

Oxide Superconductors

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This article briefly reviews ceramic superconductors from historical and materials perspectives. It describes the factors that distinguish high-temperature cuprate superconductors from most electronic ceramics and places them in the context of other families of superconducting materials. Finally, it describes some of the scientific issues presently being actively pursued in the search for the mechanism for high-temperature superconductivity and the directions of research into new superconducting ceramics in recent years.

I. Introduction

DURING the long history of electronic oxide ceramics before 1986, even the most astute observer would have found few clues predicting the revolution in materials science and physics that those materials would eventually unleash. Oxide ceramics are an important part of electronics technologies because of their electrically insulating, optical, and dielectric properties, but very rarely for their ability to conduct electrical current. Insulators such as steatite, dielectrics such as SiO_2 and Ta_2O_5 , piezoelectrics such as lead zirconate titanate (PZT), optical materials such as LiNbO_3 , and the transparent semiconductor indium tin oxide (ITO) can be considered as representative of the large class of metal oxides with real and potential applications in electronics technologies. Although such materials are sophisticated and complex when considered from any point of view, their technological usefulness in electronics generally results (with the exception of ITO and a handful of other materials) from their ability to block or highly resist the passage of electrical current and, as an important consequence in some cases, their transparency at optical wavelengths.

These important characteristics of most oxides are related to a fundamental chemical difference between the metallic elements and oxygen: the difference in their electronegativities. These

differences in electronegativity result in semiconducting or insulating materials, with forbidden energy gaps between the highest occupied orbitals in the solid derived from oxygen electronic states and the lowest unoccupied orbitals derived from the metal electronic states. The technical applications of electronic ceramics depend very highly on the materials scientist's manipulations of these energies, the introduction or elimination of defects that alter the distribution of energy states and/or their occupancy by charge carriers, and other factors such as the polarizabilities of the component atoms.

Not all metal oxides are transparent. Transition-metal oxides have been used since ancient times as pigments because of strong optical-frequency localized electronic absorptions between different excited states of the electrons in the transition-metal d orbitals, which lead to color. As electronic conductors, however, i.e., as competitors for copper wire, with few exceptions, they have never been of significant technological interest. Their principal consideration as electrical conductors has come primarily from their stability under high temperature, chemically extreme conditions where metals are not expected to be thermodynamically stable, as, for example, is found in electrodes for magneto-hydrodynamic generators.

This whole picture was stood up side down in late 1986 with the discovery of superconductivity at surprisingly high temperatures in an electronically conducting oxide based on lanthanum, barium, copper, and oxygen. Superconductivity is the passage of electrical current with *zero* resistance below a certain critical temperature (T_c). The best superconductors known at the time, to be described below, were metallic compounds, not ceramics, as one might expect as a consequence of the (no longer obvious) general fact that metals are good electrical conductors and oxides are not. Good superconductors do not have to be good metallic conductors above their superconducting transition temperature, however, and the fundamental characteristics that result in superconductivity at high temperatures in the copper oxides have little to do with any type of conventional understanding of the electronic properties of materials. In fact, more than a decade after their discovery, there continues to be no universally accepted theory for why these materials are superconductors. No one working in the field in the early days could possibly have foreseen that this would be the case after so much work and thought had been devoted to the problem.

All reviews on topics that are the subject of active on-going research are necessarily snapshots in time. The same has been true for reviews of the status of research in high-temperature (high- T_c) superconductivity. Many of the reviews of this topic published in

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Centennial Feature

the past decade are of considerable value, and they are not be duplicated here. The references in those reviews,^{1–10} especially Ref. 1, serve to provide the primary sources for much of the information summarized in the present article. References to more-recent work or work complementary to what is found in those reviews are included here. The occasion of this centennial review series in ceramic materials is used to present a more tutorial and historical perspective of the topic, with strong emphasis on the structural and chemical aspects of the story. Although widely viewed as a revolution in condensed matter physics, it is equally valid to view the breakthrough of high- T_c superconductivity in copper oxides as a revolution in materials science and ceramic materials. The pace of discovery of new materials has slowed from its peak in the late 1980s, making a catalog of the known oxide superconductors and their “history” as understood at the turn of the millenium somewhat longer lived than it would have been a decade ago, and that comprises a significant proportion of this review. In this context, a set of uniform representations of oxide superconductors emphasizing their relation to the important perovskite structure type, in terms of the packing of metal–oxygen polyhedra, is presented.

The scientific issues under study at the present time primarily involve the precise determination of the details of the electronic and magnetic characteristics of the oxide superconductors in an attempt to get at the vexing microscopic heart of the problem of why superconductivity occurs in the cuprates. The appearance of superconductivity at high temperatures in such oxides has revealed a glaring hole in our understanding of the way magnetism and electrical conductivity are intertwined and related in transition-metal-based compounds in general—both an embarrassing and wonderful event in materials science and condensed matter physics. Magnetism and superconductivity continue to be the “Jekyll and Hyde” of oxide superconductors—they are clearly intimately related and may be different sides of the same personality—but, until we catch them directly in the act of changing from one to the other, we may not know exactly what their relationship is. The issues for the nonexpert may appear obscure, but they can be presented in a way that shows why they are interesting, and they are addressed in this review. To understand what a surprise the high- T_c copper oxide superconductors were, a brief summary of the superconducting materials under active research at the time of discovery of the cuprates also is included, as is a description of the oxide superconductors known before 1986—the precursors to the revolution. The progress in materials processing of ceramics and the progress toward the ultimate application of oxide superconductors, topics central to continuing investment in the field, are not reviewed here, because that is better done by experts in that area.

II. Distinguishing Characteristics of Copper Oxides

There are several chemical, structural, and electronic aspects of the copper oxide superconductors that distinguish them from other electronic oxides, even those that are electrically conducting. The great majority of conducting oxides studied in the past have as their basis the motion of electrons in energy bands that are formed from the interactions of the d orbitals of the transition metals present. The individual transition-metal atomic orbitals overlap and interact, forming a band of allowed energy states that is partially filled by the electrons available. The energy states of the oxygens play only a minor or insignificant role, a reflection of the same type of electronegativity difference that results in the bandgap in the majority of oxides. Examples of this type of conducting oxide are compounds such as V_6O_{13} , whose electronic conductivity is essential in its use as a possible cathode in experimental secondary batteries. In the copper oxides, however, the difference in energy between the oxygen and metal orbitals is very small, resulting in electronic energy bands in which the oxygen orbitals play a major role in the vicinity of the highest occupied electronic states. Thus oxygen is as highly involved in the conductivity as is copper, a rare situation in conducting oxides.

The second, and most interesting factor, especially from the physicists' point of view, derives from the electronic configuration of the Cu^{2+} ions that form the basis for the superconducting compounds. The electronic configuration for Cu^{2+} is $3d^9$: nine of the ten available d -orbital energy states are filled. In the Cu–O coordination polyhedra (octahedra, pyramids, and squares) that form in the cuprate superconductors, these energy levels are nondegenerate. The t_{2g} orbitals, which are directed between the oxygen atoms, are at low energy and, therefore, are completely filled with electrons (six). The shapes of the Cu–O coordination polyhedra are such that there are four near in-plane oxygen neighbors and one (pyramidal) or two (octahedral) apical oxygens more distant when present. This makes the energies of the orbitals with “ z ” components (i.e., toward the apices) lower because of lower repulsion from the oxygen orbitals. The result is that the nine-electron configuration has a single unpaired electron in the $dx^2 - y^2$ orbital (Fig. 1b), which points toward the in-plane oxygens. The single unpaired electron carries a spin of $1/2$. This low spin value allows for the possibility of nonclassical (e.g., quantum mechanical) interactions between spins in the solid, which is different from the more familiar case of the spins in ferrites, for example, where the interactions between the larger spins (e.g., spin $5/2$ for Fe^{3+} in Fe_3O_4) can be described by more conventional physics.

In isolated atoms, these orbitals are discrete energy states, but, in solids, where the atoms are close together, the orbitals interact, and the sharp atomic energy states become bands of energies. The similar energy of the O $2p$ states and the Cu $3d$ states leads to the situation shown in Fig. 1(c). The electrons fill half of the Cu $dx^2 - y^2$ -derived band, and the high-energy part of the oxygen-derived band has almost the same energy as the highest occupied copper states. This is more complicated than in the usual electronic oxides, but the complexity continues. This type of picture would predict that Cu^{2+} oxides with the superconducting structure types

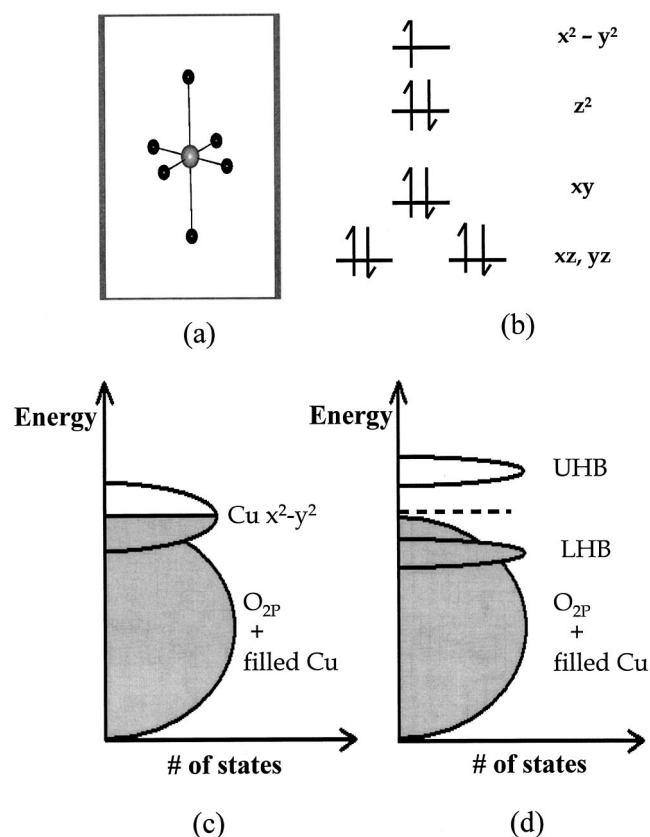


Fig. 1. (a) Cu–O coordination polyhedra found in copper oxide superconductors. (b) d electron configuration for Cu^{2+} . (c) schematic picture of the energy states in copper oxide superconductors, and (d) split $dx^2 - y^2$ band for interacting electrons in cuprates (UHB is upper Hubbard band and LHB is lower Hubbard band).

should be *metallic* conductors (e.g., the electrons are in a partially filled band with available energy states close by). They are, instead, electrical *insulators*. The standard picture for the electronic properties of solids assumes that the electrons are not interacting with each other, only with the underlying atomic lattice. In the copper oxides, this is not the case—they *do* interact. This realization came very early in the history of the field, causing great joy, continuing headaches, and great opportunities for theoretical physicists. It is this unexpected interaction that is one of the reasons why it is taking so long to understand the mechanism of high- T_c superconductivity. This interaction had been observed in other materials before the high- T_c superconductors; it was the focus of the work of Sir Nevill Mott.¹¹ Probably because there was no real compelling reason to determine the details, the ideas were incompletely formed and incompletely explored from the experimental viewpoint before the advent of high- T_c superconductors.

The interaction between electrons is greatest in half-filled bands, which is exactly the case for the cuprates. The addition of the second electron to the $dx^2 - y^2$ orbital takes a significant amount of extra energy, because it is repelled by the electron already present (called by the physicists the “on-site repulsion energy”). The result is that the energy states for the second electron are higher than those for the first electron, and there is a gap of nonallowed energies between the two. The bandgap between the highest occupied oxygen states and the empty part of the now split-in-two Cu $dx^2 - y^2$ band (Fig. 1(d)) is what leads to the insulating behavior.

What exactly happens when electrons are added to or taken away from the electronic ground state shown in Fig. 1(d), for the particular geometry of the copper–oxygen lattice in cuprate superconductors, is the big problem that, to date, has not been solved. A generalized view of the structure of cuprate superconductors is shown in Fig. 2. At their electronic heart are infinite CuO_2 planes (Fig. 2(a)) made from a checkerboard-like pattern of the in-plane basal squares of the CuO_4 coordination polyhedra (such as the octahedra shown in Fig. 1(a)) sharing corners with each other. Each of the four oxygens in the CuO_4 square is shared with another copper, resulting in 180° (or $\sim 180^\circ$) Cu–O–Cu bonds and an overall stoichiometry of CuO_2 . Between these CuO_2 layers are other layers, known as “charge reservoir layers” (Fig. 2(b)). These layers serve to control, through chemistry, the number of electrons in the available electronic states in the CuO_2 planes and to electronically connect or isolate the CuO_2 planes in the third dimension. The key to determination of the superconducting transition temperatures within the family of cuprates depends in large part on the chemistry of these charge reservoir layers.

In the copper oxide superconductor parent materials, the Cu^{2+} spin 1/2 ions (one unpaired electron per copper in the $dx^2 - y^2$

orbital) in this CuO_2 plane are ordered antiferromagnetically at a high temperature, and the material is insulating, as previously described. The high antiferromagnetic ordering temperatures indicate that the copper spins are coupled very strongly. Superconductivity is induced when the electron count on the CuO_2 plane is changed from one electron per copper site: i.e., the compounds are doped to make the formal copper valence different from Cu^{2+} , typically higher. This is accomplished through manipulation of the charge reservoir layer, either by adding oxygen, by partial substitution of one atom of higher or lower valence for another, or by the naturally occurring electron count present because of the valences of the atoms in the compound. Examples of these three cases are the inducement of superconductivity on oxygen intercalation from $\text{YBa}_2\text{Cu}_3\text{O}_6$ to $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the “123” compound, the partial substitution of strontium for lanthanum in a solid solution in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, and the naturally occurring copper valence in the stoichiometric compound $\text{Tl}_2\text{Ba}_2\text{CaCu}_3\text{O}_8$. In semiconductor language, the parent compound is doped by either electrons or holes, and the antiferromagnetic ordering changes to superconductivity. This happens at an excess electron doping of ~ 0.2 electrons per copper (the formal reduction of the Cu to $\text{Cu}^{1.8+}$) or on the introduction of electron deficiency (hole doping; the formal oxidation of the Cu to $\text{Cu}^{2.2+}$). At higher doping concentrations, the materials become “normal” metallic conductors and are non-superconducting. A generic electronic phase diagram based on many experiments has been developed over the past decade to represent what happens as a function of electron concentration, and it is shown in Fig. 3.

Understanding superconductivity becomes complicated when we take the next step, and this is where the intellectual action has been concentrated in this field for some time. Hole doping is, by far, the most common case, and we must consider now what exactly happens to the holes in the electronic bands in Fig. 1(d). It appears they should be going into oxygen p states. If this is the case, then we must consider what apparently happens to a particular copper ion on doping. The Cu^{2+} keeps its 1/2 spin (the copper orbitals are not at the Fermi level and would not change electron count on hole doping), and the hole introduced is centered on oxygen p states: The spin (the unpaired electron on the copper) and the charge (the doped hole on the oxygens) are *separated*. The most prevalent belief is that the doped hole is in the electronic states in the square of four oxygens surrounding the copper. The system becomes less magnetic on doping, because the hole in the oxygen states also has a spin, in the opposite direction as the copper spin, and effectively cancels it out.^{12,13}

We now consider what happens when this entity with zero net spin and one deficient electron (called a Zhang–Rice singlet) moves to carry current. It has to move through a lattice of strongly

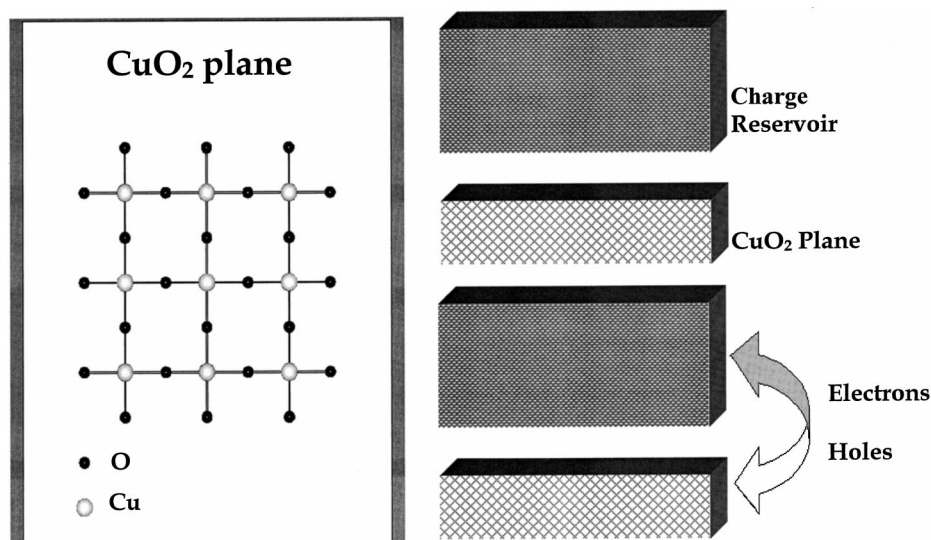


Fig. 2. (a) CuO_2 planes made from CuO_4 squares sharing corner oxygens and (b) schematic view of the electronic layers in copper oxide superconductors.

