

Room Temperature Superconductors

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Received November 1, 1994

Superconductivity is a unique state of matter. Below a critical temperature, T_c , a superconductor exhibits no resistance to the flow of electrical current. Another special attribute of a superconductor is its giant diamagnetism. Superconductors also show unique junction properties. The superconducting state is destroyed if either a critical current (J_c) or a critical magnetic field (H_c) is exceeded. The unique properties of superconductors can be utilized for a wide variety of applications. Superconducting wire can be used for power transmission and in generators, transformers, motors, and magnets. A growing use for superconductors is for energy storage devices termed SMES for superconducting magnetic energy storage. Thin films of superconductors are used in several microwave applications. Devices based on superconducting films also give us our most sensitive detection of magnetic fields and may give rise to a new generation of faster computers. Superconductors are used to levitate trains and to produce frictionless bearings. These are just a few of the many possible applications for superconductors, but the actual use of these amazing materials is limited by the fact that they must be cooled to very low temperatures to become superconducting. Currently, the highest T_c for any superconductor is about 135 K at 1 atm. If the Holy Grail of room temperature superconductivity could be achieved, the impact on our lives could be enormous. However, a useful room temperature superconductor for most applications must possess a T_c somewhat above room temperature and must be capable of sustaining superconductivity in the presence of magnetic fields while carrying a significant current load.

Recent discoveries with superconductors increase the likelihood that chemists will play the leading role in synthesizing new materials which are superconducting at room temperature. The high-temperature superconductors are thermodynamically unstable at room temperature and at temperatures where they exhibit superconductivity. Their kinetic stability is generally good under these conditions, just as it is for many other metastable materials such as diamond and common glasses. Most of chemistry is actually based on metastable compounds, a fact that apparently does not occur to many chemists. A chemist's interest in synthesizing a particular compound is usually unrelated to whether or not the compound might represent a global minimum in a particular system. Chemists' lack of concern about the true thermodynamic stability of compounds is well illustrated by the fact that organic chemistry is not considered to be based on phase equilibria in systems

containing carbon, hydrogen, oxygen, and nitrogen. Chemists have great expertise in the synthesis of metastable compounds, that is, trapping a system in some local, rather than global, minimum. However, it appears that this expertise may be pushed to new limits to produce the elusive room temperature superconductor. New synthesis strategies will likely be required. The biggest barrier to achieving this Holy Grail is, however, that we lack a fundamental understanding of the ingredients necessary to produce superconductivity at room temperature. Lacking such understanding, we can only assume that some of the characteristics of the copper oxide based superconductors provide the clue to obtaining a room temperature superconductor. We will return to the subject of just what characteristics we might seek for a compound to be a room temperature superconductor.

Background

Superconductivity was discovered¹ by accident in 1911. Mercury developed this property when it was cooled in liquid helium. The possibility of superconductivity had not been anticipated, and its existence was initially greeted with great skepticism. Once the phenomenon of superconductivity was accepted, it was sought in many metals (Figure 1). A theoretical understanding of superconductivity came very slowly. It was not until 1957 that a satisfactory theory was set forth.² Although this BCS theory was met with some initial suspicion, it was soon generally accepted. In this theory, conduction electrons are attracted to one another to form singlet pairs (Cooper pairs). A critical test of useful theory lies in its ability to make significant predictions. The BCS theory passed this test admirably. Starting with BCS theory, Josephson³ predicted unique junction characteristics for superconductors. Such junction properties were then demonstrated by Anderson and Rowell at Bell Labs.⁴ Despite the many successes of BCS theory, it has not been very useful in the search for high-temperature superconductors. Once superconductivity was found in a particular system, BCS theory did, however, offer some guidance on optimizing T_c in that system.

