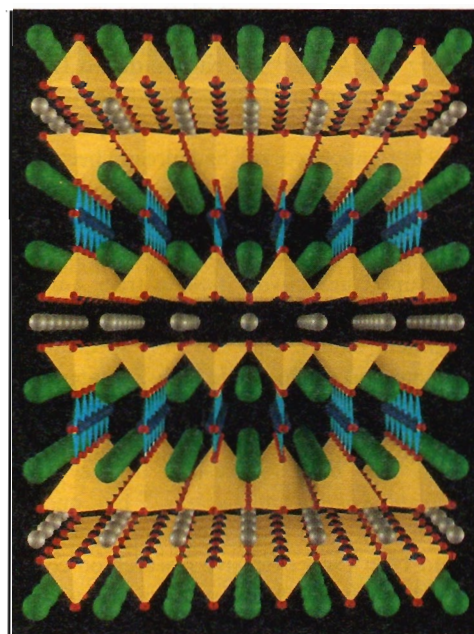


Fig. 3.  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , the green spheres represent barium. For color coding see Figure 1.

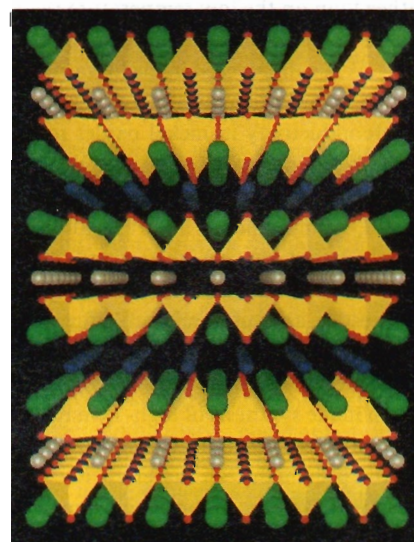


Fig. 4.  $\text{YBa}_2\text{Cu}_3\text{O}_6$ ; note the complete absence of oxygen in the inter-barium plane, resulting in a purely tetragonal structure. For color coding see Figure 1.



oxygen atoms are removed from the chain positions and it is now generally accepted that, through this process, the CuO chains function as variable "charge reservoirs" for the CuO planes. For occupation 6.5, all copper ions have a nominal charge of +2 and one might expect to find an antiferromagnetic insulator in analogy to  $\text{La}_2\text{CuO}_4$ . This is indeed very close to what is actually observed. Variation in oxygen content is a general property of all copper oxide perovskites, and it has become conventional to represent this in their chemical formulae, e.g.,  $\text{La}_2\text{CuO}_{4-y}$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ , etc. Oxygen content is a key factor in determining both the structural and superconducting properties of 1-2-3. As can be deduced from Figures 3 and 4,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has orthorhombic cellular symmetry, whereas  $\text{YBa}_2\text{Cu}_3\text{O}_6$  is purely tetragonal. An "orthorhombic-tetragonal" transition is observed at an oxygen level near 6.5. Once thought to be directly related to the disappearance of superconductivity, it is now believed to point to an order-disorder transition<sup>[14]</sup> in chain oxygen occupation which averages macroscopically to tetragonality as detected by usual powder diffraction methods. The loss of superconductivity arises from depletion of CuO plane carriers by chain oxygen removal. Much attention has been paid to this topic and the subsequent relationship between oxygen ordering, phase separation and  $T_c$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  as a function of  $y$ .<sup>[15]</sup>

Before leaving this discussion of 1-2-3, mention must be made of one of its unusual features compared to traditional superconductors. Almost all rare earth elements will substitute in the yttrium position of the 1-2-3 structure<sup>[16]</sup> and still yield materials with transition temperatures in the 80–90 K range, in spite of each rare earth ion possessing a magnetic moment, usually a situation that kills superconductivity in low- $T_c$  materials. The robustness of the superconducting state in 1-2-3 in the presence of such a dense concentration of paramagnetic sites is still not completely understood, and the answer may eventually provide a clue to the mechanism of high- $T_c$  superconductivity.

The next round of discoveries began in early 1988 with the announcement of the bismuth<sup>[17]</sup> and thallium<sup>[18]</sup> family of layered copper oxide compounds. Figures 5 and 6 contain the two- and three-layer members, respectively. The thallium form of the latter, the so-called "2223" structure (Fig. 6) holds the current reproducible record transition temperature, 125 K, and was referred to in Section 1 as the first high- $T_c$  material to receive a US patent. Interestingly, the single-layer precursor to these compounds had also been previously fabricated and studied at the University of Caen.<sup>[19]</sup> Today, over a year after their discovery, a number of important questions remain open. It is still not clear why the  $T_c$  in some cases seems to scale with the number of intimately adjacent CuO layers. For example,  $\text{La}_{1.82}\text{Sr}_{0.18}\text{CuO}_{4-y}$ , with essentially only one layer, has a  $T_c \approx 40$  K, whereas  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  and  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+y}$ , with two, are at 90 and 110 K, respectively, and then  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ , containing three adjacent layers, reaches all the way to 125 K. That this is not universal behav-

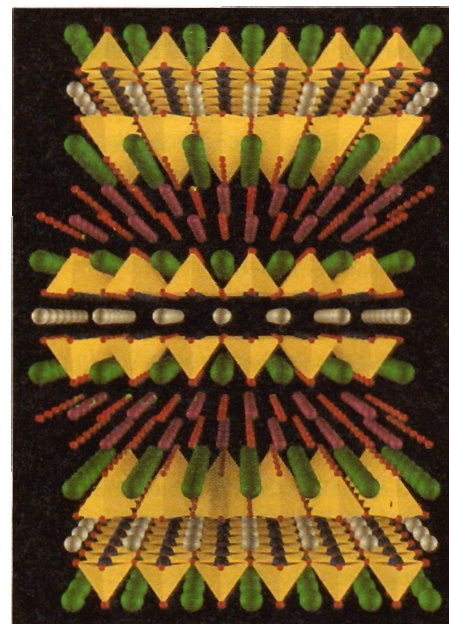


Fig. 5.  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+y}$ ; the magenta spheres represent thallium sites and the green barium as in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ; however, in this structure, the grey spheres are calcium, which can also be substituted by yttrium, thus reducing the carrier concentration. For other color coding see Figure 1.

ior is evident from the 122 K transition temperature found for the four-CuO layer compound.<sup>[20]</sup> The  $T_c$  does not seem to increase with decreasing CuO interplanar spacing either, inasmuch as this distance is smaller in the two-layer compounds than in the three-layer, yet the  $T_c$  is higher in the

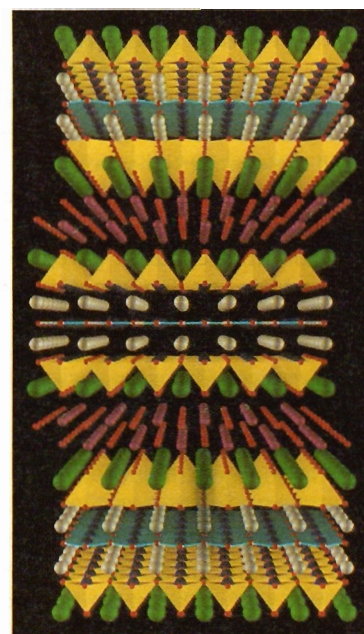


Fig. 6.  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+y}$ ; same representation as  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+y}$  (Fig. 5). For the remaining color coding see Figure 1.



latter. Associated with this issue is the exact transition temperature for the Bi 2021 and Tl 1021 structures. Two groups have reported a  $T_c \approx 80$  K for the former compound,<sup>[21]</sup> yet extensive efforts in other laboratories have failed to confirm these high values, typically obtaining  $T_c < 10$  K.<sup>[22]</sup> Therefore, any intrinsic dependence of  $T_c$  on the number of layers or layer spacing is not presently obvious and remains an open question. Indeed, can one isolated CuO layer alone sustain superconductivity?

Another mystery surrounding the bismuth and thallium compounds is the source of the carriers producing superconductivity. If one uses the ionic state of Cu as the summand for counting charge within the stoichiometric structures of all these compounds, one obtains exactly  $\text{Cu}^{2+}$ , thus these materials should ideally be Mott-Hubbard insulators! Whether the carriers originate from subtle conduction band overlap effects, as in semi-metals, or, which is much more likely, from cation deficiency and/or oxygen excess, remains to be seen.

Structural defects as a source of excess charge is an area of intense current investigation in these materials. The general role of doping, defects, oxygen content and carrier concentration in all high- $T_c$  materials are central topics of study and key subjects for debate. There is an apparent dependence of the  $T_c$  on carrier concentration that has been demonstrated for a wide variety of materials, independently of the carrier source. The range of superconductivity has both upper and lower carrier concentration limits, as shown by the work of Torrance, et al.,<sup>[23]</sup> who, through doping  $\text{La}_2\text{CuO}_{4-y}$  to high Sr levels by carrying out the reaction in a high pressure oxygen environment, found that above a certain carrier concentration, roughly 0.3 holes per  $\text{CuO}_2$  plane-molecule, the high- $T_c$  state disappeared but the metallic state remained. This finding has potentially important theoretical implications as to whether bulk superconductivity exists over a wide or narrow range of carrier concentration as a universal property of high- $T_c$  materials, and whether the materials involved undergo subtle structural changes at the high doping levels at which these properties are observed.