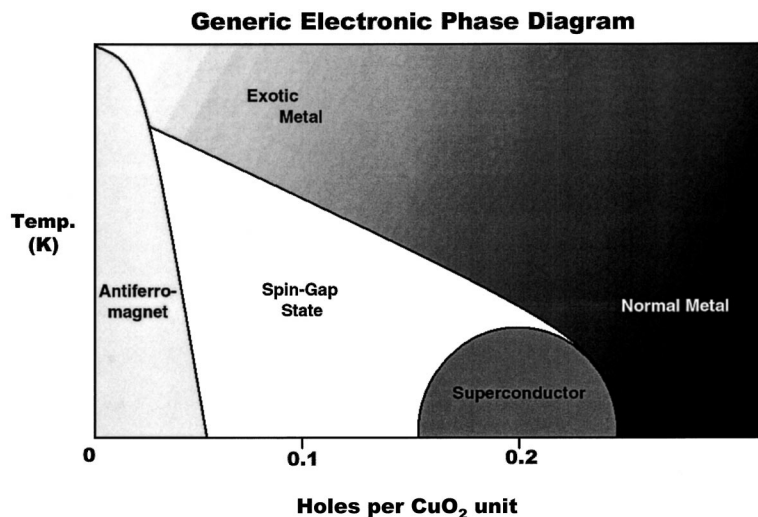


Fig. 3. Generic electronic phase diagram for copper oxide superconductors.²⁹

antiferromagnetically coupled copper spins, a problem that condensed matter physicists previously had not considered. Many believe that this exotic conduction process is the key to the whole problem. Somehow, at just the right concentration of these entities wandering around in the CuO₂ plane, their complex interactions result in superconductivity. Sophisticated neutron-scattering measurements have confirmed that the interactions between spins remain present in the superconducting materials, even though they no longer show conventional magnetic ordering. Complicating the whole issue are spectroscopic results that suggest that the overall electronic picture moves toward the case shown in Fig. 1(c) on doping, i.e., a conventional electronic band structure. Some believe strongly that it is one peculiar characteristic of this recovered, otherwise normal looking, band structure (known as a van Hove singularity) that results in the superconductivity.

This whole story is completely different from and much more complex than what people were thinking a decade ago. It is certainly not believed (sometimes vigorously) by all the theoretical physicists working on the problem, and it is difficult to judge whether it will ultimately prove to be correct. It does seem to set out many of the issues that need to be addressed before the problem can be completely understood. There is evidence for other factors to consider as well, such as the possible influence of electronic excitations and the coupling of the charge carriers to the lattice. Sometimes one wonders whether it is similar to the story of the person who loses a ten dollar bill in the street at night and looks for it under the lamppost because that is the only place where he can see: Some of the ideas about why superconductivity happens in the cuprates are much easier to explore experimentally than are other ideas and necessarily get all the attention. It is wonderful, really, that something so remarkable as superconductivity at very high temperatures in relatively simple transition-metal oxides, such as the cuprates, could continue to be an enigma after so much thought has been devoted to the problem. An excellent review of the detailed state of our current understanding of cuprates in specific and of transition-metal compounds in general can be found in the review by Imada, Fujimori, and Tokura.¹⁴

III. Intermetallic and Oxide Superconductors Known before 1986

A very brief explanation of superconductivity and some of the phenomena associated with it are in order. (An excellent, accessible description of the topic can be found in the book by Vialdi.¹⁵) Superconductivity is the ability of some materials, at temperatures below a certain critical temperature (T_c), to conduct electrical current with zero electrical resistance. There are some very

important limitations on this zero resistance state—to be described shortly—particularly when it comes to the practical applications of superconducting materials.

Superconductivity was discovered in the laboratory of Kamerlingh Ohnes in Leiden, Holland, in 1911. Ohnes was testing a theory about the resistivities of metals at very low temperatures, only then possible because of the liquefaction of helium. It was believed that the electron gas in a solid might freeze out at absolute zero and that metals would become insulating. Instead, their resistivities were found to decrease as the temperature was decreased, and experiments indicated that more-pure metals would attain lower resistivities. Mercury was the metal that could be most easily purified at that time, and, therefore, it was of particular interest. It was found to suddenly lose all resistance to current flow just above 4 K. The practical implications of the discovery were immediately obvious, but it was quickly realized that elemental superconductors would never be of any practical value. Ordinary resistivity reappeared when certain current limits (the critical current, J_c) and certain magnetic fields (the critical field, H_c) were exceeded. Both were too low for superconductors to be useful. Lead and niobium have the highest superconducting transition temperatures (9.3 and 7 K), tungsten has the lowest (0.01 K), and many are not superconducting.

Two important discoveries were made during the 1950s. Compound superconductors had been known for some time, with particular attention paid to materials based on niobium. One set of such materials, the A15 compounds (described below), were found to have relatively high T_c values, 10–20 K. More importantly, they were found to be able to conduct very large amounts of current and withstand high magnetic fields without becoming normal metals. In these materials, the magnetic field first penetrates the superconductor at low magnetic fields (the lower critical field, H_{c1}) but does not destroy the superconductivity. The field penetration causes normal metal regions within the superconductor, called vortices. There is a wide region of field strengths where superconductivity and the vortices coexist in the material, and zero resistance continues to be displayed, as long as the vortices do not move. Materials chemistry and processing are critical in “pinning” the vortices in their places, a very important area of research. Finally, at a much higher applied field (the upper critical field, H_{c2}), the superconductivity is fully destroyed. These compounds and alloys—called “type II superconductors” because of this important distinction in behavior from the superconducting elements (called “type I superconductors”), where the field penetrates all at once—were realized to hold the key to practical applications of superconductivity. They form the basis for current uses of superconductors, most importantly in the high-field magnets used in magnetic

resonance imaging (MRI). (Copper oxide superconductors are extreme examples of type II superconductors, with H_{c1} values on the order of hundreds of Oersteds, and H_{c2} values on the order of millions of Oersteds.)

The other important event of this period was the development of a theoretical model that finally successfully explained how superconductivity could occur. The theory was proposed by John Bardeen (the inventor of the transistor), Leon Cooper, and J. Robert Schrieffer (the BCS theory) in the late 1950s. BCS theory explains that, below the critical temperature in superconducting materials, pairs of electrons are formed, for which the possible energy states are quantized. The energies of the possible states are sufficiently high that the electron pairs cannot absorb the low energy from the lattice vibrations and other low-energy events in the solid. They cannot absorb the energy of the normal scattering mechanisms experienced by ordinary conducting electrons and, therefore, move completely freely through the solid. (In a sense, this is analogous to window glass passing visible light without absorbing it—light is insufficiently energetic to excite the electrons from the ground state to the lowest excited state.) Experiments soon showed that the electrons in the pairs, expected to repel each other because of their like electrical charge, were held together by an attractive interaction mediated through coupling of the electrons to vibrations of the underlying crystal lattice (“electron–phonon coupling”). This coupling is at the basis of what is now called “conventional” superconductivity. It is operating in most known superconducting materials but is clearly not responsible for superconductivity in the copper oxides.

Although the field of superconductivity research in the 1980s before the advent of high- T_c superconductivity was very small by later standards, it was an intensely intellectually active field and not “sleepy” as is often described in the popularizations of the high- T_c story. Although there had been no new families of very-high- T_c materials discovered since the 1960s, there was significant activity in more esoteric, but forefront, areas. These areas included, for example, the interplay between magnetism and superconductivity, later to become an even more urgent issue in the cuprates.

The pre-1986 high- T_c standards were intermetallic superconductors of the A15 structure type. These were alloys of niobium or vanadium with the metals aluminum, silicon, germanium, tin, gallium, etc., with the formula Nb_3X . The crystal structure, shown in Fig. 4, consists of a primitive cubic array of X atoms with niobium or vanadium atoms in pairs in each of the faces of the cube. The niobium (vanadium) atom network forms nonintersecting one-dimensional chains. The highest T_c for these materials is 23.4 K, for the metastable alloy Nb_3Ga , which can be synthesized only under nonthermodynamic conditions, i.e., in thin-film form.

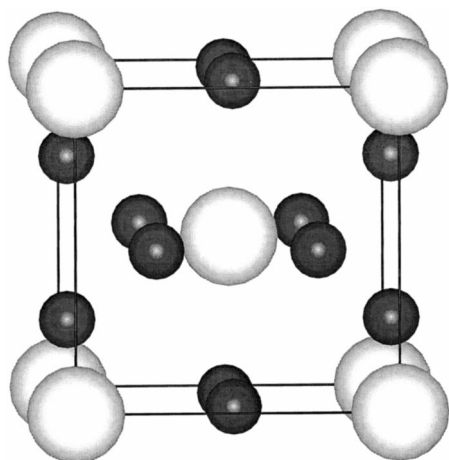


Fig. 4. The crystal structure of Nb_3Ge^{30} ((●) niobium and (○) germanium).

These materials completely defined, by example, what the community believed as the important characteristics of high- T_c superconductors.

- (1) Good superconductors should be metal alloys.
- (2) High symmetry is necessary (preferably cubic, with simple structures).
- (3) The electronic density of states must be high.
- (4) The highest- T_c superconductors are those that are structurally unstable or metastable (because the forces that result in superconductivity tend to tear crystal structures apart or make them distort into lower symmetry and unacceptable structures if they get too strong).
- (5) Structural distortions that lower the electronic density of states at the Fermi level and superconductivity compete with each other.
- (6) The physics that leads to superconductivity at high temperatures is very well understood, and the highest possible T_c can be calculated (30 K); therefore, T_c might go higher with more research, but not too much higher (perhaps the most dangerous intellectual limitation).

Materials that were not believed to function by a conventional pairing mechanism were, in fact, being studied in the early 1980s, but their T_c values were very low. These were based on alloys of uranium and cerium with other metals.¹⁶ One of the more famous of these materials, $CeCu_2Si_2$, with $T_c < 1$ K, is shown in Fig. 5. The superconductivity in these materials is derived from the hybridization at the Fermi energy of the cerium or uranium f orbitals, which are very narrow in energy, with the more-extended d orbitals of other metallic atoms in the crystal structure. The conduction electrons then travel in an electronic band that is very narrow in energy, resulting in that they act as if they have very large effective masses. The effective mass of the conduction electrons in $CeCu_2Si_2$, for example, is 1500 times the mass of a free electron. These materials are consequently called “heavy Fermion superconductors.” Electrons traveling in narrow bands typically lead to magnetism, not superconductivity, and the study of these materials was intensely pursued for that reason. The low T_c values of heavy Fermion superconductors seemed to indicate that unconventional mechanisms for superconductivity would lead

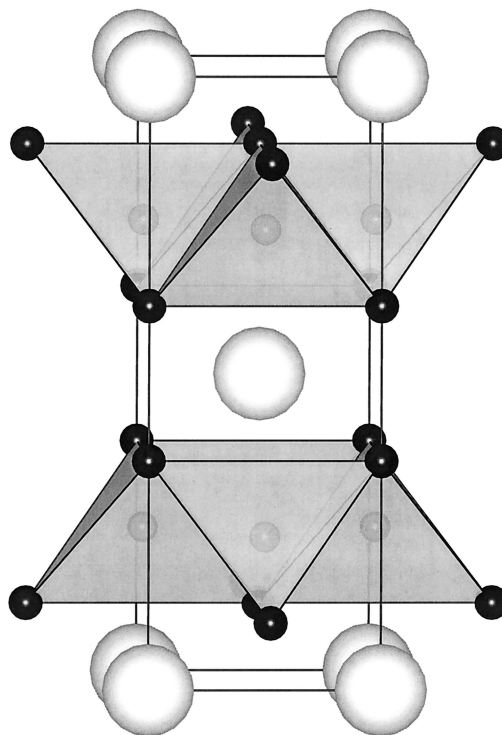


Fig. 5. Crystal structure of $ThCr_2Si_2$ ((○) thorium, (●) chromium, and (●) silicon; $CrSi_4$ tetrahedra are shown).³¹

only to lower T_c values than what was known for the more-conventional alloys.

Intermetallic compounds were not the only materials studied. Another family of superconductors studied in the early 1980s was that whose structural and chemical complexity rival those of the cuprates. These were the "Chevrel phase" chalcogenide superconductors.¹⁷ The highest T_c was known for the compound PbMo_6S_8 (14 K). Again, the T_c value was not as high as that of the A15 structure materials, and, therefore, the basic understanding of superconductivity was not challenged. Similar to the cuprates, they are part of a very large chemical and structural family. Several members of the family are superconducting. The crystal structure of PbMo_6S_8 is shown in Fig. 6. At the electronic heart of the structure is an Mo_6 cluster in the shape of an octahedron. This Mo_6 cluster can be considered to consist of atoms on the faces of a cube whose corners are occupied by sulfur atoms. This octahedron within a cube is a strongly bonded electronic entity, the Mo_6S_8 cluster, and it is the basis for many inorganic compounds. The lead atoms lie between the cubes. The Mo_6S_8 cubes are linked electronically to each other because some of the molybdenum on the Mo_6 octahedra are bonded to sulfur at the corners of neighboring Mo_6S_8 cubes. There are many interesting chemical variants of this structure, especially derived from putting different atoms in the positions of the lead atoms, ranging in size and chemical character from lithium through lead. These materials distinguish themselves by having very large H_{c2} values for the disappearance of superconductivity (as do the cuprates). The first detailed studies linking the superconducting properties in this family to the existence of chemical defects in the structures were announced at the time high- T_c superconductivity was announced, but the subject was quickly dropped. Despite considerable research into their structures and properties, these materials may be a potential source of interesting new materials science, because the relationship between structure, defect chemistry, and superconductivity was never fully explored.

Few superconducting oxides were known before 1986. For the most part, they had transition temperatures that were low compared with the known intermetallic superconductors, and, although they were of considerable scientific interest, they did not strongly challenge the status quo. One of the earliest known superconducting oxides was NbO , shown in Fig. 7. Its structure presages in some ways that of the cuprate superconductors, in that it can be considered as being made from NbO_4 squares. These squares, however, share corners in such a way to bring the highly chemically reduced niobiums in close proximity to each other, forming a strongly bonded intermetallic network. The conduction electrons are in a band of essentially metallic niobium character, and, therefore, the oxygen plays only a minor, if any, role.

Two types of oxide superconductors studied before the cuprates had classical oxide structure types, one based on the spinel

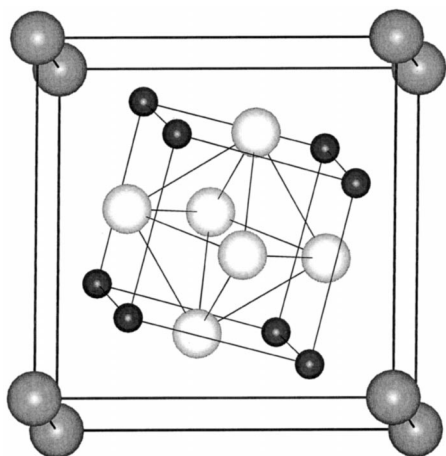


Fig. 6. Crystal structure of PbMo_6S_8 (●) lead, (○) molybdenum, and (●) sulfur.³²

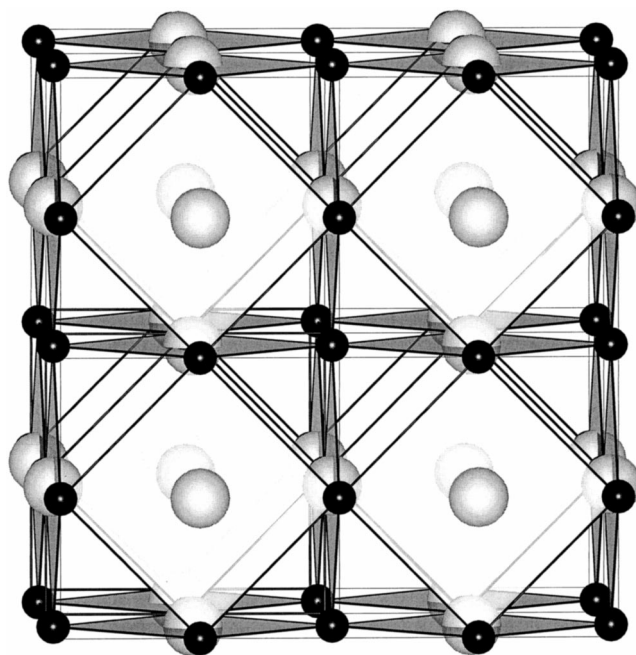


Fig. 7. Crystal structure of NbO (○) niobium and (●) oxygen; NbO_4 squares are shown.³³

structure and one based on the tungsten-bronze structure. Oxide spinels are well-known for their magnetic properties and have been extensively studied. The lithium titanate spinel LiTi_2O_4 was found in 1973 to be superconducting at 13 K. It is a normal spinel, with lithium in the tetrahedral sites and titanium in the octahedral sites. The effective titanium valence is $\text{Ti}^{3.5+}$, and all titanium sites are equivalent. The titanium-oxygen octahedra share edges in three sets of intersecting chains running along the cubic [111]-type directions. Although the crystal structure (Fig. 8) is that of a classical oxide, the electronic analysis of the compound shows that the conduction electrons are in a band of strong titanium-dominated character. Although many magnetic spinels are known, the number of superconducting spinel oxides is very limited. Some normal chalcogenide spinels, such as CuRh_2S_4 and CuRh_2Se_4 , however, are known to be superconducting. The copper in these latter materials is formally monovalent and not involved in the superconductivity.