According to BCS theory, T_c could be increased by increasing the density of states at the Fermi level or by decreasing phonon frequencies. Unfortunately, increasing T_c by either method tends to lead ultimately to an instability. Increasing the density of states at the Fermi level is a route to localization of the electrons in these states. Indeed, we frequently

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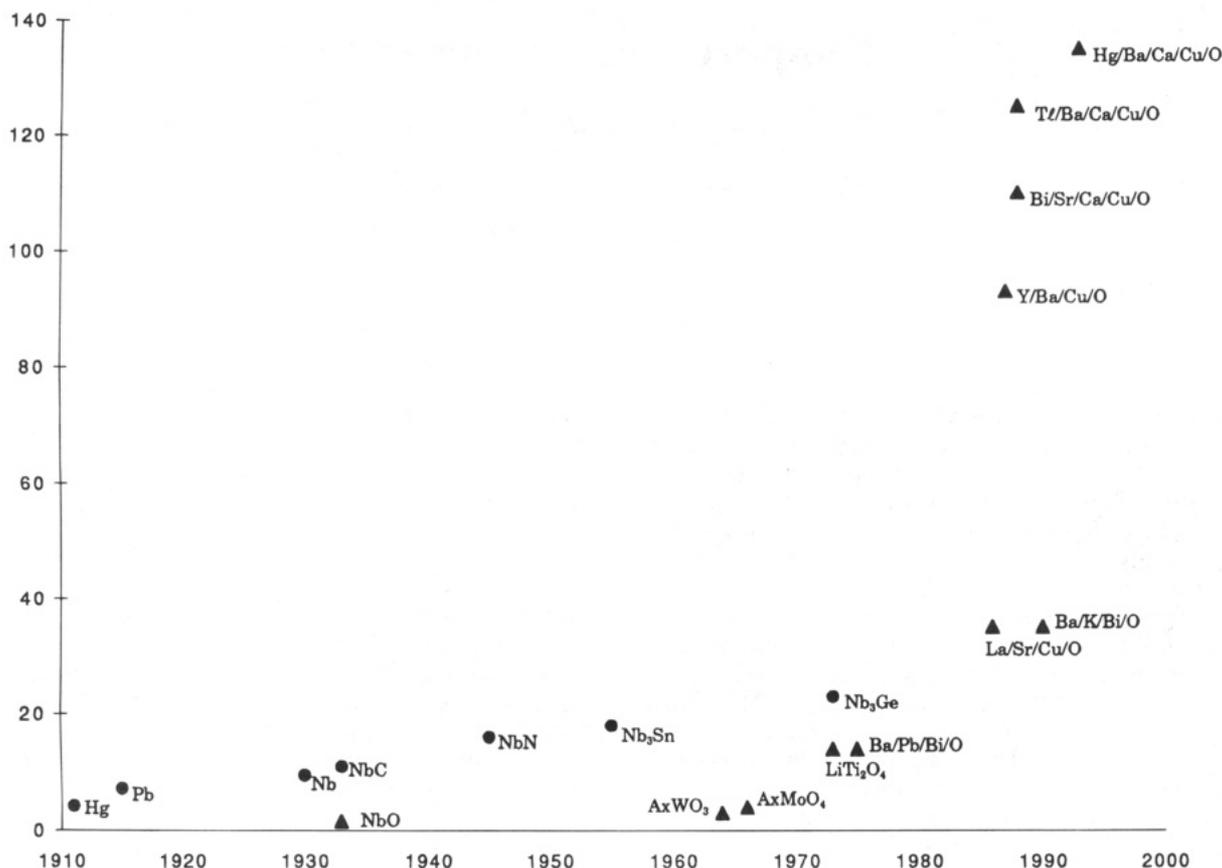


Figure 1. Superconducting T_c (K) vs historical time.

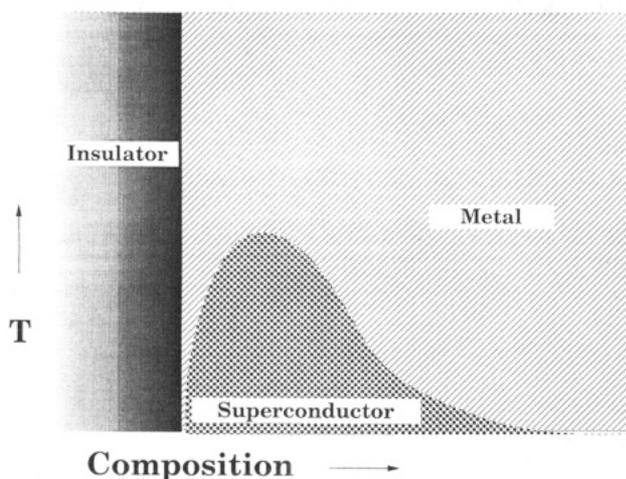


Figure 2. Schematic phase diagram showing the occurrence of superconductivity at the boundary between regions of metallic and insulating behavior.

