High T_c Oxide Superconductors

M. Brian Maple, Guest Editor

The recent revolution in high temperature superconducting materials has generated a wave of intense excitement and activity that has swept through the scientific community, attracting the attention of the news media and general public as well. The reason for this is twofold: the unexpected occurrence of superconductivity at such high temperatures is of immense scientific interest, and the new high temperature oxide superconductors may have important technological applications.

Based on a large amount of experimental information and (presumed!) theoretical understanding, the prevailing view prior to 1986, when high temperature superconductivity in oxides was discovered, was that the maximum value of the superconducting transition temperature T_c of any material would not increase much above ~23 K, the high T_c record held since 1973 by the A15 compound Nb_3Ge. In fact, between 1911 (the year H. Kammerlingh Onnes discovered superconductivity) and 1986, T_c only increased at an average rate of ~0.25 K per year. However, within the last two years the maximum T_c value of the new copper oxide superconductors has risen at an average rate of ~50 K per year to its present value of ~125 K! Thus, superconductivity near or above room temperature no longer seems out of the question, as it did a few short years ago! Moreover, the oxides were generally regarded as the least likely candidates for high T_c superconductivity due to their low concentrations of charge carriers. An understanding of the origin and nature of high T_c superconductivity in the new oxide compounds constitutes one of the most important and challenging scientific problems that has emerged in recent years.

The new high T_c superconducting oxides hold great promise for technology, ranging from large-scale applications involving superconducting magnets, motors, generators, and transmission lines to small-scale applications such as SQUID magnetometers and digital electronic components based on Josephson junction devices. However, formidable technological obstacles remain to be surmounted, such as the fabrication of conductors with high critical current densities and thin films that are compatible with silicon and other electronic materials.

The articles in this issue of the MRS BULLETIN give an overview of the developments that have taken place in high T_c superconductivity during the past two years; due to the vastness of the field, they are not intended to provide a comprehensive review. This issue also commemorates the second anniversary of the December 1986 Fall Meeting of the Materials Research Society in Boston, where initial research results were reported, touching off an explosion of research on the high T_c oxides in the United States and throughout the world!

One of the most striking aspects of all presently known high T_c superconductors with T_c's greater than ~30 K is that they are copper oxides with layered perovskite-like crystal structures, all possessing CuO_2 planes. Like its predecessor $Ba(Pb_{1-x}Bi_x)O_3$, which has a maximum T_c of ~14 K, the system $(Ba_{1-x}K_x)BiO_3$, with a maximum T_c near 30 K, has a cubic perovskite crystal structure. The series of T_c = 95 K $RBa_2Cu_3O_{7-\delta}$ superconductors, where R = rare earth element, has a crystal structure which, in addition to CuO_2 planes, contains CuO chains which appear to play an important role in the superconductivity of these materials. I.K. Schuller and J.D. Jorgensen describe the crystal structures of the various families of high T_c oxide superconductors and the relationship between the crystal structure and the superconducting properties.

The material responsible for the indications of superconductivity at ~30 K in the groundbreaking experiments of J.G. Bednorz and K.A. Müller[1] is $(La_{2-x}Ba_x)CuO_{4-\delta}$, where δ is the oxygen vacancy concentration and $x \approx 0.15$. Superconductivity has since been found in several $(La_{2-x}M_x)CuO_{4-\delta}$ systems, where M is one of the divalent alkaline earths Ca, Sr, and Ba, with respective maximum T_c's of ~20 K, ~40 K, and ~30 K, or the alkali metal Na with $T_c \approx$ 20 K. Surprisingly, the undoped parent compound $La_2CuO_{4-\delta}$ is an insulating antiferromagnet with a Néel temperature $T_N \approx 250$ K and a magnetic moment $\mu \approx 0.5\ \mu_B$ per Cu^{2+} ion. The substitution of the monovalent or divalent M cations suppresses the antiferromagnetism and transforms the material into a superconducting metal. Superconductivity, magnetism, and the physical properties of the $(La_{2-x}M_x)CuO_{4-\delta}$ (M = Ca, Sr, Ba, and Na) are described in the article by Z. Fisk, S-W. Cheong, and D.C. Johnston.

The discovery of superconductivity at ~90 K in material now known to have the chemical formula $YBa_2Cu_3O_{7-\delta}$, where δ = 0.1, by M.K. Wu, C.W. Chu, and their co-workers[2] gave a great impetus to the field of high T_c superconductivity in oxides, since it broke the 77 K liquid nitrogen temperature barrier. Shortly thereafter, superconductivity with $T_c \approx$ 90–94 K was discovered independently by several groups in the lanthanide analogues $LnBa_2Cu_3O_{7-\delta}$ where Ln is a lanthanide element except for Ce, Pr, Pm, and Tb. J.T. Markert, B.D. Dunlap, and I survey the abundance of experiments that have been performed on the remarkable $RBa_2Cu_3O_{7-\delta}$ compounds. Among the topics considered are superconductivity, antiferromagnetic order involving both the Cu^{2+} ions and the R^{3+} ions, and the effects of chemical substitution on the superconducting and normal state properties.