The tungsten-bronze family of oxides is structurally related to perovskites. These materials are best known in ceramic technology as excellent ferroelectrics. $\text{Ba}_2\text{NaNb}_{10}\text{O}_{30}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ (BSN) are two good examples. Compounds with alkali metals in tunnel sites and tungsten-oxygen octahedra are superconducting and can adopt cubic, tetragonal, and hexagonal structures. The crystal structures of the tetragonal and hexagonal tungsten-bronze alloys are shown in Figs. 9 and 10. Although the octahedra share corners in all the structure types, resulting in an extensive W-O-W bonding array, the electronic states near the Fermi level are believed to be dominated by the metal orbitals—the tungsten 5d states. Oxygen again is believed to play only a minor role. There is a wealth of rich solid-state chemistry and classical materials science in the relationships among stoichiometry, relative sizes of the interstitial ions, electron count, and superconductivity in these phases. The hexagonal tungsten-bronze alloys are the best superconductors in the family, with T_c values up to ~ 7 K. There is an apparent relationship between superconductivity and magnetism in the copper oxides; similarly, there is an apparent relationship between charge density wave behavior and superconductivity in the tungsten-bronze alloys. Charge density waves are a collective electronic state, in which the conduction electrons become partially localized in particular chemical bonds and, therefore, are no longer conducting. The wavelength and direction of the charge density waves are directly determined by the wavelength and

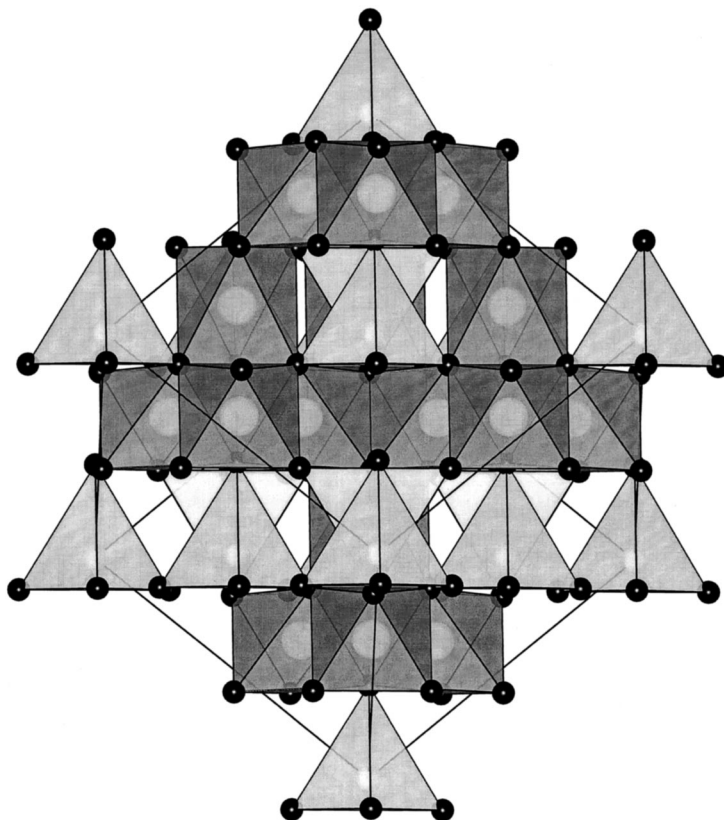


Fig. 8. Crystal structure of LiTi_2O_4 (● oxygen; TiO_6 octahedra and LiO_4 tetrahedra are shown).³⁴

direction of the electrons at the Fermi level. The localized charge is coupled to the lattice, causing periodic lattice distortions through movements of the bonded atoms from their mean positions. This type of collective electron state directly competes with superconductivity. Although these materials were extensively studied in the 1960s and 1970s, they may deserve further study, because new ideas have been formed in the past decade concerning the behavior of complex electronic solids.

More influential as precursors to the cuprates are perovskite-related superconductors. In the 1970s, it was found that SrTiO_3 , a classical ferroelectric perovskite, can be made superconducting through small amounts of electron doping—generally obtained by doping a small percentage of niobium on the titanium sites. The superconducting transition temperature is <1 K. This might not be significant, except that the creation of superconductivity by doping a semiconducting ferroelectric, even with a T_c at an extremely low temperature, piqued the interest of J. G. Bednorz and K. A. Müller, suggesting to them that oxides might someday be the source of new types of superconductors from a scientific standpoint.

The real precursor of the cuprate revolution was barium lead bismuth oxide, found to be superconducting in the 1970s.¹⁸ This superconductor was made from the perovskite solid solution of the insulating compound BaBiO_3 in the metallic compound BaPbO_3 , e.g., with bismuth and lead randomly mixed in the perovskite $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$. There is one important feature of the metallic compound BaPbO_3 that was apparent to the community at large in the early 1980s. This was that the similarity in energy of the lead and oxygen valence orbitals meant that the conduction electrons were traveling in a highly hybridized electronic band, one which had significant oxygen character as well as significant lead character: a different case from what is usually encountered in conducting oxides. Moreover, BaBiO_3 is an exotic insulator. It is a classical perovskite, but instead of having Bi^{4+} , as would be suggested by simple electron counting, there are actually two different types of bismuth in the crystal structure, with localized valences near Bi^{3+} and Bi^{5+} . The Bi^{4+} is said to be “disproportionated” into Bi^{3+} and Bi^{5+} . This is simply understood from a

chemical point of view, in that Bi^{4+} would have a single electron in a $6s$ orbital, a highly energetically unfavorable configuration ($6s^2$ is a lone-pair configuration). These bismuths are ordered in alternating B sites, forming a double perovskite. In other words, the formula can be written as $\text{Ba}_2\text{Bi}_2\text{O}_6$, in analogy with compounds similar to $\text{Ba}_2\text{LaNbO}_6$, a more familiar type of ordered $3+/5+$ perovskite. The crystal structure of BaBiO_3 is shown in Fig. 11.

The idea behind attempting to find superconductivity in the mixed $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ perovskite solid solution was to smoothly vary the electron count across the metal-to-insulator transition as a function of bismuth content. Superconductivity appears at the boundary between the metallic and insulating phases, at ~ 12 K, at the relatively low bismuth concentration of $x = 0.25$. This superconducting transition temperature could be completely explained by the classical electron–phonon coupling mechanism. Nonetheless, the relatively high T_c in a perovskite structure and the admixture of metal and oxygen states at the Fermi energy captured the interest of a few physicists around the world, all becoming an important part of the early work in copper oxides, but especially stimulating Bednorz and Müller to pursue oxide perovskites further.

Although the vast majority of workers in the field believe $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ to be a conventional superconductor, I, for one, am not convinced. An alternative explanation is that the charge disproportionation of bismuth is at the heart of it and that an unconventional electronic mechanism is at work. Against my view is that the oxygen isotope effect (the shift of superconducting transition temperature with mass of the components, described in more detail below) is large, indicating strong coupling of the electrons to the lattice, consistent with a conventional mechanism for superconductivity. In favor of my point of view is the dramatic increase in T_c that occurs when the electronically active ion is completely bismuth, and the electron count adjustment is performed entirely by solid solution on the large-atom site: $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ was found in 1988 to have a T_c of 30 K.¹⁹ Another member of this family, made with antimony in solid solution with

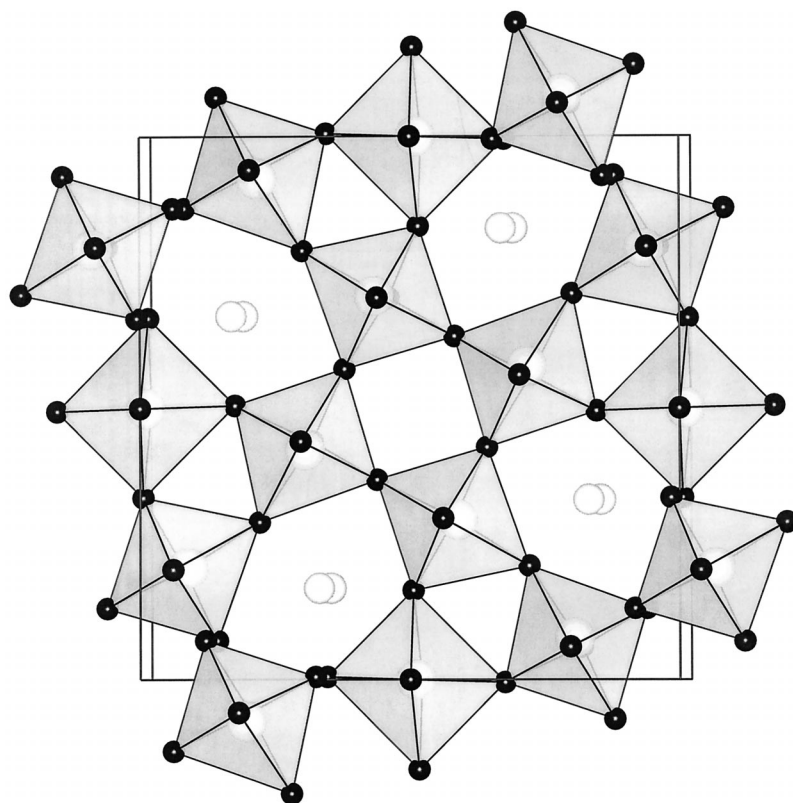


Fig. 9. Crystal structure of $\text{Na}_{0.28}\text{WO}_3$.³⁵ In this figure and the structural figures to follow, metal–oxygen coordination environments are shown as polyhedra. Oxygen are represented as small black circles and transition metals as small gray circles. Larger atoms, such as lanthanides, alkaline earths, and alkalis are shown, for clarity, as large circles without coordination polyhedra. For the important less-electropositive elements in the charge reservoir layers in the cuprates, such as lead, bismuth, tellurium, and mercury, the coordination polyhedra are shown.

lead on the B site, $\text{BaPb}_{0.75}\text{Sb}_{0.25}\text{O}_3$ has a T_c of 3.5 K. The order of magnitude difference in T_c values for these compounds never has been explained. These materials are not the subject of active research at the time of this writing, and they are perhaps most widely viewed as being of interest primarily because of their influence on the researchers to later discover high- T_c superconductivity.

IV. Discovery and Development of Copper Oxide Superconductors

The excitement that electrified the physical science community after the discovery of superconductivity above the temperature of liquid nitrogen in early 1987 spread into the popular press and from there to the public at large. There were many newspaper stories, TV news reports, and several best-selling books written about the events surrounding the initial discoveries. These popularizations made some into heroes, some into villains, some minor players into geniuses, and some major players invisible. None of them ever matched my view of what actually happened. The accounts in this country seemed always to be a blend of the actual facts with American cultural values and stereotypes—such as our national pride, our desire to root for the underdog, and our need to associate remarkable historical events with the great deeds of individuals rather than the collective efforts of many different people.

Hopefully, by considering the above summary of the world of superconductivity as it was in 1986, the reader has enough background to appreciate what a remarkable discovery the two scientists Georg Bednorz and Alex Müller made and published in late 1986.²⁰ They broke all the rules about what electronic ceramics could do and what good superconductors should look like. Pursuing their own idea about how superconductivity might occur in oxides, they were looking for superconductivity in

perovskite structure oxides based on nickel and copper. They attempted for some time to find superconductivity in nickel oxides, without success. They then turned to copper oxides, carefully considering the reports of metallic conductivity in the ternary cuprate $\text{La}_4\text{BaCu}_5\text{O}_{13}$ by the group led by the French chemist Bernard Raveau. Their initial report, cautious and objective, published in *Zeitschrift für Physik*, reported the possible existence of superconductivity in the La-Ba-Cu-O chemical system, an oxide ceramic, at the surprisingly high temperature of 28 K—not that much higher than was known for the best intermetallic superconductor (23 K), but in a completely different type of material. The actual chemical compound responsible for the observed superconductivity was not known. The results of their work became known in the very small circle of scientists interested in superconductivity in November 1986.

While Bednorz and Müller continued to work on their discovery in Switzerland, two groups on opposite sides of the world began to follow up on their work immediately: one at the University of Tokyo and one at the University of Houston. Both groups reported some of their preliminary results at the annual meeting of the Materials Research Society (MRS) in early December 1986. The group at the University of Tokyo was under the leadership of the visionary materials scientist and physicist Shoji Tanaka. Tanaka, like Bednorz and Müller, believed that there was something very unusual about the superconductivity in barium lead bismuth oxide and was very quick to realize the possible importance of the discovery. The group at the University of Houston was under the leadership of C. W. (Paul) Chu, well-known in the community of scientists working on superconductivity in the United States and an expert in the measurement of the properties of materials under very high applied pressures. Similar to the others in the story, he believed that superconductivity in exotic materials at unexplainable temperatures was possible, and his group moved quickly to look into the Bednorz and Müller announcement.

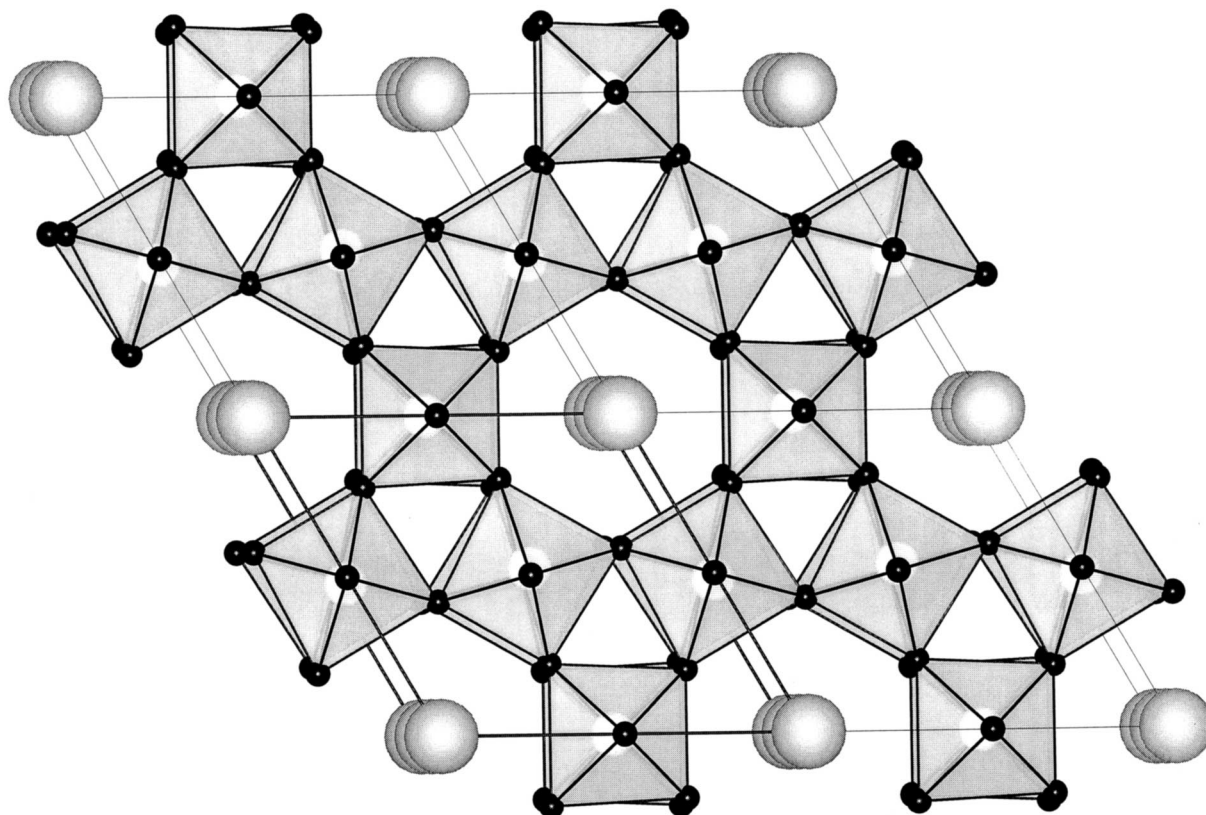


Fig. 10. Crystal structure of $\text{Rb}_{0.27}\text{WO}_3$ (see Fig. 9 for legend).³⁶