In this same arena, i.e., the production and role of carriers in CuO high- $T_c$  compounds, several new material developments of extreme interest have occurred recently. One was the synthesis of  $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$  by Siegrist, et al.,<sup>[24]</sup> a structure consisting of an ideally infinite stack of CuO planes, with no apical oxygens attached, separated by Ca and Sr ions. The formal valence of copper in this structure is +2 and the material is insulating with no reports of successful doping either rumored or published. One might expect difficulty in doping with holes because of the lack of an apical oxygen in the local copper-oxygen coordination. Precedence can be found for this assertion in the case of the  $\text{Nd}_2\text{CuO}_{4-y}$  class of compounds which differ from their  $\text{La}_2\text{CuO}_{4-y}$  cousin in that in the former no apical oxygen is found and doping with alkaline earths does not produce itinerant carriers.<sup>[9]</sup> With this knowledge, it is interesting to speculate whether the central CuO plane in the 2223 structure of

Figure 6 is "dead" in the sense that it cannot sustain holes.

However, Tokura, et al.,<sup>[25]</sup> have recently made the exciting discovery that doping the Nd 2-1-4 system with the tetravalent rare earths Ce and Th yields superconductors with onset temperatures in the 20–30 K range. The electron donating properties of the dopants would lead one to expect the carriers to be electrons as opposed to holes, and this expectation is indeed supported by the sign observed for the Hall and Seebeck effects.<sup>[26]</sup> However, a note of caution must be made regarding the concept of holes and electrons in metals, especially as revealed by the Hall effect and thermoelectric power. Strictly speaking, these terms are only appropriate for semiconductors where the "effective mass approximation" holds, as witnessed by the positive sign these experiments give for common metals like copper and gold. In fact, the thermopower changes sign in single crystal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  and bismuth 2212 with respect to crystallographic direction, being negative, or electron-like, parallel to the copper oxide planes, and positive, or hole-like, perpendicular to them.<sup>[27, 28]</sup> Therefore, these measurements can be misleading and at best indicate the type of majority normal state carriers and not necessarily whether these, or minority carriers of opposite sign, pair to give superconductivity. In historical retrospective, it is interesting to note that the sign of the Seebeck effect for all *undoped* lanthanide 2-1-4 compounds, save La itself, is negative.<sup>[9, 29]</sup>

The synthesis of these new materials is not trivial.  $\text{CeO}_2$  dissociates very slowly and it is difficult to obtain uniform cerium concentration by the usual calcining techniques. Moreover, the electrons donated by Ce or Th notwithstanding, it is still necessary to vigorously reduce the samples in order to obtain superconductivity. On reduction, a number of subsidiary lattice superstructures also result.<sup>[30]</sup> The significance of the oxygen reduction and its effect on structure and superconductivity are presently not well understood. Overall, interpretation of measurements on these "n-type" systems is hampered by both dopant and oxygen inhomogeneity. The dopant disorder aspect is somewhat ameliorated by doing single crystal growth in a CuO flux,<sup>[31, 32]</sup> but the crystals still have non-uniform oxygen distribution and flux inclusions. It has been universally observed that the resistivity of these materials does not follow the linear dependence on temperature above the  $T_c$  common to all previous copper oxide superconductors; however, it is likely that this behavior is due to the disorder problems just discussed. Recently, a two-step calcination technique has been devised, where  $\text{CeO}_2$  and  $\text{Nd}_2\text{O}_3$  are first pre-reacted at high temperature followed by a second, lower temperature calcination of the resulting product with CuO.<sup>[33]</sup> The ceramic material thus obtained displays a much more uniform cerium and oxygen concentration than material prepared by the usual technique, and for which a plot of  $\rho$  vs.  $T$  approaches near-linearity.

One of the most interesting developments with respect to the  $\text{Nd}_2\text{CuO}_4$  structure class has been the first successful use



of fluorine, introduced by reacting appropriate amounts of  $\text{NdF}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{CuO}$ , to produce a high-temperature superconductor ( $T_c \approx 20$  K).<sup>[34]</sup> This was also the first example of anion-doping in high- $T_c$  materials. The chemistry of the reaction appears quite complex, requiring much more fluorine (i.e.,  $\text{NdF}_3$ ) in the starting mixture than remains in the final product. It is probable that the fluorine that does react stays with its Nd partner throughout calcination and thus occupies an oxygen site coordinated with Nd (see Fig. 2), especially since attempts to dope using  $\text{CuF}_2$ , ostensibly placing F on a CuO planar oxygen site, did not result in superconductivity.<sup>[35]</sup>

Does the advent of the n-type high- $T_c$  compounds signal a new round of materials discovery? At first, the prospect seemed encouraging, but further reflection and subsequent events have not proved all that promising. To successfully introduce electrons through tetravalent cation or fluorine doping seemingly requires a host material without apical oxygens coordinated to the CuO planes, and, so far, only the  $\text{Nd}_2\text{CuO}_4$  and  $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$  systems have been found to have this feature. There are no reports to date of successful cation doping of the latter compound. For fluorine doping, there is the added constraint that an oxygen site chemically remote from the CuO plane must be available for occupation, which is at present a property of the  $\text{Nd}_2\text{CuO}_4$  structure alone. On the other hand, if the Bi or Tl 2223 compounds could be prepared as electronically neutral host systems, electrons could in principle be induced on the central CuO by tetravalent cation or fluorine doping on an appropriately remote cell site. It will be interesting to observe what progress is indeed made in n-type materials, especially whether transition temperatures as high as in the previous hole systems can be achieved.

One of the most enigmatic of the high- $T_c$  compounds is the one that has "no- $T_c$ " at all! This is  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ , the only member of the lanthanide 1-2-3 family that is not metallic and not superconducting.<sup>[36]</sup> There were early indications that its unit cell was tetragonal and it was thought that this might be the reason for its lack of superconductivity, in analogy to the original belief about reduced  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ . However, it is now known that fully oxygenated Pr 1-2-3 is orthorhombic but still not superconducting.<sup>[37]</sup> The most plausible explanation for the missing superconductivity is that Pr is known to be in the oxidation state +4 in some of its oxides and if the same were true in  $\text{PrBa}_2\text{Cu}_3\text{O}_7$ , no excess positive charge would be available for conduction. However, this picture is not without difficulties, inasmuch as core level spectroscopy and some structural features are more in accord with a  $\text{Pr}^{3+}$  ionic state. An in-depth analysis of magnetic measurements and structural data<sup>[37]</sup> as well as the results of resonant photoemission measurements<sup>[38]</sup> now indicate that Pr in Pr 1-2-3 can indeed be thought of as trivalent, but with strong hybridization of its outer 4f orbitals with the 2p states on its nearest neighbor oxygens which also happen to be shared with copper in the adjacent CuO planes. The excess negative charge in these bonds localizes itinerant holes

traveling on the planes on a time scale sufficiently long to disrupt metallic transport and hence superconductivity, yet sufficiently short not to cause discernible changes in the Pr charge state or overall cell parameters. I believe similar arguments explain the extremely rapid loss of superconductivity with Zn substitution for Cu in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ , where the planar holes scatter inelastically off the filled Zn 3d orbitals hybridized with O 2p orbitals.<sup>[39]</sup>

Until mid-1988, all existing high- $T_c$  compounds had been members of the copper oxide perovskite family. Then, a high- $T_c$  non-copper oxide material,  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-y}$ , was discovered by Cava, et al.,<sup>[40]</sup> with an onset temperature near 30 K. On the scale of now known transition temperatures, this is not terribly high. However, had this discovery occurred in the absence of the copper oxide systems, it would have been a sensation. Interestingly, that this compound might be superconducting was predicted theoretically by Mattheiss, et al.,<sup>[41]</sup> demonstrating that, occasionally, the famous "Matthias Rule" (no superconductor was ever theoretically predicted) can be violated. It appears that  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-y}$  is a structural extension of  $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_{3-y}$ , the prototypical oxide superconductor, whose transition temperature is around 13 K, and which received much study in the years between its discovery<sup>[42]</sup> in 1975 and the advent of high- $T_c$  materials. The origin of its high transition temperature and pairing mechanism, just as for the copper oxide systems, remains presently unclear. Unlike the latter compounds, a significant isotope effect as well as no evidence of magnetic activity is found in the BiO materials; however, it has been suggested by Batlogg, et al.,<sup>[43]</sup> that the coupling might originate from charge density wave mediated pairing in analogy to the various spin density wave models proposed for the copper oxide superconductors. The observed isotope shift is then explained by these workers as a side effect of strong coupling between the charge density waves and the lattice, a coupling often observed in such systems. Another interesting difference between these two material systems is that the low field properties and flux dynamics in the BiO compounds are quite traditional, in that they resemble much more those of the low- $T_c$  type-II superconductors, than do the properties and dynamics of the copper oxide family.