find superconductors in systems where small variations in composition cause a shift from insulating to conducting properties (Figure 2). Superconductivity occurs in the metallic region as the metal–insulator boundary is approached. At first, T_c increases, consistent with an increase of electron density at the Fermi level. Then, superconductivity abruptly disappears with the onset of electron localization. The same forces causing T_c to increase ultimately result in the destruction of superconductivity. The conduction band splits into a lower filled band and an upper empty band. This splitting can be driven by electronic factors (density of states at the Fermi level or correlation effects) or by a lattice instability (soft phonons).

Increasing T_c through softening of phonon modes is conceptually different from increasing the density of states at the Fermi level. The ultimate result, however, tends to be the same because the softened phonons lead to a displacive phase transition with concomitant localization of electrons. A path to higher T_c suggested by BCS theory is that we frustrate the transition to the localized state. This approach appears to remain valid today despite the fact that a theory is lacking for the high-temperature superconductors. Thus, even before the advent of the cuprate superconductors, some had concluded that metastability was a characteristic of high-temperature superconductors. A few days before his untimely death, Bernd Matthias announced⁵ that he would renew attempts to synthesize all of the compounds he had failed to prepare as candidate superconductors. He and others⁶ were convinced that high T_c and metastability were intimately connected.

There was also an unfortunate consequence of predictions from BCS theory. Reasonable assumptions led to the conclusion that phonon-mediated BCS superconductivity would not exist above 30–40 K. Fortunately, this conclusion did not dissuade everyone in their search for superconductors with higher T_c .

Oxide Superconductors

Although some oxides, such as ReO_3 , are excellent metals, oxides are better known as insulators than as conductors. Most researchers did not consider oxides as fertile territory for the discovery of new supercon-

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ductors. Superconductivity was observed⁷ at about 1.5 K in NbO in 1933, but this received little attention at a time when other niobium compounds were known to be superconducting at temperatures near 10 K. During the 1960s, several new oxide superconductors were discovered, but again T_c 's were low relative to those of the metals and intermetallic compounds (Figure 1). Then in the 1970s, oxide superconductors were found with T_c 's of about 13 K. This was considered high-temperature superconductivity in those days! In the 1980s, oxides surpassed metals for the record high T_c . Raising T_c from 4 to 23 K required 60 years. In less than 10 years, T_c was raised from 23 K in Nb₃Ge to 135 K in HgBa₂Ca₂Cu₃O₉.

The cuprate superconductors are all based on CuO₂ sheets where the oxidation state of copper is close to 2, but it must not be exactly 2. Compounds with the CuO₂ sheets are antiferromagnetic insulators if the oxidation state is 2 or very close to 2. The cuprate superconductors are all mixed-valent compounds, most of the type Cu(II,III) but some of the type Cu(II,I). The charge on the CuO₂ sheets is thus always negative. This must then be balanced by positive charge between CuO₂ layers, and there are many ways in which this can be accomplished. By adjusting the copper mixed valency, nearly all the compounds containing CuO₂ sheets have been induced to become superconducting.

There is no consensus on the theory for superconductivity in cuprates. Initially, some felt that this must be an entirely new type of superconductivity. Instead of the usual Cooper pairs of electrons, the superconducting electrons might be single electrons or a triplet pair. Experiments quickly established that the superconducting electrons in cuprates are singlet pairs just as had been earlier concluded in BCS theory. Indeed, the basic tenets of BCS theory still appear to be valid. While in conventional superconductors the attractive interaction between electrons is phonon mediated, it is believed that something other than, or in addition to, phonons is providing the required electron-electron attraction in the cuprate superconductors.