Two important things were revealed in the early work of these two groups, aside from their confirmation that the surprising announcement of the European team was indeed correct. Chu's group found that the superconducting transition temperature in the original formulation increased significantly under the application of pressure; i.e., T_c increased as the crystal lattice got smaller. The Japanese group was attempting to determine which compound in

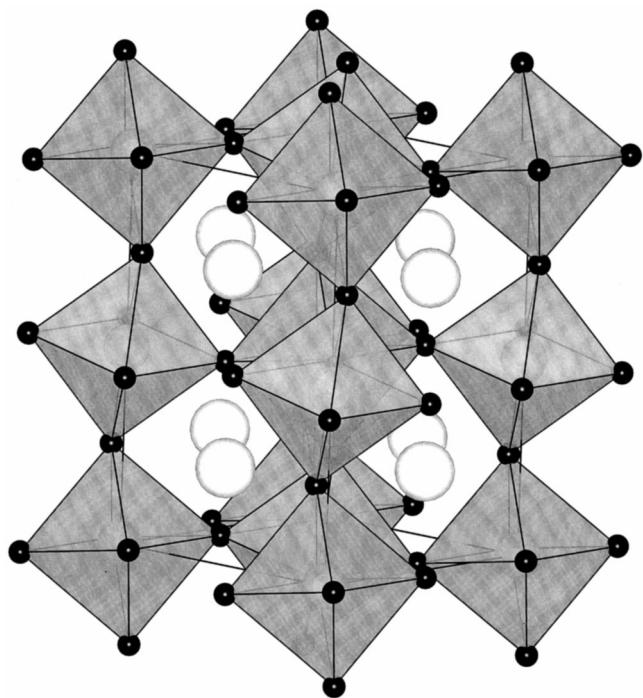


Fig. 11. Crystal structure of BaBiO_3 (see Fig. 9 for legend).³⁷

the La-Ba-Cu-O chemical system was actually superconducting. I was sitting in the seminar room at Bell Laboratories a few days after the MRS meeting at an impromptu talk given by Koichi Kitazawa from the University of Tokyo when a telephone was brought into the room and he called from the United States to the laboratory at the University of Tokyo (where it was 3 a.m.) to get the report that they had just determined that the superconducting compound was the layered K_2NiF_4 -type oxide solid-solution $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. The crystal structure is shown in Fig. 12. A few more groups, including ours at Bell Laboratories, began its research after the MRS meeting, and, before Christmas 1986, the strontium analog of the K_2NiF_4 -type compound, $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$, was found to be superconducting at the then astonishingly high temperature of 38 K, consistent with the high-pressure results that smaller lattices (strontium is smaller than barium) might lead to higher transition temperatures.

Almost everyone in the scientific community remained oblivious to what was happening. Although many of those who noticed argued that the new materials could easily be explained by a conventional picture for superconductivity, theoretical physicist and Nobel laureate Philip Anderson published a paper very early arguing that an exotic and completely unconventional mechanism must be behind the superconductivity. The few groups actively pursuing the problem worked through the holidays and through New Years 1987. It was clear that something remarkable might happen any time. A report then appeared from the group of Z. X. Zhao at the University of Beijing that very tiny amounts of superconductivity occurred in the original Bednorz and Müller formulation at a temperature of 58 K. I can remember that copies of the article announcing the result in the Beijing Peoples Daily newspaper (in Chinese of course) were very hot items for a week or so and that the only recognizable character in the article was the chemical symbol "Pb," prompting considerable effort on our part to find Chinese colleagues who could tell us what lead had to do with it (they had used superconducting lead metal as a standard for

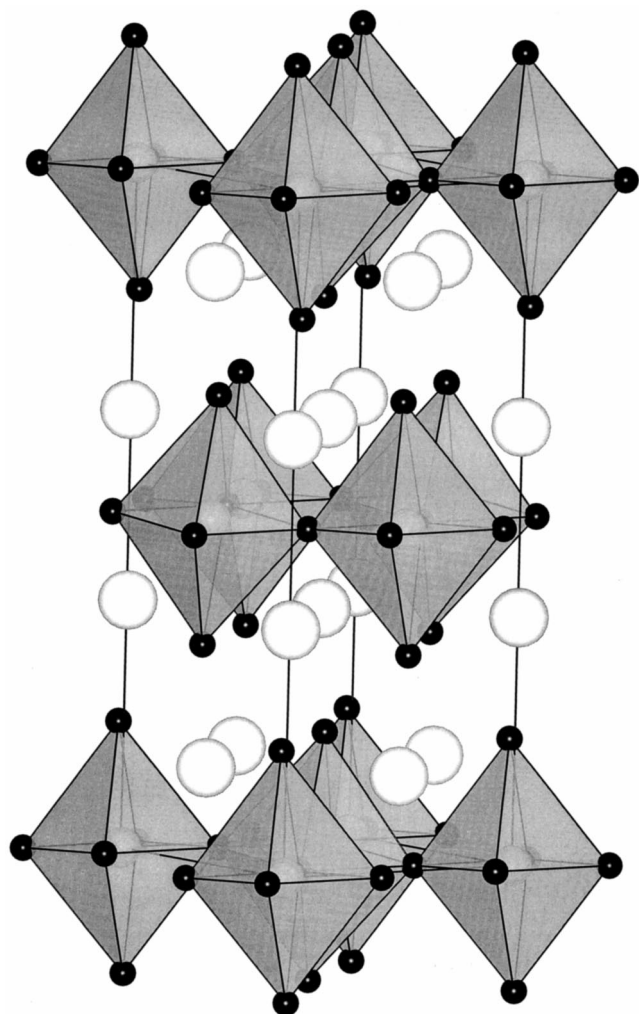


Fig. 12. Crystal structure of La_2CuO_4 (see Fig. 9 for legend).³⁸

calibration). This result could not be reproduced in other laboratories, was soon eclipsed, and, therefore, is often omitted in the telling of the story. In retrospect, it was correct, because later research would show that there was indeed a higher-temperature superconductor in the La-Ba-Cu-O system (of the 123 type). Things were already getting almost out of control—there were stories circulating about spies and secret late-night telephone calls; we probably will never know exactly what was going on.

Then came the event that attracted everyone's attention. The story began to circulate that M. K. Wu at the University of Alabama and Paul Chu at the University of Houston (Wu was one of Chu's former students) had found a superconducting copper oxide with a transition temperature of >90 K. The superconductor was also rumored to be green, by people who had actually *seen* it, which was a bizarre claim, inconsistent with what most believed to be possible for a conducting oxide, but given that, if true, everything we knew was wrong anyway. They had substituted the smaller atom yttrium for the lanthanide lanthanum in the original Bednorz and Müller formula in an attempt to shrink the lattice, as was suggested by their high-pressure data, and the T_c had gone up by an incredible 50 K!

This is the part of the story that has been told many times in the popular accounts. The original paper was submitted with the incorrect chemical components preventing the leaking of the results by the referees (always claimed to be an inadvertent error by the authors, but something that would have been a very good idea anyway). The initial report did not identify the superconducting compound and suggested that this was such a departure from the ordinary that the superconductivity might not be due to a

compound at all, but rather due to complex electronic interactions at chemical interfaces. The identification of the superconducting compound (the 123 superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$) soon revealed a completely different crystal structure than that of the Bednorz and Müller superconductor, and the era of high- T_c superconductivity had begun. The 123 superconductor, the first found to have a transition temperature above the temperature of the boiling point of liquid nitrogen (77 K), remains one of the few that is considered to have the potential for real commercial application. (As of the time of this writing, more than a dozen years after the determination of its composition and the filing of the patent applications, the U.S. Patent Office is yet to determine who rightfully holds the patent to this material. Aside from the ancient Zen question: "What is the sound of one hand clapping?" no other single question, it seems, has ever been more difficult to answer.)

Now that superconductivity above the temperature of liquid nitrogen was a reality, all types of new applications might be envisioned for superconducting materials, based on the fact that expensive, difficult to handle liquid helium would no longer be needed to cool the superconductors to temperatures close to absolute zero. Many were quite enthusiastic about what could happen, and there was much speculation about how our lives might someday be changed by the discoveries of the past few months. One had to be particularly stoic or bitter not to be caught up in the excitement, and some scientists outside of the maelstrom were not happy about the attention these developments were getting in the popular press. This was not, however, business as usual for science, and there was no reason to treat it as such.

The new 123 superconductor, similar to many electronic ceramics before it, was found to have a widely variable oxygen stoichiometry. The oxygen content determined whether it was superconducting. A few scientists quickly realized that this ability of the 123 compound to breathe oxygen in and out would allow them to test whether the superconductivity in copper oxides could be due to the same mechanism operating in the intermetallic superconductors. They remembered that the "conclusive evidence" for the conventional understanding of superconductivity by coupling of the electrons to the vibrations of the crystal lattice was proved by the observation of a change in superconducting transition temperature with the mass of the constituent atoms—an isotope effect. The transition temperature in the electron-phonon picture is proportional to the frequency of the lattice vibrations, and the frequency of lattice vibrations, in turn, depends on the square root of the mass of the vibrating atoms. The oxygen vibrational modes were speculated to result in the high T_c values in 123; therefore, replacement of the normally present ^{16}O by ^{18}O should lower the phonon frequencies and T_c if this was a conventional superconductor. ^{18}O did lower the frequency of the vibrational modes, but T_c changed little. These could not be conventional superconductors!

The crystal structure of the 123 superconductor (Fig. 13) was surprising and very unlike the structure of any oxide perovskite that previously had been observed: a fact that has always struck me as fitting for such a historical material. There were two significant differences between this material and the K_2NiF_4 -type forerunners. The first was that there were two layers of CuO_2 planes in close proximity instead of one. The second was that there were remarkable one-dimensional chains of corner-shared CuO_4 squares running along one crystallographic direction. Which of these new features was responsible for the unbelievable increase in the superconducting transition temperature became the topic of much discussion and speculation. This speculation was soon to be ended, however, by the discovery of the next new class of materials.

The French group under Bernard Raveau, which knew more about the chemistry of this type of material than anyone else on the world, soon announced the existence of another new type of superconductor, based on the substitution of bismuth for lanthanum in La-Sr-Cu-O. This new superconductor (" $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ "), which was found to have a crystal structure different from 123 and the K_2NiF_4 materials, ultimately turned out to be the first of a gigantic class of new materials to follow. Its T_c was <10 K,

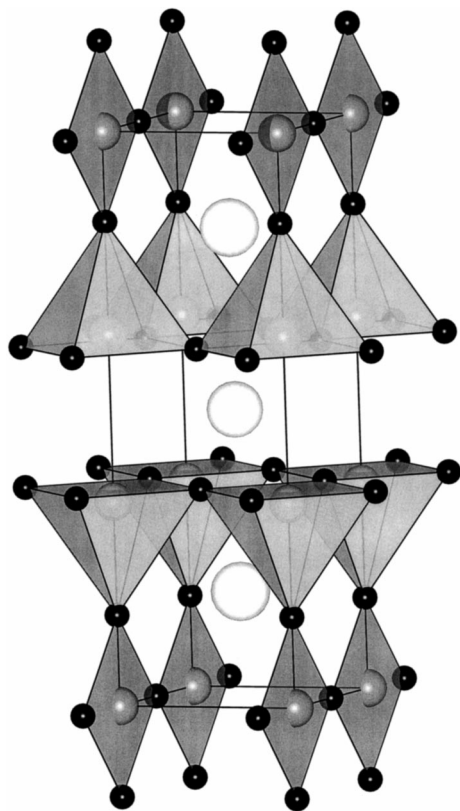


Fig. 13. Crystal structure of YBa₂Cu₃O₇ (see Fig. 9 for legend).³⁹

however, and it attracted relatively little attention at first, because most were struggling to understand what could be going on in the 123-based materials. Excited by the developments in the new superconducting materials, T. Maeda, from NIRM in Tskuba, Japan, began experimenting with the French superconductor by adding other elements to the mixture. What he found changed everything. By adding calcium to the mixture, the superconducting temperature of Bi-Sr-Cu-O increased to >80 K, and there was good evidence that parts of the sample were superconducting at temperatures near 100 K. In the now often repeating pattern, the composition and structures of the superconductors were not known, and another race to identify the superconducting compound or compounds was initiated.

The crystal structure of the 80 K superconductor in the Bi-Sr-Ca-Cu-O system is shown in Fig. 14. The approximate formula is Bi₂Sr₂CaCu₂O₈ (the real formula has deviations from these simple integer ratios of constituent atoms). There are no copper oxide chains and, therefore, that ended all discussion about whether those chains could be the reason for the high T_c in the 123 compound. What this does have in common with the 123 compound is a double layer of CuO₂ planes. Eventually the superconductor in this system with an even higher T_c (~ 110 K) was isolated. Its ideal formula is Bi₂Sr₂Ca₂Cu₃O₁₀: It had *three* sets of nearby CuO₂ planes. This compound, stabilized by partial substitution of lead for bismuth and the 123 superconductor YBa₂Cu₃O₇ are to this day the high- T_c superconductors most likely to see practical application. This is the point in history (1988) when it was realized that higher T_c values were more likely in compounds with a larger number of CuO₂ planes in proximity. This remains the general rule, although several materials with single CuO₂ layers are now known to have superconducting transition temperatures near 90 K. This was also the time when the common function of the chains and the bismuth oxide layers in these new materials was realized to be that of a charge reservoir, serving to control the amount of electron or hole doping in the CuO₂ planes.

1988 was a very good year for the discovery of new superconducting materials. It became clear that the way to find a new

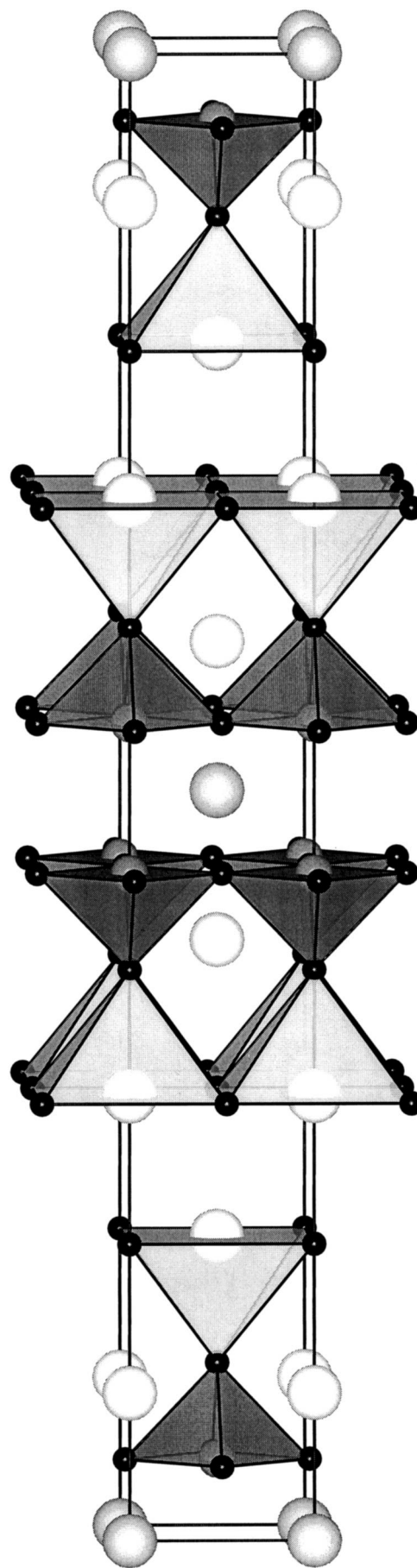


Fig. 14. Crystal structure of Bi₂Sr₂CaCu₂O₈ (see Fig. 9 for legend).⁴⁰

superconductor was to find a new atomic constituent to put into the charge reservoir layer and then to change the number of CuO_2 planes. This was easier said than done, but soon to follow were materials with thallium and lead in place of bismuth in the intermediary layer, stacked with different numbers of CuO_2 planes. Thallium and lead are analogous in size, electronegativity, and chemistry to bismuth, but, because of serious complications in the synthesis of the compounds, they are nontrivial extensions of the bismuth-based materials. The key to their accommodation in the CuO_2 -based perovskites is that their size is such that edge-shared octahedra and pyramids in bismuth, lead, and thallium oxygen layers have the same in-plane size as corner-shared CuO_4 squares; this is the same size criterion that determines whether the perovskite structure is stable in any chemical system. The thallium-based materials had as their distinguishing characteristic very high superconducting transition temperatures, holding the record for a very long time; they also were "self-doped." Because of the relative energies of thallium and copper orbitals, there is natural doping of the CuO_2 layers at the stoichiometric compositions. One of these materials, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, is shown in Fig. 15. The lead-based compounds had as their distinguishing characteristic a more complex charge reservoir layer than had been previously seen, involving Pb^{2+} pyramids and Cu^+ sticks, both chemically reduced species in equilibrium in the same compound with chemically oxidized $\text{Cu}^{2.2+}$ in the superconducting layers. One of these materials, $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_8$, is shown in Fig. 16. These lead-based materials also had the characteristic that, because of their complexity, they could not be made in as many variants as had been seen previously for other families and that their T_c values never were as high as the members of other families with an equivalent number of CuO_2 planes.