The continual and constant appearance of new high- $T_c$  materials is one of the most encouraging aspects of the present state of the field. Although further verifiable increases in the  $T_c$  have not taken place since early 1988, the number of materials discovered has still progressed apace, now totalling, depending on how one defines "new", some 60–70 high temperature superconductors. Figure 7 illustrates the relative manner in which the rate of new material discovery has exceeded the rate of increase in the  $T_c$ . In the long run, sustaining the rate of new materials uncovered may prove more important to the basic understanding of high- $T_c$  superconductivity than incrementally raising the  $T_c$ . A transition temperature of 125 K, and even 93 K, is sufficient for many applications. However, as the number of new compounds



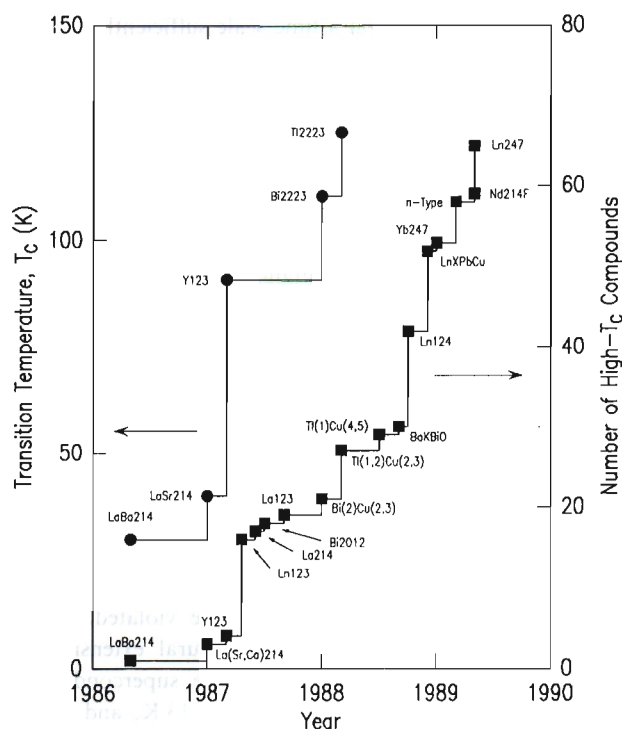


Fig. 7. Plot of increases in the  $T_c$  and in the total number of high- $T_c$  materials from the time of the initial discovery to the present. Most of the symbol labels are self-explanatory: Ln stands for the rare earth elements (most of them); X for an alkaline earth; the numbers in parentheses, e.g.,  $Ti(1,2)Cu(2,3)$  means the series with both single and double TiO layers as well as double and triple CuO layers; and F in Nd214F represents fluorine substitution on an oxygen site.

continues to grow, both in quantity and complexity, the basic paradigm of materials science—synthesis, processing and characterization—assumes greater and greater importance. Many of the new systems, as witnessed by the “n-type” materials, require closer control of these parameters now than previously. These are definitely not as “easy as 1-2-3” to make. At IBM Almaden, we often find the conditions required to repeat the work of others to be quite different than those which were published. For example, frequently we find the stated reaction temperatures to be too high. The way in which furnace temperatures, quenching rates and ambient reaction atmospheres are determined vary from lab to lab. For high- $T_c$  materials in general, many processes, such as oxygen annealing, may be quite out of control especially when compared to prevailing standards of, say, semiconductor technology.

Several times throughout this Section I have referred to the 125 K thallium 2223 compound as holding the currently highest verifiable transition temperature. In the past four years, there have been a number of reports of USOs (Unidentifiable Superconducting Objects), some with a  $T_c$  as high as 400 °C! To date, none of these reports have been reliably and independently reproduced.<sup>[44]</sup> Occasional reports of extraordinarily high transition temperatures have always been a peculiar aspect of the history of superconductivity, and their continuation into the era of high- $T_c$  materi-

als is no real surprise, only the large number of exaggerated claims, at present greater than thirty, is new. This increased frequency can be partially rationalized by the fact that high- $T_c$  work has attracted so many new researchers from other fields, many with no previous experience in superconductivity. It would not be constructive to dwell on individual cases in this review; however, there are a few general features common to these reports. Many times they involve four-probe resistivity measurements made on multi-phase, high resistance samples. Despite its apparent simplicity, the four-probe technique can often yield anomalous results on such samples and a number of independent checks must be made during the measurement.<sup>[45]</sup> Other reports involve complex thermal cycling, sometimes in the presence of an ambient gas such as nitrogen or oxygen. In such cases, errors in thermometry can arise, or artifacts in resistivity caused by adsorbed water vapor in poor vacuum can occur.<sup>[46]</sup> In the former instance, besides the possibility of the ambient increasing the thermal barrier between sample and thermometer, there is the distinct chance that a porous ceramic sample containing a small amount of “conventional” high- $T_c$  material will soak up and hold liquid nitrogen or oxygen as it is cycled below 77 K, which is then retained on warming thus giving the appearance of a much higher  $T_c$  until the absorbed cryogen boils off. At the risk of sounding sanctimonious, nothing beats the application of sound experimental procedure to check every possible source of anomaly . . . and then to make every effort to cooperate with the scientific community to have the result independently verified. This last point is particularly important. In every case known to me, save one, when a truly new high- $T_c$  material was discovered, it was independently reproduced almost immediately. This was even the case when trace amounts of superconductivity were found in undoped  $La_2CuO_4$ , a very ephemeral and sample processing dependent experiment.<sup>[47]</sup> The one exceptional case so far was the independent confirmation of superconductivity in fluorine-doped  $Nd_2CuO_4$  which followed the original report by several months.<sup>[35]</sup>

Finally, before leaving this Section, I will discuss briefly a few recent developments in organic superconductors. These were the first class of materials thought likely to yield high transition temperatures, a belief in part motivated by the excitonic pairing models originally proposed by Little.<sup>[48]</sup> Beginning in the early 1970's, much attention was given to planar  $\pi$ -bonded molecular crystal cyano-quino-dimethanide (TCNQ) and sulfur/selenium fulvalene (TTF, TMTSF) compounds, but it was not until 1980 that superconductivity was discovered in Lewis acid complexes of TMTSF.<sup>[49]</sup> Until then, various quasi-one-dimensional charge and/or spin instabilities would destroy the metallic normal state at relatively high temperatures, but in these latest compounds, the Fermi surface has sufficient two-dimensionality to maintain the metallic state to temperatures low enough to permit the possibility of superconductivity. At first, transition temperatures were of the order 1 K occurring only under 10 kbar pressure, but rapid progress has since been made with one



material,  $\kappa$ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ , displaying an onset of superconductivity near 12 K at ambient pressure.<sup>[50]</sup> No universally accepted theory for the pairing mechanism in these organic superconductors exists at the present time; however, spin density wave instabilities are usually present as well as superconductivity and it could be that one of the magnetically mediated pairing models under consideration to explain the high- $T_c$  effect in ceramics may indeed apply. Plotted against year of discovery, the slope of the rise in the  $T_c$  for organics is quite dramatic, especially when compared to the traditional low- $T_c$  compounds. Whether this trend will continue is problematic. In the organics, the  $T_c$  has so far scaled empirically with unit cell volume—the larger the volume, the higher the  $T_c$ . In the current record material, the cell volume is around 1700 Å<sup>3</sup>, a huge size, and it is difficult to conceive a crystallographically stable structure much larger. Further progress in raising the  $T_c$  in organics will probably depend on discovery of a different class of compounds apart from the current materials, perhaps paralleling the recent history of inorganic superconductors.

### 3. Superconductivity in High- $T_c$ Materials—Experiment

Experimental studies of the superconducting state of high temperature superconductors fall into two general categories. The first involves those which probe microscopic properties on the atomic level with the purpose of shedding light on the basic mechanism of high- $T_c$  superconductivity, and the second, macroscopic properties which affect application parameters like critical fields and currents. The framework governing microscopic properties of the conventional low- $T_c$  materials has been the well-known and highly successful Bardeen-Cooper-Schrieffer (BCS) theory developed in the mid-1950's and later extended by *MacMillan* and *Eliashberg*, whereas the theory encompassing macroscopic behavior has been the equally successful Ginzburg-Landau-Abriksov-Gorkov (GLAG) empirical model which evolved during the late 40's to early 60's.<sup>[51]</sup> The principal thrust of most high- $T_c$  experimental activity is directed toward exploring the applicability of these two monumental theories to the new materials, the relative degree to which this can be accomplished experimentally will be discussed in this Section. The possibility that a new microscopic theory may be necessary will be addressed in the next Section.

Several key features are manifest in the BCS theory for conventional superconductors. Of these, the most important is that the supercurrent is carried by paired electrons (or holes) which are formed as one passes below the  $T_c$  and whose binding energy is revealed by the opening of a gap ( $2\Delta$ ) in the far-IR spectrum of the otherwise continuous single particle (Drude) excitations common to all normal metals. Subsidiary features involve the physical mechanism responsible for pairing—phonons, in the case of conventional superconductors—and the symmetry of the pair wave

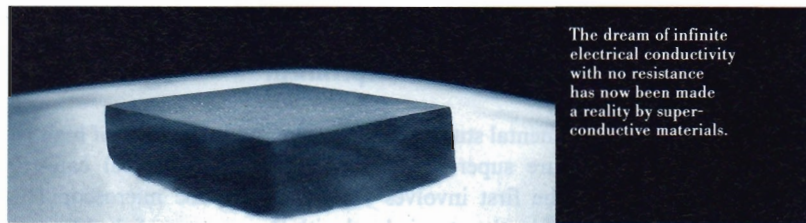
function. It is important to emphasize that phonons are not an integral part of the BCS-MacMillan-Eliashberg model as any bosonic field, such as the excitons proposed by *Little* for organic systems,<sup>[48]</sup> will satisfy the mathematical conditions of the theory. The key feature of BCS is that pairs exist only below the  $T_c$  and that the resulting macroscopic quantum state pervades the entire material.