Metastability

Strong evidence for the metastability of cuprate superconductors came first with YBa₂Cu₃O_{6+x}. The synthesis of this compound proceeds through two steps. First, the basic structure is established at a composition where x is much less than 1. This compound is usually prepared under true equilibrium conditions, but the compound prepared under those conditions is not superconducting at any temperature because the value of x is too low. Secondly, x in YBa₂Cu₃O_{6+x} is increased through an oxidative intercalation reaction. Mixed valence is thus induced in the CuO₂ sheets, and superconductivity occurs up to about 93 K when x is close to 1. All attempts to prepare YBa₂Cu₃O₇ directly failed regardless of temperature or oxygen pressure. Eventually, calorimetry data on the Y/Ba/Cu/O system were obtained.⁸ These results

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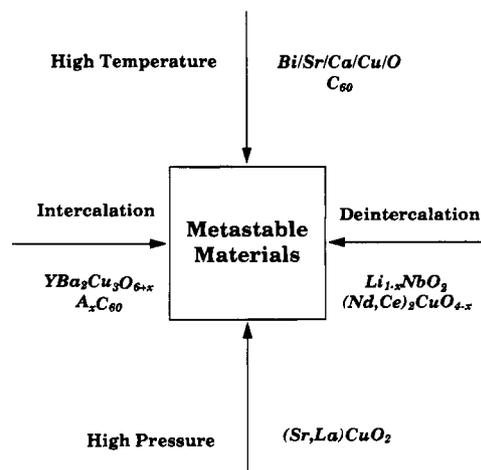


Figure 3. Some of the approaches to preparing metastable superconductors.

confirmed that both YBa₂Cu₃O₇ and YBa₂Cu₄O₈ are metastable.⁹ The case for metastability in cuprates with higher T_c is even more compelling.

There are many ways to synthesize metastable compounds (Figure 3). The intercalation approach just mentioned is a method commonly used by solid state chemists. Intercalation of MoS₂ leads to many interesting superconductors.¹⁰ One can also use deintercalation. The first application of this technique to the oxide superconductors was with the tungsten bronzes.¹¹ The T_c of Rb_xWO₃ was increased by decreasing x . Later semiconducting LiNbO₂ was converted to superconducting Li_{0.5}NbO₂ by a deintercalation reaction.¹²

Quenching from high temperature or high pressure is very commonly employed to produce metastable materials such as glass and diamond. The approaches to the metastable materials indicated in Figure 3 can, in principle, all start from a point of true thermodynamic equilibrium. Subsequently, the conditions are changed or the composition is changed under non-equilibrium conditions. The net result in any of these cases may be a metastable material.

The intercalation and deintercalation reactions are just two of many approaches that chemists use to coax certain elements to form structures which do not represent global thermodynamic minima. Sometimes, we use different catalysts to direct the same reactants to different local minima. Frequently, we use different reactants to make compounds with the same composition but with different structures in different local minima. For the oxide superconductors, the structure produced can depend on how that composition is nucleated as a solid. The usual structure of SrCuO₂ does not contain CuO₂ layers. However, growing SrCuO₂ on a SrTiO₃ substrate can produce a metastable form of SrCuO₂ which does have the CuO₂ layers apparently required for superconductivity in cuprates.

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Table 1. Features of High- T_c Superconductors

metastability
disorder
electrons nearly localized (poor metal)
high covalency
antibonding conduction band (σ^* better than π^*)
mixed valency which includes d^1 , d^9 , or s^1
proximity of 6s or 6p bands
layered structures
pseudotetragonal symmetry
noncubic local environment
light elements present
magnetic interactions

Commonalities and Trends

Current theory provides little or no guidance in our pursuit of room temperature superconductivity. We must, therefore, establish the common features of the superconductors with high T_c . From those features, we can seek out trends which might lead to higher T_c . Although it is a relatively simple task to collect together the common features (Table 1), it is impossible at this time to reach consensus on which features are relevant to obtaining superconductivity at room temperature.

We have already discussed the metastability of high- T_c superconductors. An intimately related feature of these materials is the high concentration of defects which are generally present in such materials. These include cation and anion vacancies and interstitials, antisite disorder, and displacements of atoms from ideal lattice sites including incommensurate superstructures. Although the CuO_2 layers ideally possess square symmetry, this symmetry seems to always be broken by either long-range or short-range deviations of the structure. It, therefore, seems unlikely that a successful theory will be based on the ideal structures usually considered.