Given the whole history so far, it should not be obvious that electron doping of a copper oxide should lead to superconductivity as well. The first of only two known electron-doped superconductors was discovered in this time period. This discovery, from the group of Yoshi Tokura at the University of Tokyo, came as a very big surprise to everyone in the field. It was based on the doping of Nd_2CuO_4 , a compound in which the CuO_2 squares in the planes are not capped with further oxygen in their apical positions (Fig. 17). The doping to reduce the formal valence of copper was eventually accomplished in two ways: partial substitution of cerium or thorium for neodymium in a solid solution and partial substitution of fluorine for oxygen in oxygen layers isolated from the CuO_2 planes. This material has been enigmatic since its discovery and remains poorly understood. It is not sufficient to prepare the material at the correct electron-doping level to obtain a superconductor. Certain complex treatments must be used to induce superconductivity, just slightly milder than conditions that clearly lead to decomposition of the phase. Moreover, for all superconducting preparations, there is a mixture of phases present with the same overall structure but with different short-range-ordered structures. No one knows which one is the superconductor or what the difference between them is. Years later, a second *n*-type superconductor was discovered, again apparently based on CuO_2 planes with no apical oxygens, but it can be synthesized only by a high-pressure synthesis technique and has not been the subject of detailed study.

The early 1990s were a grueling period if your business was the discovery of new oxide superconductors. All the simple combinations of elements that could be explored by conventional synthesis had been attempted, and the new superconductors that were found were structurally and chemically complex, did not have T_c values that rivaled the materials already known, and did not, in general, appear to be pointing to any new aspects of the physics of the materials. Nonetheless, the truly hardy did find new materials with new types of intermediary layers, such as those based on intermediary layers of GaO_4 tetrahedra (Fig. 18) and NbO_6 octahedra (Fig. 19). There was, however, a continuing undercurrent of research in new materials that was to have serious consequences in the years to follow: one of the most interesting stories associated with the discovery of oxide superconductors.

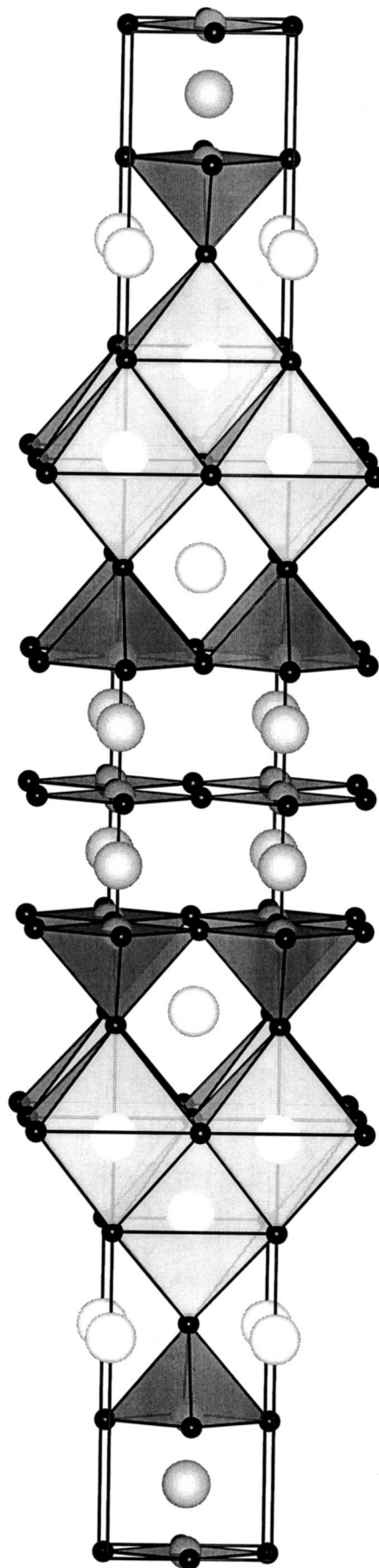


Fig. 15. Crystal structure of $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (see Fig. 9 for legend).⁴¹

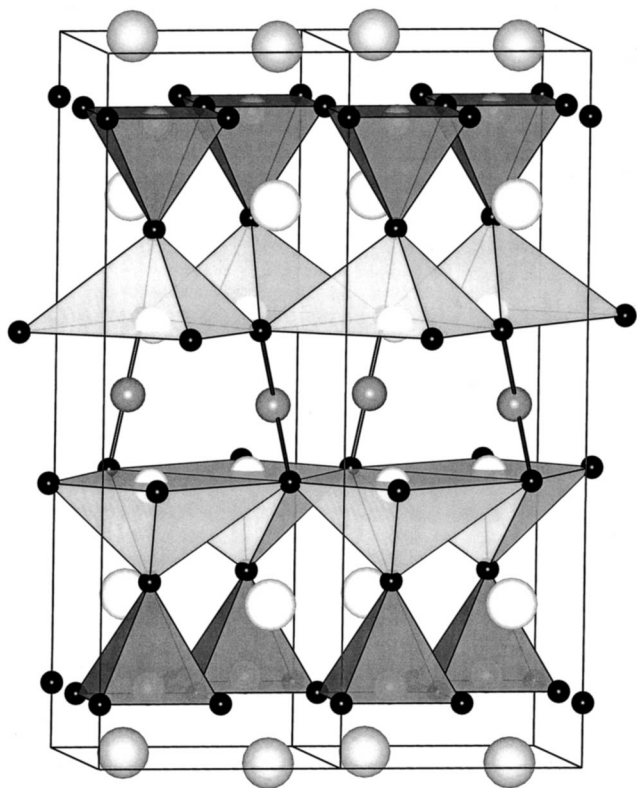


Fig. 16. Crystal structure of $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$ (see Fig. 9 for legend).⁴²

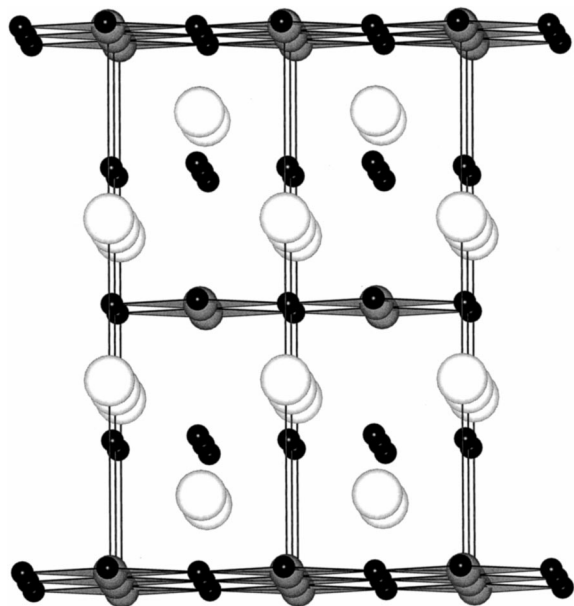


Fig. 17. Crystal structure of Nd_2CuO_4 (see Fig. 9 for legend).⁴³

The story begins in 1988, when Bob Roth and co-workers, studying the phase-equilibrium diagram for the Sr-Ca-Cu-O chemical system as part of a much larger project to characterize the important (and complicated!) Bi-Sr-Ca-Cu-O chemical system, found a remarkable chemical compound of composition $\text{Ca}_{0.84}\text{Sr}_{0.16}\text{CuO}_2$. The composition of the compound was very precise, with no measurable variability, at this peculiar Ca:Sr ratio. The determination of the crystal structure by Theo Siegrist showed that this was a compound made entirely of CuO_2 layers separated by alkaline-earth layers made of a solid solution of calcium and strontium mixed *randomly* but at one particular ratio.²¹ This

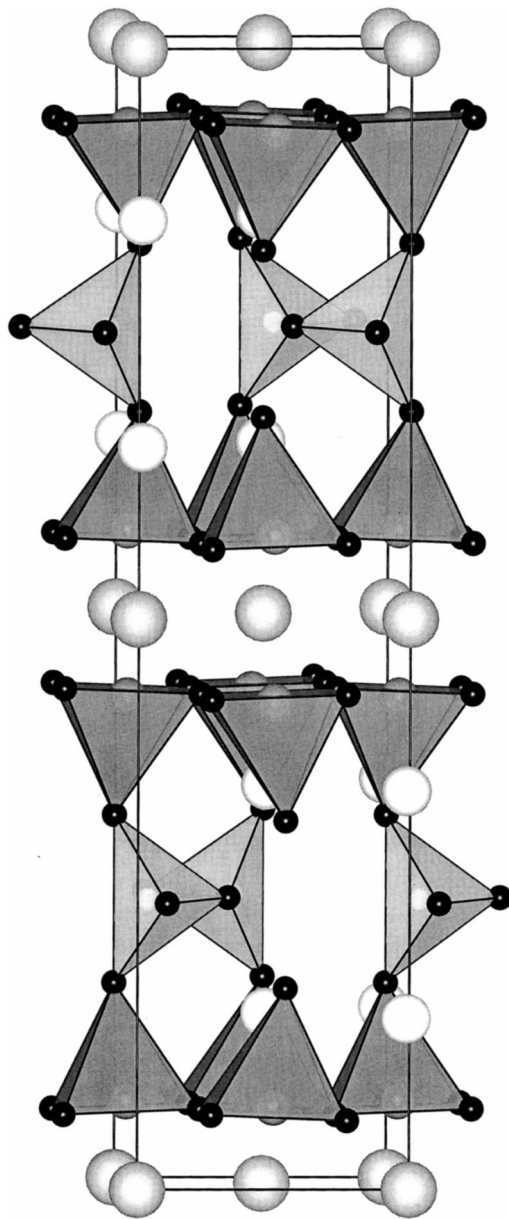


Fig. 18. Crystal structure of $\text{GaSr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_7$ (see Fig. 9 for legend).⁴⁴

important material is variously known as the “parent structure of the cuprate superconductors,” or “the infinite-layer phase.” It consists only of the electronically active CuO_2 planes responsible for superconductivity (Fig. 20). If it could be chemically doped, then its T_c might be extremely high!

However, it apparently could not be done easily. The precise Ca:Sr (whose sizes differ by only 10%) ratio needed to form the compound indicates that the compound is sensitive to about the 0.1% level to the precise matching of size of the CuO_2 plane to the Sr + Ca spacing layer. All attempts at doping by conventional means failed, apparently because of this extreme size sensitivity. Then came an important insight from the group of M. Takano in Japan: Because of the great differences in compressibility of the alkaline-earth–oxygen and copper–oxygen bonds, synthesis under high pressures might allow the range of relative sizes of the atoms in the compound to be expanded. Synthesis under high-pressure/high-temperature conditions often leads to the formation of phases that are metastable only under ordinary conditions of pressure (e.g., diamond!). Thus, in 1989, a year after the announcement of the existence of the phase, the Japanese group reported that, during synthesis at 40 000 or more atmospheres (4 GPa) of pressure at 1000°C, the stability of the all-layer phase could be expanded to a

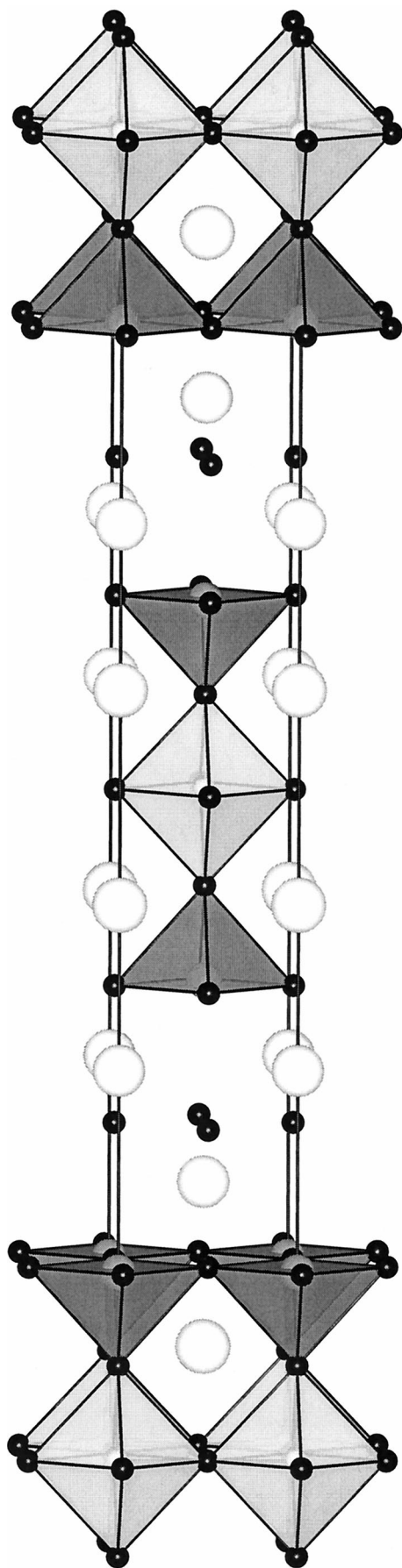


Fig. 19. Crystal structure of $\text{NbSr}_2(\text{Nd,Ce})_2\text{Cu}_2\text{O}_{10}$ (see Fig. 9 for legend).⁴⁵

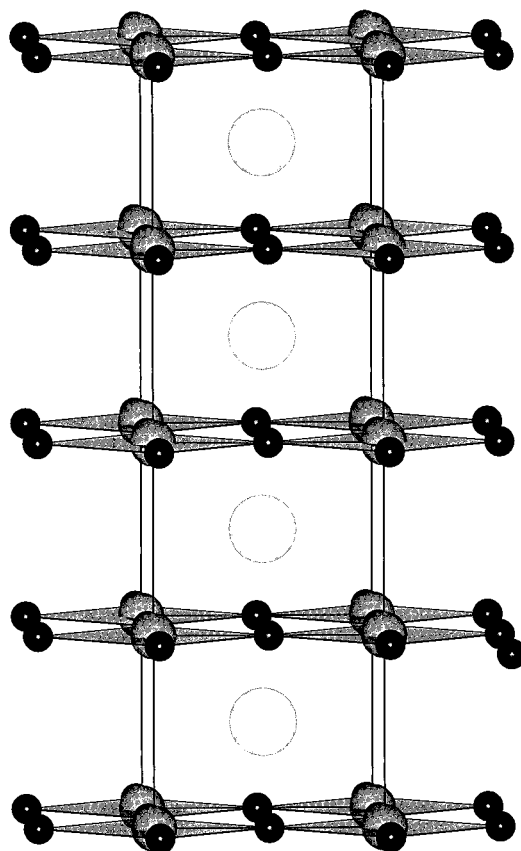


Fig. 20. Crystal structure of $(\text{Sr,Ca})\text{CuO}_2$ —the "infinite layer phase" (see Fig. 9 for legend).⁴⁶

wider range of sizes, notably to *larger* sizes, including mixtures of strontium and barium on the alkaline-earth site. When these larger atoms went in, they forced the expansion of the CuO_2 plane to allow them to fit. At the time, there were few groups in the world with the type of synthesis apparatus that could be used for this type of experiment.

For the most part, nobody seemed to notice this structural and synthetic undercurrent. Then, two years later, the group of John Goodenough realized that the larger range of sizes attainable at high pressures might allow the doping of the compound, in particular *n*-type doping, for which the Cu–O bond with lower formal charge would be expected to be relatively long. They announced, three years after the discovery of the phase, that *n*-type superconductivity with $T_c = 40$ K could be induced in the infinite-layer phase in materials of formula $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ by synthesis at 25 kbar (2.5 MPa) and 1000°C .²² The community at the time was, however, notably one-dimensional in thought (the only thing that mattered was T_c), and the low T_c of this material did not at first generate a perturbation in the direction of the field in proportion to its importance. Things changed radically in late 1991 and in 1992 when a Japanese group announced the existence of superconductivity at temperatures up to 110 K in the *p*-type-doped infinite-layer phase.²³ The doping was accomplished through the introduction of strontium deficiency in randomly arranged defect layers in the all-layer phase of composition $\text{Sr}_{1-x}\text{CuO}_2$ synthesized at 60 kbar (6 MPa) and 1000°C . At a T_c of 110 K, people took notice. The most important consequence of this notice was that it became evident to many that high-pressure synthesis was the road to the discovery of new superconducting materials and could break the logjam plaguing the field for the past four or more years.