It is now fairly well established that the supercurrent in high- $T_c$  compounds is carried by charged pairs,<sup>[52, 53]</sup> so they in fact exhibit a necessary, but not sufficient, characteristic of BCS. By virtue of the absence of an <sup>18</sup>O isotope effect,<sup>[54]</sup> most workers would also accept that the lattice, or the phonons therein, does not play the significant role in pair-binding that holds for conventional superconductors. Two questions then arise for experimentalists to answer: 1) What is the strength of the coupling, and, 2) what is the mechanism providing the attractive interaction to form the pairs?

As might be expected, part of the answer has been sought in a variety of optical and tunneling studies on high- $T_c$  materials from the visible to the far infrared. In principle, optics, along with tunneling experiments, provide two of the most direct probes of coupling properties. For example, an appropriate analysis of tunneling data can yield the complete frequency spectrum of the fermion-boson interaction. Tunneling is perhaps the most ideal of all experiments that probe the superconducting state. Unfortunately, application to high- $T_c$  compounds is limited by the currently low state of materials perfection and perhaps ultimately by the very short coherence length (crudely, the diameter of the paired holes or electrons). The most that present data clearly indicates is a gap in the derivative I-V characteristic appearing below the  $T_c$ . Early measurements were widely scattered with respect to the value of the gap energy, especially in bulk 1-2-3, but recently more mutually consistent data has been obtained.<sup>[55]</sup> The issues confronted in attempts to use optical properties as a tool for understanding coupling mechanisms and determining gap energies are summarized in an extensive review article by *Timusk* and *Tanner*.<sup>[56]</sup> The optical data, usually acquired by near-normal incidence reflectance techniques, is very rich in structure, and requires rather elaborate numerical analysis to extract the underlying dielectric response function which connects to the physics one is trying to understand. Therein lies the prime difficulty with optical experiments. In having so many optical excitation and decay channels open in these materials (electronic, vibronic, magnetic), the optical spectrum of high- $T_c$  compounds is far more complicated than the simple Drude-like response of elemental metals and superconductors. In the near infrared, an uncharacteristically strong frequency dependent dielectric response is observed. Some have interpreted this behavior in terms of an electronic gap which may possibly be mediating an excitonic coupling mechanism,<sup>[57]</sup> while others have associated it with a frequency dependent itinerant carrier scattering time and effective mass.<sup>[58]</sup> This latter picture implies there exists strong coupling, or dressing, of the single particle carriers with high energy boson excitations which, at



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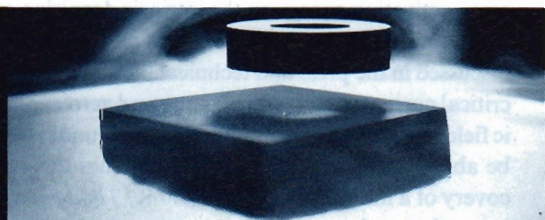


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sufficiently low temperatures, gives rise to pairing. These are quite separate views of the same data. In terms of a BCS-Eliashberg-MacMillan framework, if the spectrum indeed contains a "mid-IR gap," then high- $T_c$  superconductivity could arise in the weak coupling limit from the large characteristic boson temperature prefactor ( $\theta$  in the simple BCS expression  $T_c \approx \theta \exp(-1/\lambda)$  where  $\lambda$  is the electron-boson coupling constant) associated with the large gap. On the other hand, the same spectrum taken as evidence for strong coupling would argue for a high transition temperature resulting from a large  $\lambda$ .

To decide the question of weak vs. strong coupling, one usually examines the ratio  $2\Delta(0)/kT_c$ , where  $2\Delta(0)$  is the value of the superconducting gap energy measured well below the  $T_c$  by either optical or tunneling methods. For weak coupling, this ratio is approximately 3.5, while for strong coupling, it can be typically 1.5–2.0 times greater. As in the near-IR, reflectance spectra taken in the far-IR in order to obtain  $2\Delta$  are complicated by overlapping, and possibly temperature dependent excitations from similar sources at higher energies which can mimic a pairing gap. Added to this is the further complication that in an ideal superconductor, the reflectance will not reveal any additional structure arising from the presence of a gap—one must have a certain amount of impurities (the so-called "dirty limit") for gap transitions to be observed. These difficulties notwithstanding, features which appear at the onset of superconductivity are observed<sup>[59, 60]</sup>, and, when taken as the gap energy, yield values of  $2\Delta(0)/kT_c \approx 7-8$ , in general agreement with tunneling data, and in support of a strong coupling viewpoint. However, not all workers agree on this interpretation, and, although recently published results by Collins, et al.,<sup>[60]</sup> appear to satisfy previous objections against the strong coupling picture, the optical question, and hence which coupling strength limit applies to high- $T_c$  materials, is still not entirely answered.

On the macroscopic side, it is now well known that all the present high- $T_c$  materials are Type II superconductors—a fact dramatically illustrated by the ubiquitous demonstrations of laterally stable levitation of a permanent magnet over (and even under!) a flat surface of the compounds.<sup>[61]</sup> Most of their macroscopic behavior is well described by conventional GLAG models. The study of one Type II property, flux penetration and its associated dynamics, exploded in 1988 and continued throughout 1989. Interestingly, these investigations began very early with the third paper published by the IBM Zürich group<sup>[62]</sup> containing observations of the time-dependent decay of diamagnetism in the superconducting state. This behavior was originally interpreted in terms of a spin-glass analogy model involving intergranular Josephson tunneling.<sup>[63]</sup> Much later, at IBM Yorktown,<sup>[64]</sup> these experiments were repeated and re-examined from the more conventional flux creep point of view traditionally applied to explain flux dynamics in Type II superconductors.<sup>[65]</sup> The principal difference found between the old low- $T_c$  materials and the new high- $T_c$  compounds is that the

"pinning" force, or resistance to vortex motion in an applied magnetic field, is orders of magnitude smaller for the latter, leading to what has been termed "giant flux creep." This phenomenon may also be responsible for the unusual vortex lattice properties observed as well.<sup>[66]</sup> Recently, a new model has been proposed for flux motion and pinning based on vortex entanglement, or "reptation," arising from the large anisotropy inherent in all high- $T_c$  copper oxide perovskites.<sup>[67]</sup> These ideas have a number of commonalities with mechanisms of structural transitions in polymers, and do not require the existence of pinning centers to explain the observed time dependence of the magnetization.

Time dependent magnetic effects have profound consequences for transport and dissipation effects in the new materials. They are responsible for the broadening of the resistive transition and loss of zero resistance in relatively modest (2 T) magnetic fields and, because they have been observed in untwinned single crystals<sup>[68]</sup> as well as ceramics, they do not appear to arise from sample inhomogeneity.

Within the context of flux creep models, Tinkham<sup>[69]</sup> has proposed a GLAG-based picture for the dependence of the creep activation energy on the intrinsic depairing critical current (note: this is not the measured critical current, usually discussed in the press and technical literature). The depairing critical current at zero temperature and zero applied magnetic field,  $J_{c0}$ , in the present high- $T_c$  compounds is estimated to be about  $10^7-10^8$  A/cm<sup>2</sup>. If one assumes the eventual discovery of a material with  $T_c = 400$  K, Tinkham's model estimates that, unless concurrent increases in  $J_{c0}$  also occur, zero resistance at room temperature would only exist in applied magnetic fields less than 10 T. This limitation would be in addition to the much stricter requirement of a usefully high *extrinsic* critical current. If correct, these considerations imply dire consequences for the practical application of room temperature superconductors.

However, there has been a reincarnation of superconducting glass concepts arising from a model recently put forward by Fisher.<sup>[70]</sup> In normal flux creep theories, a true zero resistance Type II superconducting mixed phase cannot occur in the absence of pinning.<sup>[65]</sup> Fisher has shown theoretically that a "vortex-glass" phase, exhibiting zero resistance, can arise from taking into account the collective motion of the vortex lines alone. Thus, a continuous transition between a normal, or "vortex fluid," state and a superconducting, or "vortex glass," state delineated on the  $H-T$  plane has been predicted. This picture is supported by an analysis of nonlinear I-V response data obtained on epitaxial films of  $YBa_2Cu_3O_{7-y}$  by Koch, et al.,<sup>[71]</sup> and "glass echo" magnetization measurements performed by Rossel, et al.,<sup>[72]</sup> on  $YBa_2Cu_3O_{7-y}$  single crystals.

The magnetic field-dependent macroscopic properties of high- $T_c$  compounds is one of the most active and interesting aspects of experimental high-temperature superconductivity at present, rivaling the search for the pairing mechanism. It remains to be seen which viewpoint will emerge the winner, or whether a suitable synthesis of the creep, entanglement



and glass models will prevail. Nonetheless, it is fascinating and appropriate that the ideas contained in the third paper of the Zürich workers have regained currency, and that the influence of this paper on the progress of the field is surpassed only by their first.