It is well accepted that a superconductor must be a poor metal, close to actually becoming a system of localized electrons. Herein lies the biggest problem for producing room temperature superconductivity. Not only is there always something competing with superconductivity, but it appears that the very forces that are used to increase T_c are also driving the system toward localization. The localized state may be a charge density wave, *i.e.*, a disproportionated system. It might also be a magnetically ordered state. In any case, we would like to frustrate the transition to the insulating state while enhancing the forces increasing T_c . One approach lies in the partially disordered lattice common to the high-temperature superconductors. This disorder can frustrate the long-range forces required for localization. Another approach is to make use of lattice symmetry to frustrate the ordered state. Disproportionation of a cation is easy in the perovskite structure, for example, $2\text{BaBi}^{\text{IV}}\text{O}_3 \rightarrow \text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$, because the cubic lattice symmetry need not be destroyed. However, disproportionation of Sn^{II} in SnP with the rock salt structure¹³ is inhibited because it cannot occur without breaking the cubic lattice symmetry.

A high degree of covalency is required. This is simply a statement that there must be adequate

mixing of cation and anion wave functions. A band must contain a significant portion of both anion and cation character if electrons are to be delocalized over the lattice. The metallic conduction in ReO_3 is not the result of direct overlap of cation orbitals. Instead, the conduction band is a $\text{Re}-\text{O}$ π^* band. In the case of cuprates, the conduction band is a σ^* band derived from $\text{Cu } 3d_{x^2-y^2}$ and $\text{O } 2p$ states. In all of the oxide superconductors, the conduction band is antibonding in character. For those with the highest T_c , (Ba,K)- BiO_3 and cuprates, this is a σ^* band.¹⁴

All of the oxide superconductors are mixed-valent compounds. One issue which arises is whether we should be considering the energetics of two or three oxidation states of a given cation.¹⁵ The tungsten bronze superconductors are $\text{W}^{\text{VI},\text{V}}$ compounds. The cuprate superconductors are either $\text{Cu}^{\text{II},\text{I}}$ or $\text{Cu}^{\text{II},\text{III}}$ compounds. However, whether compounds with $\text{Cu}^{\text{II}}\text{O}_2$ layers are metallic or not can be related to the proximity of the $\text{Cu}^{\text{I,III}}$ state relative to the Cu^{II} state. Furthermore, the disproportionated state may be directly related to the electron-electron attraction required for superconductivity.¹⁶ Thus, crucial charge fluctuations in the CuO_2 layers may depend on the momentary coexistence of Cu^{I} , Cu^{II} , and Cu^{III} .

The superconducting cuprates all have structures with CuO_2 layers. The long-range dimensionality may be important. Alternately, this might simply be a reflection of the need for a local symmetry around copper which is not cubic or even close to cubic. Compounds of the type LaCuO_{3-x} can be prepared at high pressure.¹⁷ No CuO_2 layers are present, and the coordination of copper is not square planar. Superconductivity is not observed in LaCuO_{3-x} perovskites at any value of x . This could be due to either local symmetry or lattice symmetry. We do not yet have enough chemistry of mixed-valent cuprates without CuO_2 sheets to answer this question. We should, however, remember that superconducting $\text{Ag}_7\text{O}_8\text{NO}_3$ is cubic with $\text{Ag}^{\text{II,III}}$ on square planar sites.¹⁸

The CuO_2 sheets stack to give structures which always have pseudotetragonal symmetry. However, true tetragonal symmetry seems always to be absent. The $\text{Cu}-\text{O}$ chains in $\text{YBa}_2\text{Cu}_3\text{O}_7$ destroy the tetragonal symmetry. An incommensurate superstructure destroys the tetragonal symmetry in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. Short-range displacements destroy the tetragonal symmetry in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$.¹⁹

It is tempting to conclude that the presence of light elements is an important ingredient of high-temperature superconductors. Unexpectedly high T_c 's have also been found in borocarbides²⁰ and fullerenes.²¹ This could be rationalized according to traditional BCS

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theory on the basis of higher vibrational frequencies for lighter atoms. It is, however, unclear that such a theory pertains to superconductors with the highest T_c .