Again, this is easier said than done, and it took several years for groups to gear up to this new expensive and elaborate synthetic method. The result was a great new flurry of discovery of superconducting compounds, starting in 1994, based almost exclusively on the synthesis of materials under high pressures. The most

notable of these are the Ba-Ca-Cu-O and Ba-Ca-Cu-C-O multiple-layer cuprates. Although not initially discovered by high-pressure methods, the synthesis of the large family of superconductors with mercury intermediary layers has been greatly facilitated by high-pressure synthesis, needed to prevent mercury from volatilizing. This is now virtually the only way these important materials are synthesized in bulk form. This family of superconducting compounds is based on intermediary layers of a single plane of O-Hg-O sticks, as, for example, is shown in Fig. 21. (Double mercury layer materials also have been synthesized.) The triple layer variant of these, $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$, is currently the high- T_c record holder at ambient pressure (134 K) and when measured at high pressure (164 K).

In the same time period, intermediary layers that involved the mixing of CO_3 groups and CuO_x polyhedra in the intermediary layers, with the charge on the superconducting CuO_2 planes controlled by the Cu:C ratio, were discovered to result in a family of superconductors. High-pressure synthesis has been used extensively to make these materials. An example of one of them is shown in Fig. 22. The highest T_c values (>100 K) in this family are obtained in the Ba-Ca-Cu-C-O system when synthesized at high pressures. A very interesting structural phenomena in the carbonate family is the discovery of a series of complex multiple-layer cuprates by the Raveau group, in which TlO - and CO_3 -based intermediary layers alternate.²⁴ Aside from the more straightforward $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ superconductors, in which single-chain CuO and double-chain CuO intermediary layers alternate, these are the only materials known with more than one type of intermediary layer in the same compound; a new type of structural principle not yet fully explored.

The influence of high-pressure synthesis and measurement continues to be profoundly felt in the field, and it is discussed in context of current directions. However, one of the most interesting parts of the story of the all-layer phase came years after the discovery that it could apparently be made superconducting. Further study of the p -type doping of the all-layer phase in 1997 by an independent group of researchers revealed that the superconductivity above 100 K in that material was not from the all-layer phase but, rather, due to inadvertent second phases based in the Sr-K-Cu-O-Cl system!²⁵ The potassium and chlorine in the superconducting impurity phases are because KClO_3 is used in the synthesis at high pressures as a source of extra oxygen (it decomposes at high temperatures to $\text{KCl} + \text{oxygen}$). Ostensibly separated from the main reactants, it nonetheless managed to get into the sample and form superconducting compounds. The superconducting compounds, later studied in more detail, are $\text{Sr}_{3-x}\text{K}_x\text{Cu}_2\text{O}_4\text{Cl}_2$ and $\text{Sr}_{2-x}\text{K}_x\text{CuO}_2\text{Cl}_2$. Sodium-doped variants are also known. The all-layer phase cannot be made into a p -type high- T_c superconductor, only into an n -type superconductor.

Only a few groups around the world continue to look for new superconductors among the copper oxides. For the most part, research in "new materials" has consisted of adding a variety of elements to already known superconductors, sometimes with the intention of exploring one aspect of the superconductivity or another and sometimes for no obvious reason. From a chemical or structural consideration, they do not, in general, represent new directions. Nonetheless, there have been some interesting discoveries in recent years. These are described in further detail in a later section.

V. Historical Sideshows and Final Count of Cuprate Superconductors

The sidetracks, sideshows, false alarms, and downright fraudulent claims in the history of the field of high- T_c superconductivity have been an ever-present and often important part of the story since the field's inception. Some of the claims of the observations of very small amounts of very-high- T_c materials (e.g., at the recurring apparent T_c value of 240 K) remain real mysteries to this

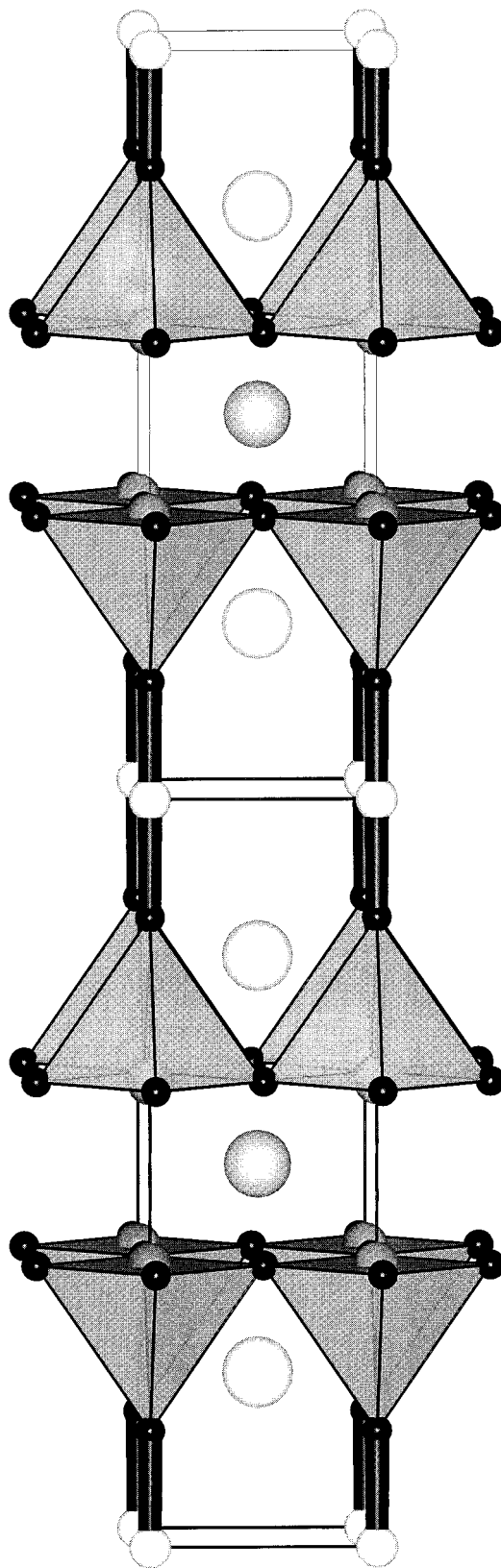


Fig. 21. Crystal structure of $\text{HgBa}_2\text{CaCu}_2\text{O}_6$ (see Fig. 9 for legend).⁴⁷

day, because no obvious flaw in logic or mistake in the experimental procedure is evident. These observations have never been reproducible in other laboratories following the reported procedure—this is logical, in a sense, because the extreme superconductivity is always present at the 1 part in 10 000 level or lower. It is impossible to estimate, however, how many hours have been

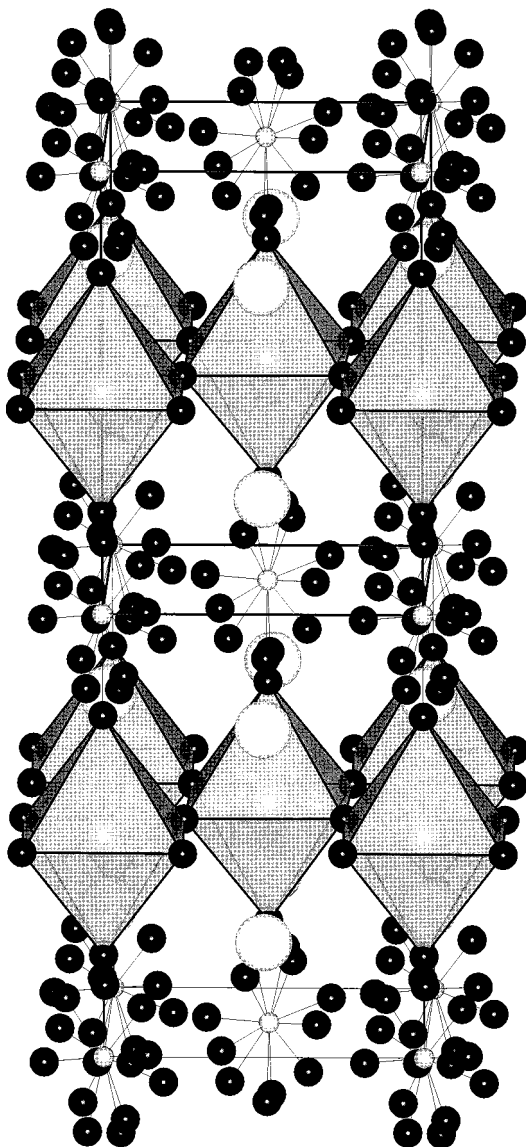


Fig. 22. Crystal structure of $(C_{1-x}Cu_x)(Ba,Sr)_2CuO_y$ (see Fig. 9 for legend).⁴⁸

spent by the materials community attempting to duplicate what appeared to be spectacular results and which were mistakes in judgment, inadvertent error, overzealousness, or outright lies. During the early years of high- T_c research, I came to call the prestigious physics journal *Physical Review Letters* the “Journal of Irreproducible Materials Science.” In the first years of research in the field, there was virtually no negative feedback by the scientific community for researchers who made these wild claims. The attention such claims got in the popular press created considerable havoc and never did the retraction of the story eventually shown to be incorrect ever get the type of attention the original announcement received. These events frustrated many scientists, especially those working outside of the field, and left some with a negative attitude for high- T_c research. The great majority of workers in the field, however, were not working in that mode. The relationship between the media and scientists that evolved during the heady days in high- T_c research may have had an influence in the disastrous “cold fusion” folly that followed, because the media were primed with the expectation of spectacular announcements in science and are never nearly as critical of scientists’ statements as they are, for example, about the assertions of politicians. In a very small way, primarily through exaggeration or error, incorrect claims about new superconductors or their properties continue to

this day. I am sure it is difficult for the nonexpert to tell what is real and what is not.

Koichi Kitazawa coined the perfect term for these announcements of outrageously high transition temperatures in 1987: USOs. This is actually a triple entendre: USO stands for “unidentified superconducting object.” The obvious analogy to UFO conjures up the appropriate implications about their verisimilitude, and the character of the people who chase them, and, finally, USO means “lie” in Japanese. USO sightings continue to this day, for example, the recent report of “superconductivity” at 91 K in the surface layer of a sodium tungsten bronze.

Some of the origins of USOs and confusing claims are presented in the following, as examples of the variety of reports that can obfuscate the issues when a group reports the existence of a “new superconductor,” making keeping track of things difficult.

(1) Experimental error or lack of scientific judgment is always the most spectacular claim; there are many examples of them in the literature. It would not be appropriate to point out particular examples. They continue to this day. Many are determined to be obvious nonsense after looking at the data for one minute, but, for some, it is more difficult to discover the mistake. An all too typical error is lack of good thermal contact between the sample and the thermometer measuring its temperature, resulting in the sample being colder than the claimants believe.

(2) There are sincerely reported and apparently experimentally sound but confusing results. The most famous example is the 240 K USO sighting caused by the “reverse Josephson effect” (even most physicists cannot easily recall exactly what that is) in Y-Ba-Cu-O. The authors claim there can be no other explanation for their observation other than parts per million of superconductivity present in their sample, turning on at 240 K. This 240 K value has appeared in many USO sightings by other groups since. I have never heard a convincing argument as to why these experiments might be incorrect, although one may have escaped me.

(3) There continue to be reports of a “new” superconductor in a chemical system that already has a known superconductor in it, made from some subset of the elements present. There are almost countless examples of these claims in the literature. One example is the report of a new layered-structure superconductor in the Ba-K-Pb-Bi-O system—the Ba-K-Bi-O and the Ba-Pb-Bi-O systems have superconductors in them, and the combination of all the elements is also superconducting, but from the known superconducting phases. It is possible for more than one superconducting compound to exist in the same chemical system, e.g., $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$, but the case has to be carefully proved. Errors of this type are difficult for nonexperts to identify. The culture of contemporary science makes it inappropriate to publish papers disagreeing with these types of reports; therefore, they reside in the literature unopposed.

(4) The superconducting phase actually comes from a combination of elements or an element not believed to be present by the experimenter. A good example is p -type superconductivity reported for the “all-layer” Sr-Cu-O phase, which actually came from Sr-K-Cu-O-Cl, as described previously. More insidious are, for example, reports of superconductivity in Sr_xNbO_y and related oxides. The superconductivity actually comes from the presence of filaments of niobium metal in the sample, or worse, from NbN, which forms very easily when there is even a small amount of residual air or nitrogen present during synthesis.

(5) A “new” superconductor is sometimes reported when the authors have merely substituted one minor constituent for another in a known superconductor. That the 123-type phase does not form in the Sr-Y-Cu-O system without being stabilized by a small amount of another metal ion mixed in on the copper chain site is responsible for an almost countless number of these announcements. A “new” superconductor is not announced every time $YBa_2Cu_3O_7$ is doped with a minor amount of some additional metal ion, and the same should be the case in the Sr-Y-Cu-O system. Partial substitution of 10–15 elements in the periodic table allows for the stabilization of the 123-type phase in this system.

Table I. Structurally or Chemically Distinct Copper Oxide Superconductors and Year of Discovery

Superconductor	Year	Superconductor	Year
(La,M) ₂ CuO ₄	1986	TlBa ₂ (Eu,Ce) ₂ Cu ₂ O ₉	1992
La ₂ CuO _{4+x}	1988		
La ₂ CuO ₄ F _x	1988	(Tl,Pb)SrCaCu variants of Tl, Ba, Ca compounds	1988
(Nd,Sr,Ce) ₂ CuO ₄	1989		
(Nd,Ce) ₂ CuO ₄	1989		
Nd ₂ CuO _{4-x} F _x	1989	GaSr ₂ (Y,Ca)Cu ₂ O ₇	1991
Sr ₂ CuO _{3+x}	1993	GaSr ₂ Ca _{n-1} Cu _n O _x	1994
Sr ₂ CuO ₂ F _{2+x}	1994	<i>n</i> = 3, 4	
(Ca,Na) ₂ CuO ₂ Cl ₂	1994	AuSr ₂ CaCu ₂ O ₇	1997
(Ca,Na) ₃ Cu ₂ O ₄ Cl ₂	1995	NbSr ₂ (Nd,Ce) ₂ Cu ₂ O ₁₀	1992
(Sr,K) versions of previous two also are superconducting		RuSr ₂ (Nd,Ce) ₂ Cu ₂ O ₁₀	1996
		and others in "1222" type with a mix of Cu and M on first Cu site (e.g., Ti, V, Cr) also known	
(La,Sr) ₂ CaCu ₂ O ₆	1990		
(Sr,Ca) ₂ (Sr,Ca) _{n-1} Cu _n O _x	1993	Cu(Eu,Ce) ₂ (Eu,Sr) ₂ Cu ₂ O ₉	1989
(<i>n</i> = 2, 3, 4)		and others in this type with a mix of Cu and M on first Cu site (e.g., Pb, Ga) also known	
PbBaSr(Y,Ca)Cu ₃ O _x	1990		
Sr _{1-x} Nd _x CuO ₂	1991		
YBa ₂ Cu ₃ O ₇	1987		
YBa ₂ Cu ₄ O ₈	1988	HgBa ₂ Ca _{n-1} Cu _n O _{2n+2}	1993
Y ₂ Ba ₄ Cu ₇ O ₁₅	1988	<i>n</i> = 1, 2, 3, 4, 5, 6	
(Cu,M)Sr ₂ (Y,Ca)Cu ₂ O ₇	1988	Hg ₂ Ba ₂ (Y,Ca)Cu ₂ O ₈	1994
M stabilized Sr 123		(Hg _{0.5} Cr _{0.5})Sr ₂ CuO ₅	1995
M = Pb, Ga, Fe, B, SO ₄ , CO ₃ , Al, (Bi + Cd)		(Hg _{0.5} Cr _{0.5})Sr ₄ Cu ₂ O ₇ CO ₃	1995
		(Ba,Sr) ₂ Cu _{1+x} (CO ₂) _{1-x} O _y	1992
Pb ₂ Sr ₂ (Y,Ca)Cu ₃ O ₈	1988	(Cu _{1-x} (CO ₂) _x) _m (Ba,Sr) ₂ Ca _{n-1} Cu _n O _y	1994
Pb ₂ (Sr,La) ₂ Cu ₂ O ₆	1988	<i>m</i> = 1; <i>n</i> = 2, 3, 4, 5; <i>x</i> ≠ 0 or <i>x</i> = 0	
		<i>m</i> = 2; <i>n</i> = 3, 4, 5; <i>x</i> ≠ 0	
"Bi ₂ Sr ₂ CuO ₆ "	1987		
Bi ₂ Sr ₂ CaCu ₂ O ₈	1988	Bi ₂ Sr ₄ Cu ₂ O ₈ CO ₃	1993
Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀	1988	Bi ₂ Sr ₅ Cu ₃ O ₁₀ (CO ₃) ₂	1994
Bi ₂ Sr ₂ (Ln,Ce) ₂ Cu ₂ O ₁₀	1990	(Tl,Pb)Sr ₄ Cu ₂ O ₇ CO ₃	1993
Tl ₂ Ba ₂ Ca _{n-1} Cu _n O _{2n+4}	1988	Ca _{13.5} Sr ₅ Cu ₂₄ O ₄₁	1996
<i>n</i> = 1, 2, 3, 4		(60 kbar (6 MPa) applied pressure only)	
TlBa ₂ Ca _{n-1} Cu _n O _{2n+3}	1988		
<i>n</i> = 1, 2, 3			