The unusual field properties of the high- $T_C$  materials also affect the way their upper and lower critical fields,  $H_{C1}$  and  $H_{C2}$ ,<sup>[61]</sup> respectively, are obtained and interpreted. Since enormous applied magnetic fields ( $> 20$  T) are required to restore the normal state of Type II superconductors, and especially high- $T_C$  compounds, at low temperature,  $H_{C2}$  is determined from the derivative dependence of the resistive transition with respect to magnetic field close to the  $T_C$ , and GLAG models are employed to extrapolate back to  $T = 0$  K. But, because of the broadening of the resistive transition by flux motion as just discussed, this traditional method cannot be applied and what the exact magnitude of  $H_{C2}$  actually is remains unclear... we just know it's large!

A similar uncertainty applies to measuring the absolute value of the lower critical field,  $H_{C1}$ . A classic method used to determine  $H_{C1}$  in Type II superconductors is to locate the field value at which the variation of magnetization vs. applied field first departs from linear behavior. However, in the high- $T_C$  materials, a slight curvature in the  $M$ - $H$  plot is invariably observed down to very low fields (about 0.1–1.0 mT (1–10 Oe)) when the measurement is done in a conventional magnetometer. In a more prosaic sense, we know from levitation experiments that flux enters at quite low fields and becomes trapped since the little levitated magnet is indeed laterally stable. Vibrating sample magnetometry on ceramic samples<sup>[73]</sup> indicates that flux enters and is trapped in applied fields as low as a few hundred  $\mu$ T (0.1 Oe). The situation is not much better for single crystals. There are several other indications that  $H_{C1}$  is small.

One is that the "Meissner fraction," that is, the amount of flux expelled by virtue of the Meissner-Oschenfeld effect compared to perfect diamagnetic shielding, when the sample is cooled in an applied external field (around 1 mT (10 Oe) in most dc magnetometers), is always even less than the actual diamagnetic shielding signal obtained by cooling the sample in zero field and then turning it on well below the  $T_C$ . One often sees "Meissner fraction" quoted as representative of the volume of a given sample that is actually in the superconducting state. Actually, for high- $T_C$  materials, it is more a measure of the flux trapped due to field penetration, and, unless the data is collected in a very small applied field, it may have little to do with superconducting volume fraction. As with  $H_{C2}$ , it is difficult to determine the exact value of  $H_{C1}$ ... we just know it's small!

The resultant problems in determining critical fields precisely in high- $T_C$  compounds in turn cause difficulties in estimating important parameters of the superconducting state, in particular, the London penetration depth,  $\lambda$ , and the pair coherence length,  $\xi$ . The ratio of these two quantities is a measure of the "Type II-ness" of the material. As will be seen

in the next Section, it is particularly important to have a good idea of the magnitude of  $\xi$ .

In this Section, I have primarily stressed measurements dealing with the superconducting state. However, I must emphasize that measurements of normal state properties are equally important. Traditionally, a number of parameters important to superconductivity are obtained from the normal state. For example, an estimate of the fermion-boson coupling constant,  $\lambda$ , can be deduced from a comparison of the temperature dependence of the resistivity, specific heat and carrier spin susceptibility above the  $T_C$ . Resistivity data can also be analyzed for the carrier mean-free-path, important in determining whether a given material is in the "clean" or "dirty" limit. In principle, optical data at Drude response energies can yield the London penetration depth, and the Seebeck coefficient the Fermi energy. However, the relevance of all these measurements to BCS-like superconductivity depends on whether the normal metallic state can be described in terms of a Fermi liquid, which is the central theoretical issue in high-temperature superconductivity, next to be discussed.

#### 4. Superconductivity in High- $T_C$ Materials—Theory

There is as yet no universally accepted microscopic theory of high-temperature superconductivity in copper oxide perovskites. The general prescription that can be given which is probably sufficient for obtaining a high- $T_C$  material is that it must contain a set of quasi-two-dimensional  $\text{CuO}_2$  planes capable of sustaining a critical density of itinerant carriers within some given concentration range. That the quasi-2D character is necessary is demonstrated by the lack of superconductivity in  $\text{La}_4\text{BaCu}_5\text{O}_{13+y}$ , which is highly metallic, in a hole concentration region adjusted by Pr doping<sup>[74]</sup> to span 0.2–0.4 holes per  $\text{CuO}_2$  molecule, but whose copper oxide backbone consists of a 3D network of chains and not 2D planes.<sup>[75]</sup> Another prominent characteristic differentiating  $\text{La}_4\text{BaCu}_5\text{O}_{13+y}$  from its superconducting relatives is that a plot of its  $\rho$  vs.  $T$  is definitely not linear, following much more closely the Bloch-Grüneisen dependence typical of most metals.  $\text{La}_4\text{BaCu}_5\text{O}_{13+y}$  is the most clear and unambiguously single phase example of a conducting copper oxide compound that is not a superconductor.

It did not escape notice for very long that the ground state of the undoped parent compound to the Bednorz-Müller discovery,  $\text{La}_2\text{CuO}_{4-y}$ , was antiferromagnetic and insulating and arose from the interaction of  $\text{Cu}^{2+}$  spins.<sup>[76]</sup> That this ground state existed and might prove critical to the occurrence of superconductivity on doping was anticipated by Anderson.<sup>[77]</sup> As time has passed, the electronic phase diagram with respect to carrier concentration shown in Figure 8 has come to be generic to all planar copper oxide superconductors. There remains disagreement over detailed features such as the true extent of the antiferromagnetic and superconducting regimes, or whether an intermediate spin glass



state exists between them. The salient point is that close by the superconducting phase lies magnetic order and this may not be just an accident without any relevance to the microscopic mechanism of high- $T_C$  superconductivity. It was also Anderson<sup>[77]</sup> who immediately pointed out that a theoretical framework suitable for describing just such a scenario had existed for some time. That framework is the Hubbard Hamiltonian,<sup>[78]</sup> shown in Equation 1.

$$\mathcal{H} = \sum_i [t(c_i c_{i+1}^\dagger + c_i^\dagger c_{i+1}) + U n_i^\uparrow n_i^\downarrow] \quad (1)$$

Here,  $t$  is the hopping or delocalization energy for holes or electrons moving between nearest neighbor sites on a square 2D lattice, with  $U$  being the on-site coulombic repulsion for two-carrier occupation subject to Pauli exclusion of equal spin directions. This deceptively simple equation contains a great richness of electronic behavior and has so far resisted analytical solution for general values of  $t$  and  $U$  and arbitrary site occupation except in one dimension.<sup>[79]</sup> It can be arguably claimed that, because of its possible relationship to high- $T_C$  superconductivity, study of the 2D Hubbard model is the most important theoretical topic in condensed matter physics today. With respect to the electronic phase diagram of Figure 8, the direction of increasing  $U/t$  is as shown. That is, as one moves from right to left, increasing the coulomb repulsion term with respect to the bandwidth, traversing the limit from Fermi liquid (far right) to quantum spin liquid (far left).<sup>[80]</sup> Nearest which limit the superconducting phase is encountered is precisely the main question of the moment in the theory of high-temperature superconductivity. The different flavors of magnetically-motivated microscopic theories of high-temperature superconductivity which now abound arise from investigating the 2D Hubbard Hamiltonian in various limits of  $U/t$ . This is difficult enough, but the real situation is even more complex.

First of all, the above equation describes particle motion only in a single non-degenerate band, whereas actually we are dealing with a highly dispersive, overlapping and degenerate states originating from Cu 3d and O 2p atomic orbitals.<sup>[81]</sup> Further important modifications can arise from the relative ionization potentials of copper and oxygen ionic states<sup>[82]</sup> and surrounding ionic Madelung energies.<sup>[83]</sup> An early theoretical concern was the question of exactly which ionic states held the carriers during transport... did they come from Cu 3d or O 2p? Initial core level and valence band photoemission spectroscopy data indicated an increase in  $O^\ominus$  states on doping suggesting the holes delocalized in the oxygen ligands. With the advent of the electron systems, these same experiments<sup>[84]</sup> show an excess of  $Cu^\oplus$ , so an ionic description of the charge transport becomes even more labyrinthian. Are there really two bands, one for holes and another for electrons? It is most likely that transport occurs in a single band comprised of strongly hybridized Cu-O bonds with a major influence on the relative amounts of d and p character exerted by the presence or absence of an apical oxygen coordinated to the CuO plane.

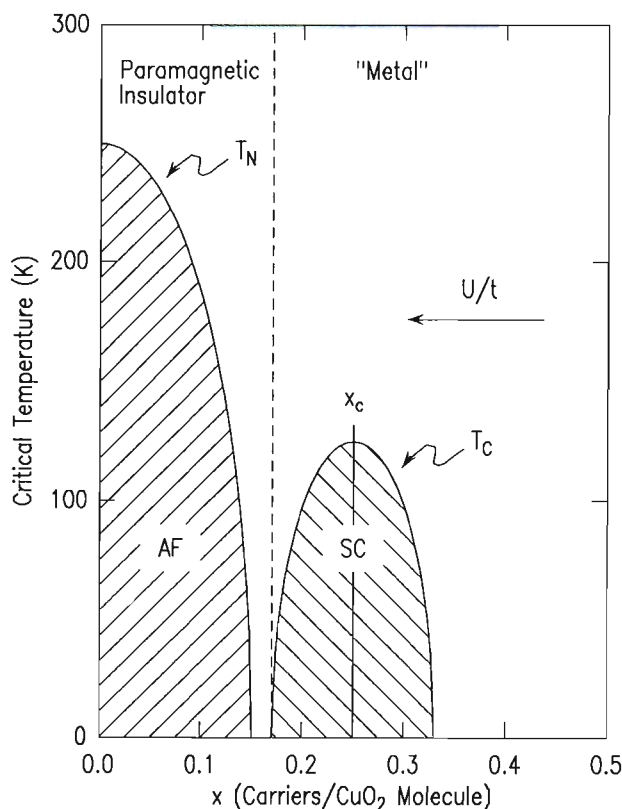


Fig. 8. Generic electronic phase diagram for the copper oxide perovskite high temperature superconductors.  $T_N$  and  $T_C$  denote the antiferromagnetic Néel and superconducting critical temperatures. The temperature and concentration scales indicate the range of values typically found in the copper oxide perovskites.  $x_c$  indicates a speculative "critical concentration" which may be the only carrier concentration at which bulk superconductivity is obtained (see text). Note that on this plot the direction of increasing Hubbard parameter ratio  $U/t$ , is in the direction shown.