Cuprate superconductors always contain additional cations. These are required to balance the negative charge of the CuO_2 sheets. They are also needed to establish a desired structure. In the case of the alkaline earths and rare earths, these cations would seem to serve no further role. However, it is the ratios of these cations to oxygen that determine the degree of mixed valency in the CuO_2 sheets. With the exception of Pr, these cations do not have levels close enough to the Fermi level to impact the $\sigma^* \text{Cu } 3d_{x^2-y^2} - \text{O } 2p$ band. When Bi, Pb, Tl, or Hg is incorporated between CuO_2 layers, a T_c enhancement frequently occurs. There is no consensus on the critical role played by these cations. They are all capable of mixed valency. It is possible that charge fluctuations due to mixed valency are present in both the CuO_2 layers and the layers containing Bi, Tl, or Hg. These charge fluctuations might interact in a way that enhances T_c . The systems become more polarizable when Bi, Tl, and Hg are added, and this could be the crucial factor in enhancing T_c . All of these elements possess a 6s or 6p band close to the Fermi level. This will lead to some 6s or 6p character in the $\sigma^* \text{Cu } 3d_{x^2-y^2} - \text{O } 2p$ band. Perhaps this enhances T_c in some way.

Traditionally, magnetic interactions have been considered to be the enemy of superconductivity. Transition metal oxides can be metallic at many different d electron concentrations of a given d shell. However, superconductivity above 4 K occurs only if a d shell is nearly empty or nearly filled. It would appear that the strong magnetic interactions due to several unpaired d electrons always prohibit superconductivity. Despite this case for magnetic interactions inhibiting superconductivity, many believe that the magnetic interactions in cuprates favor superconductivity.

There is one widely accepted correlation with T_c in the cuprates. There is an optimum ratio of oxidation states in these mixed-valent materials. The $\text{Cu}^{\text{II}}/\text{Cu}^{\text{III}}$ or $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ ratio should be close to 5. The exact ratio of oxidation states which gives the highest T_c depends on the system. Those systems giving the highest T_c 's do so at lower $\text{Cu}^{\text{II}}/\text{Cu}^{\text{III}}$ ratios. The Cu–O distances will, of course, correlate with $\text{Cu}^{\text{II}}/\text{Cu}^{\text{III}}$ and $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ ratios. Thus, there will be the expected correlation between Cu–O distance and T_c . Other correlations with T_c have been proposed, for example, with Cu–Cu interplanar distance, Cu–O–Cu angles, and number of immediately adjacent CuO_2 sheets.

Room Temperature Superconductivity

Superconductivity at room temperature will likely require some form of electron–electron attractive force to produce singlet pairs. Fortunately for chemists, we can view this as a real-space phenomenon. In traditional superconductors, the electron–electron attraction and pairing was viewed as occurring in momentum space. In real space, these electrons might be 2000 Å apart. In the high-temperature superconductors, the two electrons making up the Cooper pair may be in neighboring unit cells. Any real-space electron–electron attractive force is now a legitimate starting point, although one which would lead to a singlet pair would seem to be preferred.

The electron–electron attractive force which I have preferred is disproportionation.^{13–15} The disproportionation reactions of Bi^{IV} to $\text{Bi}^{\text{III}}/\text{Bi}^{\text{V}}$ and Cu^{II} to $\text{Cu}^{\text{I,III}}$ give electron–electron attraction to form singlet pairs. Linus Pauling wrote to me as soon as he learned that I had suggested that the electron–electron attraction in oxide superconductors might be related to such disproportionation processes. He had found²² in 1938 that gold in CsAuI_3 was disproportionated into Au^{I} and Au^{III} , and he suggested that substitutions into this compound might also give a superconductor. I agree, but perhaps this superconductivity will require high pressure. It has been shown²³ that, at high pressure, insulating $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{I}_6$ converts to metallic $\text{CsAu}^{\text{II,III}}$. If appropriate $\text{Au}^{\text{II,III}}$ or $\text{Au}^{\text{II,I}}$ compositions can be produced in this perovskite structure, I would expect superconductivity, but I would not predict T_c . Unfortunately, the disproportionation process also tends to give electron localization. The key to room temperature superconductivity may be in defining a new type of electron–electron attraction which does not so readily lead to electron localization.