Considering all the above, the materials I believe to be unique superconducting copper oxides, with the date of their first report, are listed in Table I. Uniqueness is taken to mean a new structure type, a new intermediary layer, or a significant difference in chemistry from previously known examples with the same structure type. (Perhaps others using a different philosophy for what constitutes a truly unique superconductor would have a different listing.) There have been many reports of "new" superconductors

in the past few years that are actually only substitutions of one type of stabilizing atom for another in a well-known structure type. This means, as far as I can tell, that only one unique cuprate superconductor was discovered in 1997 and none in 1998. The list presented here represents my best assessment of the current situation and is slightly different from earlier versions I have published. The compounds are organized by type of intermediary layer and number of CuO₂ planes in Table II, generally accepted to be the

Table II. Classification of Copper Oxide Superconductors by Intermediary Layer and Number of CuO₂ Planes

Intermediary layer	(CuO ₂) _n						M ₂ O ₂ + 2CuO ₂
	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6	
AO (A = Ln, Ca, Sr, Ba)	X	X	X	X			
CuO or (Cu,M)O		X					X
2CuO		X					
PbO-Cu-PbO	X	X					
2BiO	X	X	X				X
TlO	X	X	X				X
2TlO	X	X	X	X			
GaO		X	X				
NbO ₂							X
RuO ₂							X
AuO		X					
HgO	X	X	X	X	X	X	
2HgO		X					
(Cu,C)O	X	X	X	X	X		
2(Cu,C)O			X	X	X		
BiO-CO ₃		X	X				
(Tl, Pb)O-CO ₃		X					
MCl	X	X					

most useful way of looking at them and seeing the patterns. Many reviews have been written about such classification schemes, and I will not treat them here. Finally, the rate of discovery of superconducting copper oxides as a function of year is presented in Fig. 23. Figure 23 shows the incubation period of 1986–1987, the banner year of 1988, the doldrums of the early 1990s, and the dramatic impact of high-pressure synthesis beginning in 1994 and lasting until 1997.

VI. Some Current Directions in Oxide Superconductor Research

After more than 12 years of active research in high- T_c superconductors, much has been learned about them, and new insight into the behavior of other materials has been attained as well, as transition-metal compounds are being reconsidered in a new light. Current research directions primarily involve the posing and answering of complex, specific questions designed to attempt to clarify the superconducting mechanism, the fabrication of experimental electronic devices, and the processing of bulk materials for large-scale applications. This review is primarily of a crystal-chemical nature, and, therefore, those three topics are best left to expert reviews elsewhere. Two areas of research into new superconducting oxides are active at this time: the investigation of cuprates with copper–oxygen geometries that are more amenable to first-principles calculation of physical properties, and the investigation of a different type of oxide superconductor, based on ruthenium oxide, in which an implied relationship between magnetism and superconductivity is also present. These are described briefly in this section.

The first area of active research in oxide superconductors has been inspired by the predictions of theorists.^{12,13} The CuO_2 planes responsible for superconductivity in the normal cuprate materials, even though geometrically simple, are very difficult to model theoretically. Theorists can model the electronic and magnetic behavior of complex one-dimensional systems exactly, but, in two dimensions, approximations must be made that to date apparently have been insufficient to allow the prediction of a superconducting state from first principles. The important insight that came to one group of theorists was that they might be able to understand CuO_2 planes, which are made from corner-shared CuO_4 squares, if they first modeled the behavior of one-dimensional chains of corner-shared CuO_4 squares. These one-dimensional chains could then be

lined up side-by-side, parallel to each other, sharing the oxygen between them, forming “ladders.” The theorists wondered whether they could model that system exactly, because the ladder is electronically and magnetically intermediate between one and two dimensions. Two chains side-by-side make a ladder with two legs. Three chains side by side make a ladder with three legs, and so on, until eventually a full plane is built. It turned out they could model them very well. When they began to look at the predicted electronic and magnetic properties of such ladder systems, they found some interesting surprises.

They found theoretically that a two-legged ladder made of Cu^{2+} and oxygen, and all ladders with an even numbers of legs, should display a “spin gap”—a range of forbidden energies in the set of allowed spin states beginning just above the ground state—exactly analogous to the electronic bandgap in a semiconductor. They also predicted that, if a system such as this could be electronically doped, then it should become superconducting. The predicted phenomenology of the behavior of the two-legged ladder was exactly analogous to that observed in the cuprate superconductors. For the three-legged ladders and all ladders with an odd numbers of legs, no magnetically or electronically unusual behavior could be observed.

Now that such behavior was predicted, could it be observed in a real material? Again high-pressure synthesis was the key. The compounds SrCu_2O_3 and $\text{Sr}_2\text{Cu}_3\text{O}_5$, with two-legged and three-legged ladder structures, respectively, were synthesized by solid-state chemists who had heard the predictions.²⁶ Their crystal structures are shown in Figs. 24 and 25. Magnetic and electronic interactions for copper–oxygen–copper arrays are very strong for Cu–O–Cu bond angles of $\sim 180^\circ$ and very weak for O–Cu–O bond angles of $\sim 90^\circ$; the magnetic two-legged and three-legged nature of the compounds are shown in the figures. Consistent with the predictions, the two-legged ladder compound showed the presence of a spin gap and the three legged ladder compound did not. Half of the prediction held true. However, it turned out to be impossible to electronically dope these materials, and the theoretical picture was not fully verified.

Continuing to pursue these ideas, there were several false starts in finding ladder systems that could become superconducting when doped. Then, in 1997, a group announced the discovery of superconductivity in a ladder system that was made by high-pressure synthesis and had to be subjected to high pressure while cooling to low temperatures to become superconducting.²⁷ The

The Rate of Discovery of Copper Oxide Superconductors

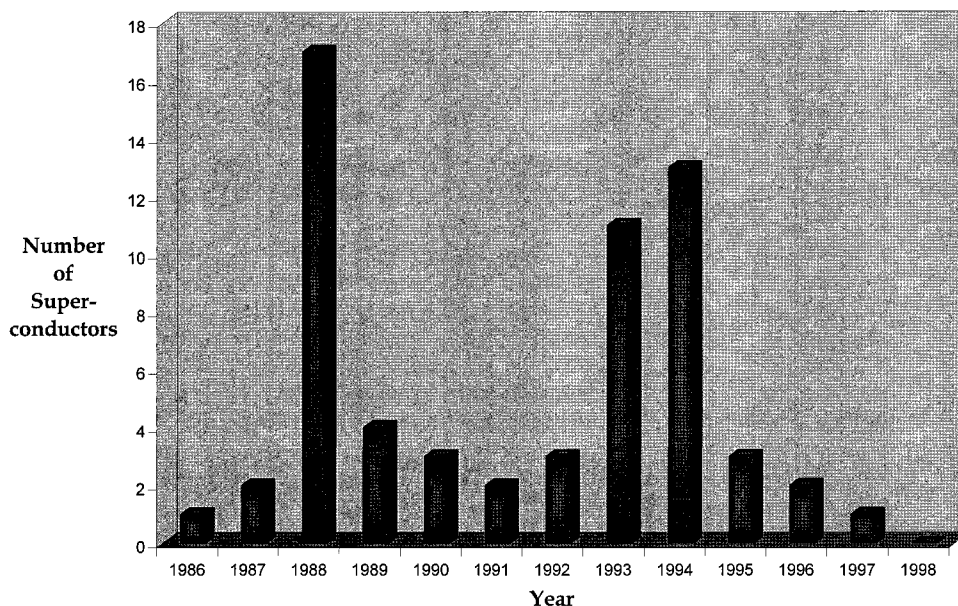


Fig. 23. Number of copper oxide superconductors discovered per year, 1986–present.

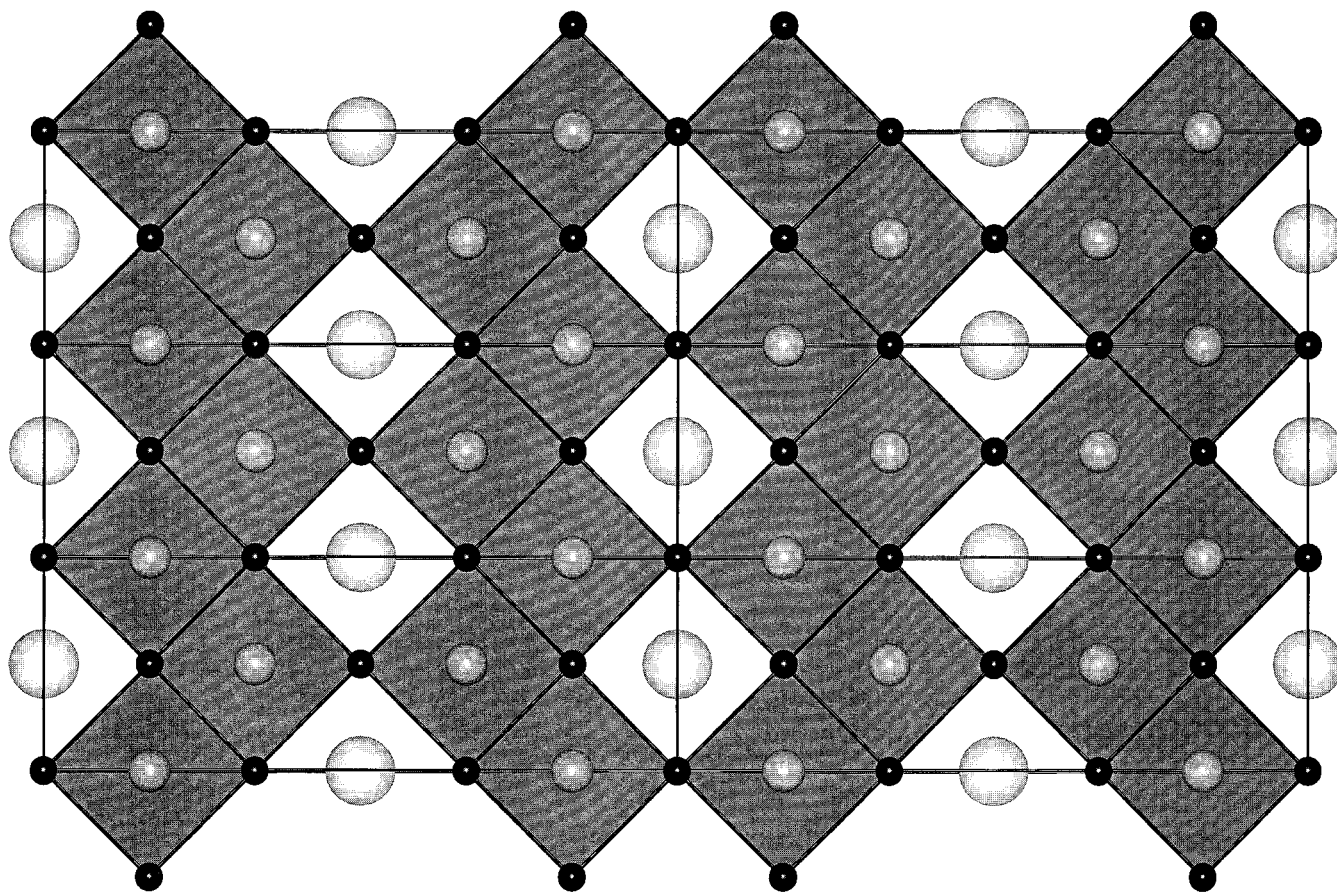


Fig. 24. Hypothetical crystal structure of SrCu_2O_3 (see Fig. 9 for legend).

superconductor announced was based on the compound $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, which had been known since the early days of high- T_c research. The crystal structure of this complex material is shown in Fig. 26. It is made from severely skewed CuO_5 pyramids attached at their vertices by badly twisted CuO chains. The bases of the pyramids form the same type of plane as is found in the much simpler compound SrCu_2O_3 , i.e., a two-legged ladder. Unlike the other materials considered as possible ladder superconductors, however, this one has a charge reservoir layer—the CuO chains—and, therefore, can be doped.

The doping process is complicated. At a stoichiometry of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, the formal copper valence is 2.25. The material is therefore hole doped as made. However, the holes are concentrated in the chains. When the solid solution $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ is made, the unit-cell dimensions change significantly, and charge is transferred from the chains to the ladder plane. Under ambient pressure conditions, the calcium solid-solution limit is $x = 10$, and there is never sufficient charge transfer to reach a superconducting state. However, synthesis under high pressure extends the upper limit of calcium solubility to $x = 13.5$. This material, however, is not superconducting. Because the calcium substitution shrinks the lattice significantly, the next step would be to subject the $x = 13.5$ material to high pressure with cooling to attempt to obtain superconductivity. That was successful, and a superconducting transition was obtained in a narrow pressure range near an applied pressure of 30 kbar (3 MPa).

Therefore, has the theory been verified and has high- T_c superconductivity been understood theoretically? Some believe so, but there is no consensus in the community at large. Time will tell. It is fair to say that much-more-sophisticated experiments need to be conducted to explore the detailed predictions of the theoretical picture. Competing theories might also be able to explain the existence of superconductivity in this compound. Also, the difficulty in making and testing the compound has severely limited its

study. The lesson on the false report of superconductivity of the all-layer compound $\text{Sr}_{1-x}\text{CuO}_2$ synthesized by the same method due to inadvertent potassium and chlorine contamination should be remembered. Study of this material in more detail would be an interesting course of research in the future.

The second area of research centers around the very-low-temperature oxide superconductor Sr_2RuO_4 . This is the first ($n = 1$) member of the Ruddlesden–Popper series, $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$. In this series, common in ternary transition-metal oxides, n is the number of RuO_2 layers. The members $n = 1$, $n = 2$, and $n = \infty$ (the perovskite) are known in the Sr–Ru–O chemical system. Their crystal structures are shown in Fig. 27. The interest in this family comes from the manner in which ferromagnetism transforms into superconductivity as a function of the number of RuO_2 layers. The perovskite SrRuO_3 is a ferromagnetic metallic conductor with a large ordered magnetic moment and a ferromagnetic ordering temperature of 160 K. The double-layer compound $\text{Sr}_3\text{Ru}_2\text{O}_7$ has a local moment at high temperatures, consistent with the spin expected for Ru^{4+} , and is a metallic conductor. The Curie–Weiss theta, indicative of the strength of the magnetic interactions between ruthenium atoms, is low, ~ 10 K. No magnetic ordering transitions are observed in this compound down to low temperatures. Thus, on going from the fully three-dimensional compound to the double-layer compound, the magnetism has changed rather dramatically—from that of a high- T_c ferromagnet with strong interactions between spins, to a (very) low- T_n antiferromagnet, with weak spin interactions. Finally, the single RuO_2 layer compound Sr_2RuO_4 shows no local moment magnetic behavior whatsoever at high temperatures—the magnetic susceptibility indicates that the electrons are completely delocalized. No magnetic transitions are observed. Instead, this material becomes superconducting at temperatures near 1 K²⁸!