All these complications notwithstanding, if we can make a separation of the transport state manifold from that of independent  $Cu^{2\oplus}$  spins,<sup>[85]</sup> and then connect them with an appropriate hopping term, a degenerate and charge symmetric Hubbard description should apply and we return to the question as to what limit of  $U/t$  should be used. The value of these parameters is not easy to determine experimentally due to local band dispersion and screening of the coulombic repulsion, and, in any event, exactly what values of  $U/t$  are considered "small" or "large" is a matter of taste on the part of each individual theoretician. Nonetheless, two completely distinct microscopic theories of high- $T_C$  superconductivity arise in each limit.

Examples of models which flow from the "small"  $U/t$  side are the "two-band" ideas of Emery,<sup>[86]</sup> the "spin bag" approach of Schrieffer,<sup>[87]</sup> and the "heavy fermion" analogy of Pines.<sup>[88]</sup> These theories fall into the BCS-MacMillan-Eliashberg formalism and are Fermi liquid based. Essentially, the phonons of the conventional theory are replaced by spin-wave excitations as the bosonic "glue" which bonds the paired fermions, presumably giving rise to high- $T_C$  superconductivity due to stronger coupling and a higher boson char-



acteristic temperature, here the magnetic exchange energy, than was the case for phonon-mediated pairing. The strongest sources of experimental support for this picture probably come from the interpretation of the dependence of the  $T_c$  on doping as an intrinsic carrier concentration effect on the Fermi energy and the single particle density of states thereat, the observation of band dispersion at the Fermi level in angle-resolved photoemission spectroscopy,<sup>[89]</sup> and the presence of incommensurate spin excitations observed above, and, at reduced intensity, below the BCS gap value,  $2\Delta(0) = 3.5 k_B T_c$  in the inelastic neutron scattering spectra of a single crystal of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-y}$  with a 33 K transition temperature and nearly complete Meissner fraction.<sup>[90]</sup>

On the other hand, the spin-mediated pairing Fermi liquid models are not without problems. The pair wavefunction contained in these theories should have non-s-wave symmetry, but both gap measurements and the temperature dependence of the penetration depth<sup>[91]</sup> suggest otherwise. Moreover, one would expect that for these models to hold, some remnant of antiferromagnetism should spill over into the metal-superconducting part of the phase diagram. On a local scale, at least, the antiferromagnetic coherence length should exceed, by perhaps several times, the Pippard coherence length of the pairs. The evidence is that they are equal or even reversed in magnitude.<sup>[92]</sup> The accommodation of these data pertaining to the superconducting wavefunction symmetry and the very short range magnetic order are the principal challenges facing the various spin-mediated pairing models.

As mentioned above, Anderson<sup>[77]</sup> was the first to exploit the nearby antiferromagnetic phase in his "resonating-valence-bond" (RVB) picture, essentially involving a Bose condensation of pre-existing normal state charged quasiparticles with unit spin ("holons"), bound to chargeless spin-1/2 solitons ("spinons") as a model for high- $T_c$  superconductivity. If one starts from the "large"  $U/t$  limit, a modification of the Hubbard model can be made which makes the appearance of the band motion of the carriers against the spin background of the  $\text{Cu}^{2+}$  spins more explicit, the so-called " $t$ - $J$ " model,<sup>[93]</sup> where  $J$  is the usual Heisenberg exchange interaction. This new Hamiltonian itself has a rich variety of solutions, including RVB. Recently, Laughlin<sup>[94]</sup> has made an interesting extension of RVB using concepts borrowed from fractional quantum statistics, sort of a half-way house between fermions and bosons, found useful in treating the fractional quantum Hall effect in semiconductors. His model predicts a gap in the quantum spin liquid (perhaps already seen in the inelastic neutron scattering mentioned above?) and a ground state with chiral symmetry (handedness). In terms of the normal state, one would expect the absence of the usual metallic Fermi surface if quantum spin liquid theories apply. Here the high transition temperatures and upper critical fields involved, perversely frustrate attempts to directly use the usual magneto-oscillatory measurement tools, e.g. de Haas-Shubnikov, which require the restoration of the normal state at sufficiently low temperatures in order to

reduce carrier scattering. These theories also predict the universally observed linear temperature dependence of the resistivity in superconducting copper oxide perovskites.

Some experimental support aside from a linear  $\rho$  vs.  $T$  plot for RVB-like models can also be found. One might expect the normal state of a Fermi liquid to contain spin fluctuations, which would not be characteristic of the RVB state. If so, then the normal state thermopower, which reflects the entropy associated with these fluctuations, when measured in magnetic fields high enough to saturate the  $\text{Cu}^{2+}$  spins, should be quenched. It is found that little change occurs in the magnitude of the thermoelectric power of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  single crystals in a field in excess of  $10 T$ ,<sup>[27]</sup> consistent with an RVB framework. In addition, the usual modification of the single particle density of states above  $2\Delta$  is not observed in the far-IR spectrum,<sup>[60]</sup> inferentially consistent with RVB.

It has been difficult to make direct experimental contact with the quantum spin liquid theories, largely because they are still in a period of development and change. Originally, no gap and unit charge for the superconducting state were predicted—later variations now contain a gap and paired charge, in common with the Fermi liquid models. Hopefully, continued work will reveal clearly distinctive features, perhaps like a chiral ground state, that can be probed experimentally. On the other hand, it may turn out to be impossible to differentiate sharply between a Fermi liquid or quantum spin liquid formalism from experiment, inasmuch as both theories are derived from limiting extremes of  $U/t$  in the Hubbard hamiltonian, and reality may lie somewhere in between.

In this Section I have dealt solely with models of high-temperature superconductivity which rely in one way or another on spin interactions. It must be said that other points of view have been proposed. There is not space to deal with all of them—I will just draw attention to one. It has been suggested that extremely strong coupling could arise from carriers pairing through a coherent plasmon-phonon interaction.<sup>[95]</sup> This picture depends on the unusual plasmon dispersion properties in two dimensions, noting that there are low-momentum acoustic plasmons present, not existing in 3D, which can now couple to the carriers along with phonons, to mediate pairing.

Mentioned previously was one experimental result which seems explainable only in terms of a Fermi liquid model. This is the dependence of the  $T_c$  on carrier concentration. Recently, the electronic phase purity of one class of materials,  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ , used to obtain this dependence has been called into question. Harshman, et al.,<sup>[96]</sup> point out there is strong evidence that  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$  is only electrically homogeneous near  $x = 0.15$ , the Sr concentration which gives the maximum  $T_c$ . Their argument is based on the fact that a rapid drop in Meissner fraction is observed as one departs from this optimum Sr doping level. Such behavior is also often observed in other high-temperature superconductors as the carrier concentration is varied away from the value giving the highest  $T_c$ , e.g.,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  as oxygen is



taken out. Additionally, the range of doping resulting in discernible superconductivity in  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$  exists only over a narrow range of Ce concentration.<sup>[125]</sup> There have been other long-standing indications that electronic inhomogeneities may be present when carrier or doping concentrations depart from the optimum level. For example, the width of the resistive transition seems almost always narrowest at the highest- $T_c$  for a given material system. Moreover, as the doping level decreases, an upturn in the gradient of a  $\rho$  vs.  $T$  plot appears as the superconducting transition is approached. This is sometimes explained as a localization effect, but it is also well known that inhomogeneous mixtures of insulating and conducting phases can give the same result. It is also interesting to note that as  $x$  increases from 0.15 in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$ , the normal state  $\rho$  vs.  $T$  relationship is no longer linear,<sup>[123]</sup> and is more like that found in  $\text{La}_4\text{BaCu}_5\text{O}_{13+y}$ , which could be taken as a sign of increasing 3D character in the electronic properties of these samples.