It may be that we will not be able to define a new type of electron–electron attractive force for our room temperature superconductor. Instead, we will have to become more clever in our attempts to thwart electron localization. There have been many reports of possible superconductivity at temperatures higher than 150 K. If any of these results are actually related to a superconductor in the sample, the amount of superconductor was very small. Such samples are always multiphase with the possible superconducting phase being less than 1% of the sample. There has been no way of determining which part of the sample showed the evidence for superconductivity. Reproducibility from sample to sample has been poor. The evidence for superconductivity in a given sample disappears with time. All of these problems are easy to understand if such superconductors with very high T_c 's are highly unstable. A microprobe technique that could indicate the region of the sample showing evidence of superconductivity would be invaluable.

The rise of T_c in cuprates has been largely the result of empirical approaches and serendipity. For example, attempts to replace Y for La in $(\text{La,Ba})_2\text{CuO}_4$ led to the formation of $\text{YBa}_2\text{Cu}_3\text{O}_7$. Robots have been developed²⁴ which can produce 30 candidate superconductors per hour.

Superconductivity has not yet been induced into cuprate oxyhalides of the type $\text{A}_2\text{CuO}_2\text{X}_2$ or $\text{A}_3\text{Cu}_2\text{O}_4\text{X}_2$ where A = Ca, Sr, or Ba and X = Cl or Br. Mixed valency of the $\text{Cu}^{\text{II,I}}$ type has apparently been introduced into the CuO_2 sheets of these compounds.²⁵ Perhaps the ratio of Cu^{II} to Cu^{I} is not quite right for superconductivity. The added polarizability of the halide ions might give rise to an enhancement of T_c when we eventually produce superconductivity in this class of cuprates. An interesting cuprate oxyhalide superconductor can be produced by intercalation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ with iodine.²⁶ Iodine Mössbauer studies²⁷

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indicate that iodine is present as the mixed-valent I_3^- species. We thus have a compound with apparent mixed valency of Cu, Bi, and I. The T_c of $Bi_2Sr_2CaCu_2O_8$ is, however, only slightly altered by iodine intercalation. It is noteworthy that I_3^- can exist in this compound because Bi^V , Cu^{III} , and even Cu^{II} normally oxidize I^- to I^0 .

Many groups²⁸ are using layer-by-layer deposition techniques to produce new, highly metastable, cuprate structures. Some of these have given indications of superconductivity at 180 K and even 250 K. However, superconductivity at these temperatures remains unverified.

We may have to move away from cuprates to obtain room temperature superconductivity. Some groups are investigating tin chalcogenides and halides. Tin diselenide becomes superconducting at 8 K when intercalated with bis(cyclopentadienyl)cobalt.²⁹ Layered structures such as $(C_4H_9NH_3)_2(CH_3NH_3)_2Sn_3I_{10}$

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show a transition from insulating to metallic conductivity with changing composition, but superconductivity has not yet been observed.³⁰

Before the advent of cuprate superconductors, compounds and alloys of niobium seemed to be the most promising for high T_c . Thus, there have been many studies of reduced niobium oxides. To date, the results have been disappointing. The highest T_c obtained¹¹ for a niobium-based oxide is 5.5 K in Li_xNbO_2 . Perovskite type niobates such as $BaNbO_3$ are metallic, or nearly metallic, but have not been found to be superconducting. Many compounds containing the Nb_6O_{12} cluster have been prepared. Despite their resemblance to the superconductors containing the Mo_6S_8 cluster, none of the niobium oxide cluster compounds prepared to date show indications of superconductivity.

The search for room temperature superconductivity will continue. Many new interesting materials will be discovered on the way. Theory may not help us in this quest, but perhaps the quest for this Holy Grail will provide the clue to a successful theory.

Support from the Air Force Office of Scientific Research is gratefully acknowledged.

AR940072T