Therefore, with a superconducting transition temperature so low, what is the interest in this material? The interest is purely

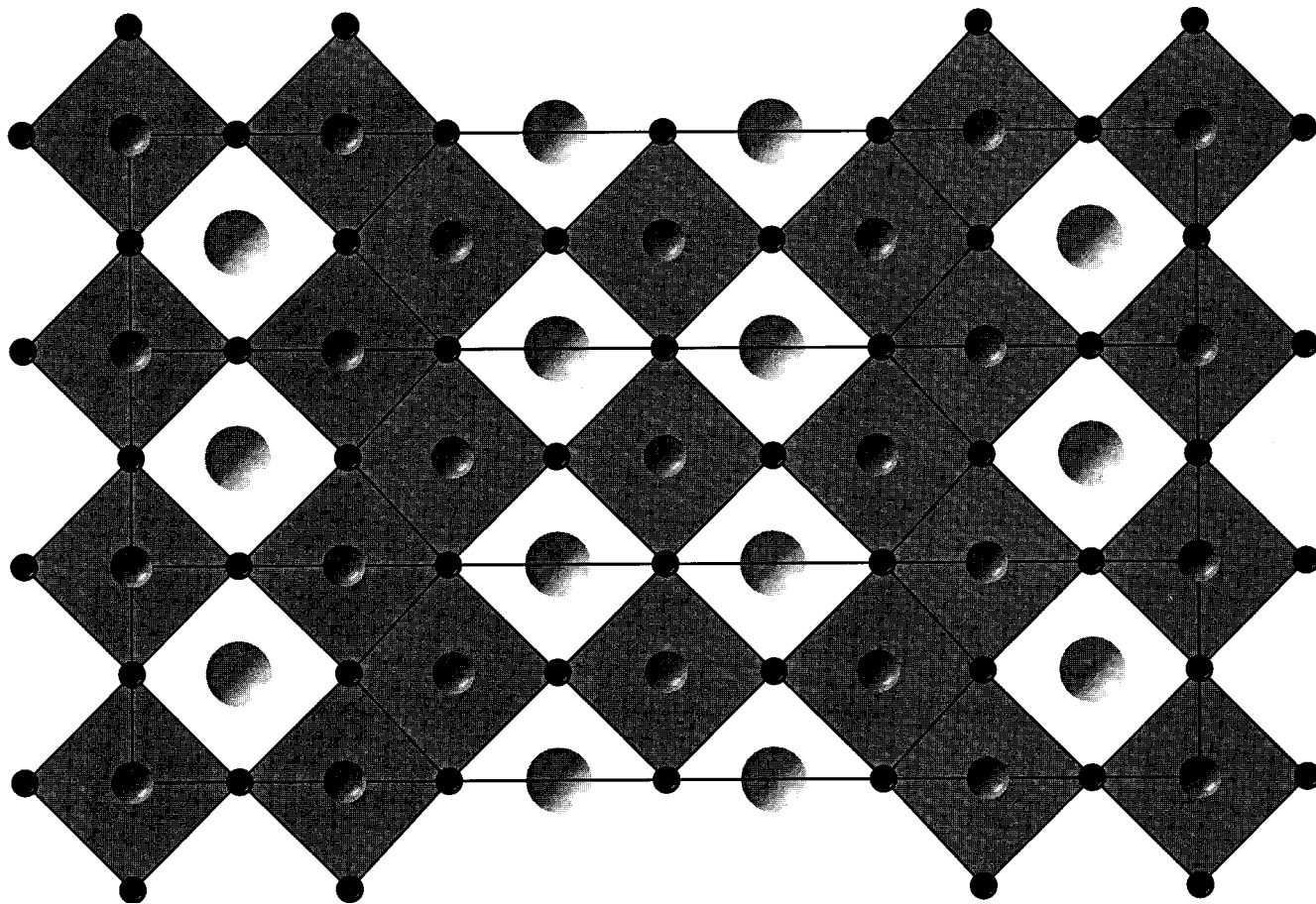


Fig. 25. Crystal structure of $\text{Sr}_2\text{Cu}_3\text{O}_5$ (see Fig. 9 for legend).⁴⁹

scientific—this appears to be another example of an oxide for which the mechanism of the superconductivity is not conventional electron-phonon coupling. Many sophisticated experiments have been performed that show that to be the case. As in the cuprates, there appears to be a relationship between superconductivity and magnetism, in this case between *ferromagnetism* and superconductivity. This is a highly unexpected relationship, because the two effects should be mutually exclusive by conventional understanding. The transition from ferromagnetism to superconductivity as a function of increasing two-dimensionality of crystal structure is intriguing, especially in the context of the importance of two-dimensionality in the cuprate superconductors: The same is true for the analogous correlation of the disappearance of the localized magnetic moment and the appearance of superconductivity.

Given that transition-metal oxides frequently walk a fine line between localized moment magnetism and delocalized nonmagnetic electron states, there are likely to be other examples of exotic superconductivity of a similar nature in other oxides. Two aspects of the results on the ruthenates, however, suggest that these interesting materials will be very difficult to find. Unlike in other oxide superconductors, in the ruthenates the presence of superconductivity is very sensitive to the presence of impurities. The superconductivity in Sr_2RuO_4 is destroyed by the presence of impurity atoms at the level of tens of parts per million, as opposed, for instance, to the case in the cuprates, where a few percent impurity concentration is needed to suppress the superconductivity. Only single crystals of Sr_2RuO_4 grown in the traveling-solvent floating-zone furnace, which grows the crystal and refines it of impurities, have been found to be superconducting. Finally, testing materials for superconductivity at temperatures near 1 K is hardly something that can be done routinely. Liquid helium can be used easily to cool samples to 4.2 K and, with some effort, to 1.8 K. A more sophisticated and expensive cooling technology, based on ^3He , is needed to test materials at lower temperatures. Not many

groups in the world have the means and the will to perform an exploratory materials program of that type.

VII. The Future

The pursuit of the microscopic mechanism for high- T_c superconductivity in the cuprate ceramics and their potential practical application has had a significant impact on the field of materials science in general. Examples of these types of influences are the development of laser ablation for the fabrication of thin films, the dramatic improvements in the energy and angular resolution in photoelectron spectroscopy, the widespread use of traveling-solvent floating-zone crystal-growth methods, and the fabrication of complex experimental magnetic and electronic devices based on oxides rather than conventional semiconductors. The impact of these developments is clearly being felt in areas outside of superconductivity research even now, and it will continue well into the future. From my point of view, the last of these—the development of the ability to fabricate new multilayer devices based on the magnetic and electronic properties of complex transition-metal oxides, including the development of the fabrication methods and the sophisticated analytical tools used in their characterization—may be the most far-reaching legacy of high- T_c superconductivity research. It has brought ceramics from the old world of technological application as bulk components into the modern world of integration into microelectronic systems. These innovations would have happened eventually in any case, but the very strong driving force of the understanding and application of oxide superconductors has greatly accelerated the pace of their development.

Constant progress is being made toward the development of fabrication techniques for making bulk conductors of high- T_c superconductors. Innovative processing methods that allow for the

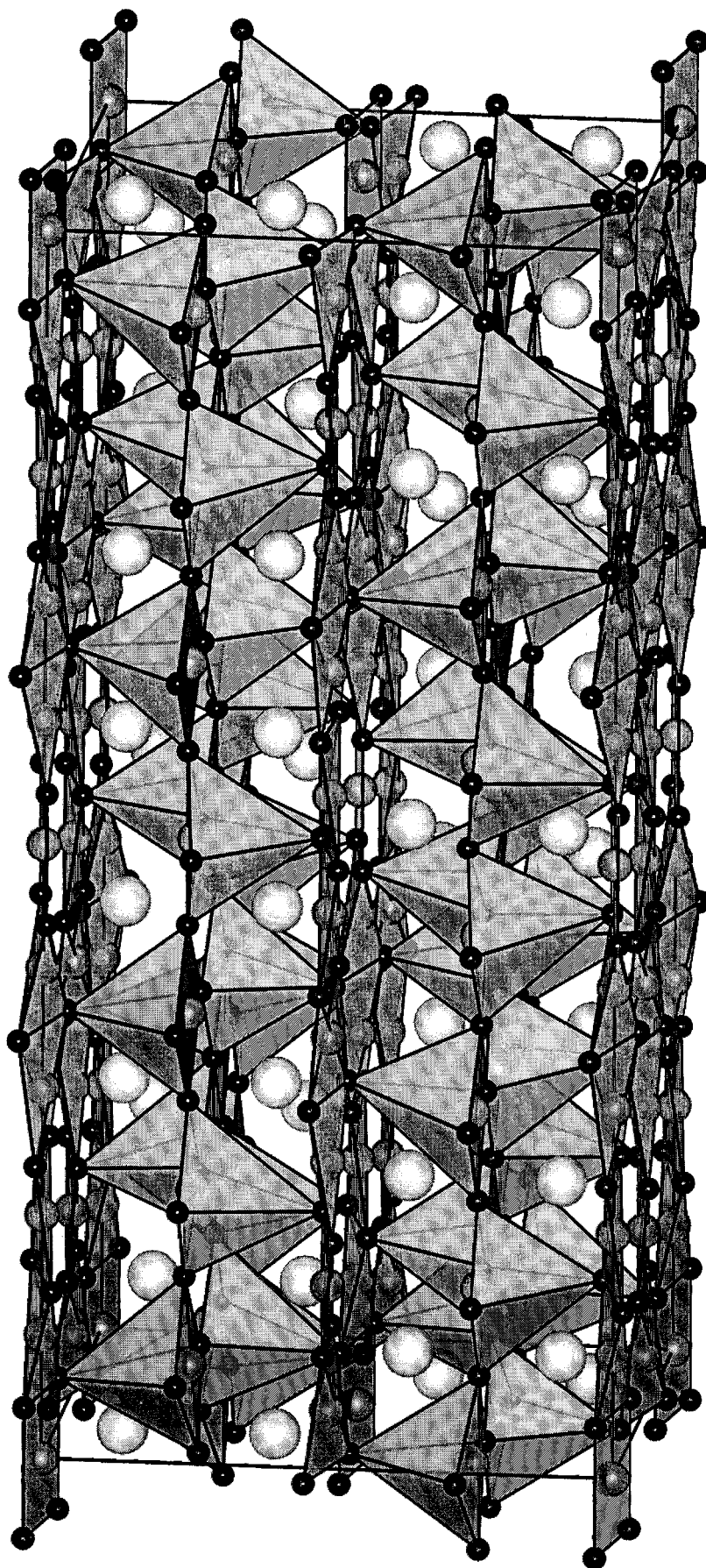


Fig. 26. Crystal structure of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ (see Fig. 9 for legend).⁵⁰

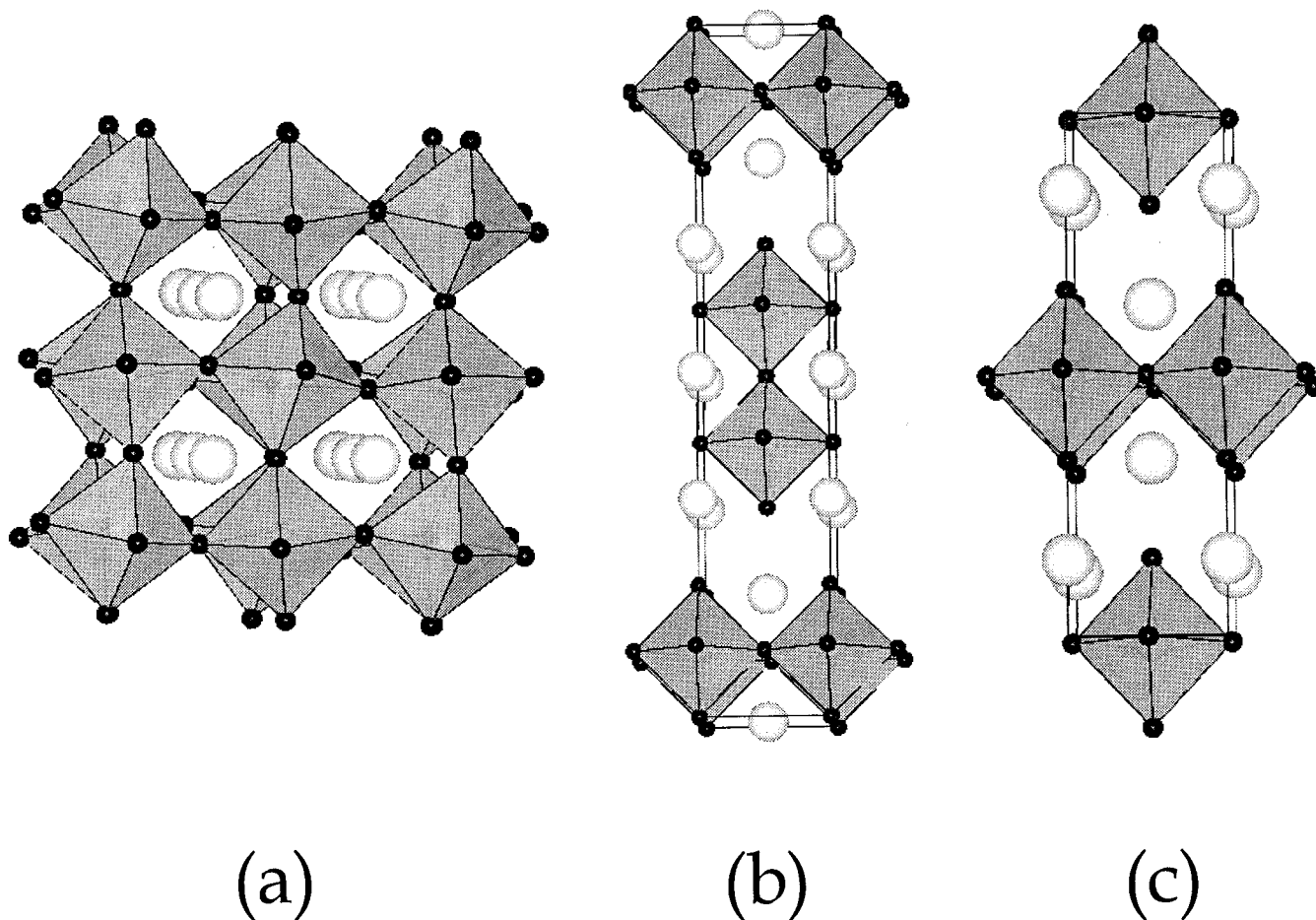


Fig. 27. Crystal structures of (a) SrRuO_3 ,⁵¹ (b) $\text{Sr}_3\text{Ru}_2\text{O}_7$,⁵² and (c) Sr_2RuO_4 (see Fig. 9 for legend).⁵³

alignment of superconducting crystallites in bulk ceramics, such that the superconducting current travels in preferred directions across grain boundaries, are presently in a stage of active research. The processing of superconducting cuprates appears to me to be one of the most important areas for research in the future in this field, because the potential of high- T_c superconductors to change the way society functions cannot be realized until problems with making them into practical materials can be solved. It is important for funding agencies and corporate research managers to take a long-term view of the possibilities for success, although the progress may in many ways often appear slow. Perhaps several concentrated worldwide consortia working within different cultural contexts, with sufficient human investment to achieve teams of critical mass, is the best way to go about this. Although the materials-processing issues are difficult, nothing has appeared to date that would preclude the eventual large-scale use of high- T_c superconductors in technologies that would impact daily life.

As far as new superconductors with even higher transition temperatures are concerned, it now does not appear likely that they will come in the cuprate family in materials amenable to conventional synthesis. The issue of practical application is not a single-variable problem, and other factors—in particular the modification of the behavior of the superconductors in high fields and high currents through innovative processing and chemical manipulation—are more important than an increase in T_c at this time. Closed-cycle refrigeration systems can be designed and built to cool the materials now available to temperatures appropriate for their use if the current-carrying and magnetic-field response issues can be resolved. On the other hand, great potential exists for the discovery of oxides with different lattice geometries or other characteristics that contribute to the understanding of the superconducting mechanism.

It is a big periodic table. It is conceivable that there will be another new family of superconductors that will display exotic or exciting superconducting properties. Perhaps the cuprates are unique in having a mechanism for superconductivity that depends on the particular set of complex factors described above, and other superconductors may not have as wildly high superconducting transition temperatures, but there is no doubt in my mind that equally unexpected superconductors will be found elsewhere as well. Materials with much more modest T_c values, in the 30–40 K range, and different processing or critical field/critical current capabilities may ultimately prove to be the ones that change the way we live. Maybe the superconductors will be oxides and maybe not, but the superconducting oxides will always be considered the first to open our eyes to the fact that anything is possible in materials science if we just keep looking.

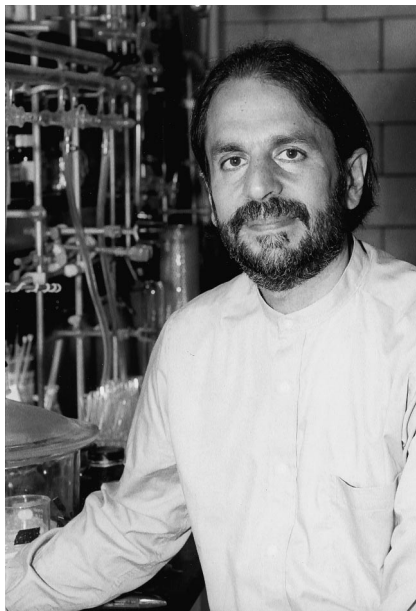
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