Could it be that there is really only one single carrier concentration, designated as  $x_c$  in Figure 8, which yields high-temperature superconductivity? Such a picture would accommodate the reduced Meissner fractions observed at any other point, but why would the  $T_c$  apparently change? Perhaps what we are seeing at all other concentrations are the effects of granular superconductivity. One could anticipate that on the scale of the very short coherence lengths indigenous to high- $T_c$  materials ( $\xi \approx 20 \text{ \AA}$ ), difficulties might arise in achieving, on that length scale, uniform doping, especially at low concentrations. Thus, a non-optimally doped material may consist locally, again on the scale of  $\xi$ , of relatively isolated small optimally doped regions, or, in essence, a granular superconductor. Figure 8 indicates  $x_c$  to be 0.25, which would be the case for the 1-2-3 compounds. There is a reasonable possibility that 0.25 could be a universal value for all copper oxide perovskites. In the La and Nd 214 systems, where the highest  $T_c$  is obtained at doping concentrations of around 0.15–0.18, undetected oxygen excess in the former and oxygen depletion in the latter could raise the actual carrier concentration to nearer 0.25. Given the questions and speculations just made, and the implications for theory, the role of carrier concentration in high-temperature superconductivity needs re-examination.

I close this Section on theory with a question: What actual values of transition temperature do the current theories predict? This is an reasonably fair thing to ask a theoretician, and the answer is  $T_c = 0 \text{ K}$ ! All present theories exploit the 2D nature of the CuO planar structure, but there can be no phase transitions of continuous symmetry, including superconductivity, at finite temperature in two dimensions. However, the situation is saved because in lower dimensions, phase fluctuations are extremely broad and can be stabilized at finite temperature via very small 3D interactions. Nonetheless, it is the interaction between CuO planes which gives rise to finite transition temperatures. How this coupling may be affected by different copper oxide perovskite

structures has received almost no attention.<sup>[97]</sup> All other things being equal between materials, such as pair coupling strength and characteristic boson temperature, the actual value of the  $T_c$  is set by the interplanar interaction.

## 5. Thin Films

Thin film activity forms its own separate sub-set of high- $T_c$  research quite apart from the study of bulk properties and the basic nature of high- $T_c$  superconductivity itself. This is because many projected applications must employ films and the economic incentive, and support, is easiest to rationalize in this area. Table 1 indicates that the number of thin film publications is rising rapidly compared to bulk, and this is true for patent activity as well. The quality of high- $T_c$  films has advanced rapidly since the first 1-2-3 layers were successfully deposited in early 1987. I do not have space here to review the entire topic and will just dwell on a few emerging developments. For further information, there have been several recent reviews posted in High- $T_c$  Update as well as articles in professional magazines and newsletters.<sup>[98, 99]</sup>

Methods of depositing metal oxide films of any type have always been tricky in that retaining oxygen in the proper stoichiometric amount in the resulting film is difficult. Usually, some sort of post-annealing in an oxygen atmosphere is required. This remains the situation for high- $T_c$  films produced by standard methods such as vacuum deposition and reactive ion sputtering. These methods have been refined and, when used in conjunction with appropriate post-annealing, yield films of 1-2-3, bismuth and thallium compounds with superconducting properties approaching, and in some aspects, like critical current, exceeding bulk materials. However, these fabrication techniques are still awkward for oxides, and recently a new approach, laser ablation, is starting to be used. Here, the source target is stoichiometric bulk material which is subject to bombardment by an intense focused laser beam producing a roughly equally stoichiometric plasma subsequently condensed on a suitable substrate. Excellent results surpassing those from more conventional deposition techniques have been obtained at Bell Communications Research, but only for very thin and small area films. These are presently the major limitations to laser ablation but it will be interesting to see if ablation techniques will eventually supplant more traditional methods of high- $T_c$  thin film deposition.

Substrate properties dominate in enabling the production of high-quality films in at least two ways: 1) by influencing the film microstructure and crystallinity, and 2) by being sufficiently robust to withstand the high post-annealing temperatures usually required. Right now, the best substrates, e.g., strontium titanate, are expensive and impractical for large area film production. They can be difficult to integrate, or are incompatible with other materials such as semiconductors, where the high dielectric constants of these ferroelectric substrates can present problems. Diffusion of sub-



strate elements into the film at the current processing temperatures required,  $\approx 600^\circ\text{C}$  at best, remains a major constraint on the choice of substrate material. Lowering of the substrate temperature is one of the principal challenges in this field today, and perhaps new deposition techniques, such as laser ablation, will help ameliorate this problem.

I pointed out earlier that current research in flux dynamics suggests the intrinsic zero resistance state in high- $T_c$  materials, especially any with higher- $T_c$  if indeed discovered, might be quite fragile. On top of this is the question of the transport critical current ( $T_c$ ) at a given temperature and applied magnetic field. In practice,  $J_c$  is always determined by extrinsic material conditions, and for this reason one should not be overly pessimistic concerning the findings from flux dynamics studies for the present materials. The nature of the pinning centers is one of the major open issues not only for thin films, but bulk material as well. In the old low- $T_c$  materials with reasonably large coherence lengths, pinning could occur on dislocations or any other imperfection with a length scale of the order of  $\xi$ . In high- $T_c$  compounds, however, pinning might be occurring on point defects due to the extraordinarily small values of  $\xi$ . This could, in principle, result in greater flexibility to "engineer" high values of transport critical current through implantation techniques.

The rapid increase in thin film development represents one of the real bright spots for potential high- $T_c$  applications. Critical currents in zero applied magnetic field exceeding  $10^6\text{ A/cm}^2$  are now being routinely obtained. Much progress has been made in achieving smoother surface topographies, a critical requirement for microwave cavity and strip line applications. The same photolithography and ion milling methods used for circuit patterning in semiconductor technology have been applied to high- $T_c$  films with great success. In addition to application prospects, high- $T_c$  films have also proved essential in a number of purely scientific investigations, especially tunneling experiments.

## 6. Applications

Exceedingly high expectations were raised in the public mind at the time of the initial high- $T_c$  discoveries regarding their potential application, both temporally and in magnitude. In the euphoria of the year one A. B.-M. (after Bednorz-Müller), even scientists with wide experience in the field of superconductivity were guilty of broadly misleading statements. Two, three and four A. B.-M. have been years of sobering up. Forgotten had been the fact that for many past proposed applications of superconductivity, liquid helium refrigeration was never a problem. Digital logic technology in high-speed computers is an excellent example. Superconductivity above the boiling point of liquid nitrogen offers no significant advantages in performance for digital Josephson devices; in fact, there are a number of distinct disadvantages to operation at higher temperature, and one is better off for

this particular application using conventional materials such as Nb and Sn. Moreover, the task of preparing massively-replicated micron-scale Josephson logic with low individual device margin limits has up to now proved to be a show-stopper for this technology even using these traditional metals, yet those past difficulties seem almost trivial when one contemplates trying the same feat with ceramic perovskites. One can safely say that, if superconductivity using low- $T_c$  materials had offered a clear and significant cost/performance advantage over current, or even projected, semiconductor and magnetic technologies, it would have already been applied commercially to computers by somebody somewhere today. There is a hard lesson here that is often not taught to young science and engineering students as they enter a career in industrial technology, and sometimes not learned at all. The most important parameter in technology is not switching speed, or critical temperature, or component density ... it's cost normalized to performance. Frequently forgotten is that any emerging technology is inevitably taking aim at a currently well entrenched one, and one that presents a moving target as well, especially if it is earning large corporations billions of dollars per year in revenue. These institutions reinvest this income in extensive R & D programs, hiring the best talent, to prolong as far as possible the lives of their most profitable technologies. This is not to say that all promising new and emerging alternatives should not be fully explored, but few will actually break through to the market, particularly the first time around. One should be continually prepared for disappointment.<sup>[100]</sup>

Added to the past difficulties encountered in applying the old low- $T_c$  materials are some new ones indigenous to high- $T_c$  compounds. The task of processing and integrating a non-malleable ceramic material, as compared to traditional metals, difficult enough themselves, seem sufficiently formidable, but there have also arisen indications that fundamental limits on attainable critical currents might exist, as discussed in Section 4. These concerns, along with other reappraisals of the prospects of high- $T_c$  technology, have given rise to a certain amount of public questioning. A recent article by *Robert Pool* in *Science* asked, "Superconductivity: Is the Party Over?"<sup>[101]</sup> I will explore this question below. Is the party really over and has the band gone home?

I start by returning to the discussion dealing with the integration of superconductivity with conventional computer technology. At first sight, it might seem advantageous to have superconducting transmission lines between active elements on a chip—after all, zero resistance would imply no pulse shape distortion. It turns out that the major performance aspects of these transmission lines are determined by their inductance and capacitance, whereas the resistive component is dominated by the impedance characteristics of the active elements themselves, especially if they are CMOS devices. To truly utilize the benefits of a zero resistance transmission line in CMOS logic, which is seen as the emerging dominant semiconductor technology, would require the use of appropriate impedance matching devices, thus increasing



overall circuit complexity. There does appear to be one window of opportunity opened by the advent of high- $T_c$  materials. This is in the area of high-end packaging to interconnect densely integrated logic modules, a function currently served by large laminated copper printed circuit boards of the order of one square meter in size, containing nearly 20 kilometers of wiring. Here the distances involved, with their attendant large resistance, might justify the use of patterned superconducting films along with the additional impedance-matching circuitry that would be needed. However, most importantly, since future supercomputer technology will almost certainly utilize liquid nitrogen cooled CMOS, packaging employing high- $T_c$  printed circuitry could piggyback on the same refrigeration system. Nevertheless, a formidable amount of work needs to be done even to assess the feasibility of such a concept, and to approach the current densities and reliability provided by the present technology.<sup>[102]</sup>

Computer applications, like those discussed above, rely mainly on thin film embodiments of high- $T_c$  materials. Fortunately, as mentioned in Section 5, there has been encouraging progress in this area. However, there are a number of applications which use superconductors in bulk form, mainly in the shape of wires, in which high- $T_c$  materials could potentially have an impact. Primary among these are long-distance power transmission and high-field electromagnets. It took over 20 years to enable the economic manufacture of low- $T_c$  wires, a particularly uncomfortable reflection when one recalls that high critical currents at high magnetic fields for NbTi ( $J_c = 100,000 \text{ A/cm}^2$ ,  $H = 10 \text{ T}$ ), the principal commercially available superconducting wire at present, and Nb<sub>3</sub>Sn were achieved on a laboratory scale almost immediately after their discovery, as opposed to the present situation for the new high- $T_c$  compounds. The manufacture of superconducting wire, regardless of the particular superconducting material, requires the assembly of thousands of filaments of the superconductor in parallel clad with a normal metal like copper. Now try to put in perspective our past experiences in bringing NbTi from discovery to the market, with the task of eventually manufacturing, in high yield at low cost, several hundred meters of continuous wire from a brittle material cousin to that in your dinner ware ... and for which gold or silver tubing is the only presently known stable cladding! Achievable critical currents, according to recent literature and news reports, sit at around  $5000 \text{ A/cm}^2$  for 10 meter lengths in zero applied magnetic field. Some isolated reports exist of  $50,000 \text{ A/cm}^2$  as determined by pulse measurements on laboratory scale samples. In all cases,  $J_c$  degrades rapidly in a applied magnetic field, to at best 50% of maximum in a 0.5 T field, due to grain boundaries and the natively highly anisotropic properties of copper oxide high- $T_c$  materials. The way matters stand right now regarding laboratory scale critical currents in high- $T_c$  wires is that they are approaching practical levels for power transmission, but are a long way from the specifications required for high-field superconducting magnets. It will be a very long interlude indeed before high- $T_c$  wire becomes competitive with current

low- $T_c$  products, whose cost is also bound to decrease in the meantime.<sup>[103]</sup>

Limited space does not allow a complete discussion of superconducting wire applications here. It is enough to point out that even if all problems regarding critical properties, large scale manufacture, and cost of high- $T_c$  (perhaps even room temperature) wire were solved, its actual application would involve peripheral political, economic and social factors of greater magnitude than the mere technological achievement. For example, a decision to implement the wide-scale installation of a superconducting transmission line network would be governed principally by present capital investment in the existing power grid, its efficiency, and the current and projected cost of source energy, as opposed to the cost of replacing it by the new technology. The solution to this economic equation would vary from society to society. It is doubtful that First World nations would find such replacement attractive at any point in the foreseeable future. On the other hand, some Third World countries of large land area with minimal power distribution facilities in place may find superconducting technology a reasonably economic growth path.

Economic and social arguments similar to those just put forth for high-power transmission lines can be made for wire applications in superconducting magnets. One often hears that liquid nitrogen refrigerated high- $T_c$  superconducting magnets would make more widespread the use of a truly marvelous medical diagnostic tool, the nuclear magnetic resonance imaging scanner, said to have at least halved the requirement for exploratory surgery in hospitals where installed, and which currently employs low- $T_c$  technology cooled by liquid helium. However, there are already many such instruments in use in hospitals all over the world, including some in very poor nations. The helium refrigerant is usually recovered and recycled with rapid and efficient liquifaction machinery. All in all, by the time practical high- $T_c$  superconducting magnets become available, the world market for this particular kind of instrument may have been saturated.

With respect to the application of high-temperature superconductivity to electromagnets for surface transportation, competing socio-economic and technical factors are also encountered. A preliminary study by the electric car division of the Ford Motor Company indicated only minimal opportunity for the personal locomotion industry, primarily because of the high efficiency of current electric motors and a superior energy/weight ratio projected for storage battery technology.<sup>[104]</sup> The use of superconducting electromagnets for levitated trains has been studied for some time, the most serious effort having been undertaken in Japan.<sup>[105]</sup> However, the major capital cost involved, given that appropriate land right-of-ways already exist, is in the highly precise track system that must be built and maintained to accommodate speeds in excess of 200 mph. Moreover, in a country such as the United States, a well-established and relatively convenient network of freeways and airports sustain the principle



portion of public and private travel. There is also sufficient space in which to build more as needed. This is not to say better and faster intra- and interurban transportation is not urgently required; however, this need can be more readily met with more conventional technology rather than with high-speed maglev trains. For example, it would be possible to service the Boston-to-Washington Northeast Corridor with an improved wheel-and-rail system capable of speeds up to 180 mph. Finally, it is worth noting that a number of scientific instruments utilizing superconducting magnets, parasitically make use of the liquid helium refrigeration to cryopump the high vacuum chambers of the unit, a function which would become less efficient using liquid nitrogen.<sup>[106]</sup>

Thus, the prospect of the huge markets once forecast for high- $T_c$  materials does not seem likely on closer and calmer scrutiny. On the other hand, there should be plenty of opportunity to exploit high-temperature superconductivity by small entrepreneurial companies seeking niche applications in various electronic areas. The first products thus to emerge are likely to have more social than economic impact, in that they will indirectly affect areas like medical research, rather than overturn entire technologies currently producing enormous revenue returns. For example, dc SQUIDS made from thallium 2223 films<sup>[107]</sup> are, at least on a laboratory scale, approaching commercially available devices fabricated from low- $T_c$  materials in their sensitivity and noise properties. The availability of high- $T_c$  SQUIDS may enable significant advances in the in vivo detection of minuscule magnetic fields emanating from nerve tissue. Here, the proximity of the detector to the magnetic field source is an important factor which is enhanced by the simplicity of liquid nitrogen refrigeration and subsequent insulation requirements as compared to liquid helium. In general, these considerations would apply to any situation requiring the detection of low magnetic fields where convenience of SQUID refrigeration was a prime factor, such as geological exploration for oil reserves in remote areas, antisubmarine early warning stations, or outer space, where, in fact, "room temperature" is below that of liquid nitrogen. Other examples of small, but important applications, that high- $T_c$  materials should enable in the short-term are compact, conveniently maintained voltage standards based on the Josephson effect, and low-loss, high-Q microwave cavities and waveguides.<sup>[108]</sup>

My discussion in this Section may strike the reader as very pessimistic, and even iconoclastic in view of early predictions, regarding the future for applications of high- $T_c$  materials. Not at all—it is just that a large dose of realism needs to be injected into current popular thinking and expectations. An appropriate perspective is given in the thoughtful and insightful review, *Superconductors: The Long Road Ahead*, by *Foner and Orlando*,<sup>[109]</sup> of the prospects for, and problems involved in, applications of high-temperature superconductivity. Nonetheless, they sum up with the following thought: "Despite the many challenges on the road to practical superconducting technologies, the recent scientific breakthroughs in the field remain extremely important. They

are the prelude to the continuing development that will make widespread superconducting applications possible ... but a great deal remains to be done." Certainly it would be very foolhardy to propose at this time that these discoveries are bound to make great changes in the way we live, but it would be even more of a mistake not to put in the hard work to find out if they indeed will. The party isn't over yet ... the band is only out on a break. We will have to wait and see what kind of music will be played in the next set.

## 7. Conclusion

To conclude, high-temperature superconductivity in copper oxide perovskites remains, in my opinion, by far the most exciting frontier of condensed matter physics, and will likely be so for some time to come. The continued arrival of new materials is a sure sign of vitality. There is no question that much outstanding science, having an impact not only on the field of superconductivity itself, but on almost all other aspects of solid state physics and materials science, has already been accomplished. But there is also no question that there are many unsolved problems remaining that will tax the finest of our scientific minds and resources promising lots of fun. In short, the impact that high- $T_c$  superconductivity has had and will continue to have on our basic understanding of condensed matter science is awesome.

However, an assessment of the impact on potential large-scale practical applications, especially in the short-term, is more uncertain. It is most likely that the first commercialization of high- $T_c$  materials will come in small electronic devices targeted at niche markets, and that the material technology will be thin film rather than bulk.

Finally, I would like to mention one aspect of the new discoveries that was totally unanticipated—the introduction of the subject of superconductivity as part of the experimental science curriculum at the primary and secondary school level worldwide, and the consequent renewed interest of youth in science as a whole by allowing them to participate directly in an activity at the forefront of modern research. The new high- $T_c$  superconductors, by virtue of their ease of synthesis and low-cost refrigeration, are readily available to schools in nations at every economic level and provide excellent tools with which to teach, not only superconductivity, but fundamental principles of solid state chemistry and the physics of electricity and magnetism. A number of kits and teaching aids have become available for classroom use ... and it all began with the fabrication and testing by magnetic levitation of 1-2-3 by a high school chemistry class in Gilroy, California,<sup>[110]</sup> in late May, 1987, four months before *Bednorz and Müller* were awarded the Nobel Prize in physics for the basic discovery! Since then, thousands of students throughout the world, not only in large countries, but also in small, have repeated similar experiments as science projects. Perhaps, instead of any of the possibilities we have discussed here, the truly large applications of high- $T_c$  technology will



occur in entirely unforeseen areas uncovered by this soon-to-emerge generation of young scientists as familiar with superconductivity as the present is with lasers and computers ... and hopefully matching their creative accomplishments as well.

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