The highest values of T_c are found in a large family of compounds of the type $(AO)_mM_2Ca_{n-1}Cu_nO_{2n+2}$ where the A cation can be Tl, Pb, Bi, or a mixture of these elements, the value of m = 1 or 2 (but is only 2 when A is Bi), the M cation is Ba or Sr, and the substitution of Ca by Sr is frequently observed. The number of CuO_2 layers, separated by Ca, within a unit cell is equal to n, and T_c increases with n up to n = 3. The highest temperature at which zero resistivity is obtained, currently 122 K, occurs in this family of materials. The structure, composition, and systematics of T_c in this system are described in the article by A.W. Sleight, M.A. Subramanian, and

C.C. Torardi.

One of the most interesting of the new high T_c superconducting materials is $(Ba_{1-x}K_x)BiO^3$ which exhibits superconductivity near 30 K for $x \approx 0.4$. This material is distinctly different from the other high T_c oxides in several respects: (1) it has a simple cubic perovskite crystal structure, (2) it does not contain copper, and (3) it does not exhibit antiferromagnetism in its insulating phase. The physical properties of the $(Ba_{1-x}K_x)BiO_3$ system are described and compared to those of the related 14 K superconductor $Ba(Pb_{0.75}Bi_{0.25})O_3$ and the copper-oxide-based superconductors in the article by R.J. Cava and B. Batlogg.

The physical properties of high T_c oxide compounds are very sensitive to the oxygen stoichiometry; changes in the oxygen composition can produce structural transformations, metal-insulator transitions, and strong variations in the transition temperatures for magnetic ordering and superconductivity. For copper-oxide-based high T_c superconductors, a common view is that the oxygen content determines the valence state of Cu, the critical parameter upon which the occurrence of superconductivity depends. The effect of oxygen stoichiometry on the physical properties, particularly those related to the superconducting transition, of the compounds $(La_{2-x}M_x)CuO_{4-\delta}$, $RBa_2Cu_3O_{7-\delta}$, and $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ are discussed in the article by J.M. Tarascon and B.G. Bagley.

Thin films of the new high T_c copper oxide superconductors have important applications in basic research and technology. A variety of techniques for fabricating high T_c copper oxide thin films, particularly electron beam and sputter deposition, are discussed by R.B. Laibowitz. He also considers some uses of thin films in tunnel junctions for measuring the superconducting energy gap, and in SQUIDs and transmission lines. Many applications of the high T_c oxide superconductors will require forming conductors for electromagnets, rotating electrical machinery, transmission lines, etc. Various novel preparation techniques for the high T_c oxide superconductors, including ceramic and metallurgical processing, melt-textured growth, novel wire fabrication, and shock compaction, are discussed in the article by W.J. Nellis and L.D. Woolf.

The unexpectedly high values of T_c and other unusual features, such as extremely short superconducting coherence lengths, small superconducting isotope effects, and the proximity of antiferromagnetism, suggest the possibility that a non-phonon pairing mechanism, perhaps magnetic in nature, is responsible for the high T_c superconductivity of the copper oxide compounds. In the final article, V.J. Emery discusses the physical properties of the oxides that are relevant to the occurrence of high T_c superconductivity, and reviews the theoretical approaches currently being taken in an attempt to solve this fascinating and formidable problem.

Two other articles that recently appeared in the MRS BULLETIN complement the selection of articles in this issue. These are "Magnetism in the High T_c Family of Compounds"[11] by S.K. Sinha[3] and "Crystal Growth of High Temperature Superconductors" by H.J. Scheel and F. Licci.[4]

As far as the future is concerned, it seems clear that new compounds with yet higher T_c's await to be discovered. Further experimentation will surely yield new information concerning the mechanism that is responsible for the high T_c superconductivity in these remarkable materials, and progress in developing a theory of high temperature superconductivity in oxides can be anticipated. In the meantime, it will be interesting to observe the advances in developing practical devices that are based on these new high T_c superconducting oxide materials.

References

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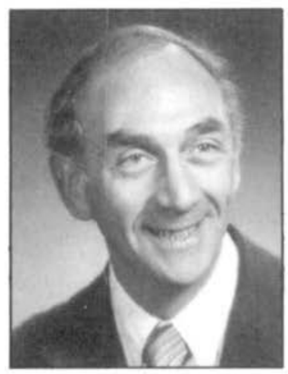
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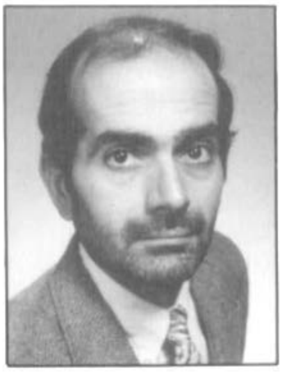

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Brian G. Bagley, a member of the technical staff in the Solid State Science and Technology Laboratory of Bell Communications Research (Bellcore), served in a similar capacity for 16 years in the Materials Research Laboratory of Bell Laboratories, Murray Hill, New Jersey. He received a PhD in applied physics, under Prof. David Turnbull, from Harvard University in 1968. He is a member of the American Physical Society and the Materials Research Society and holds an adjunct appointment as a professor of materials and metallurgical engineering at Stevens Institute of Technology.

Bertram Batlogg is head of the Solid State and Physics of Materials Research Department at AT&T Bell Laboratories, Murray Hill, New Jersey. He holds a diploma in physics from ETH Zurich, Switzerland, where he also received his doctorate in natural sciences in 1979. After joining Bell Laboratories that same year, Batlogg began research on materials-related solid state physics, with an emphasis on many-body problems. In particular, he has studied mixed-valent rare-earth compounds and heavy-fermion superconductors and magnets. In addition, he has explored in detail the unusual superconducting properties of $Ba(Pb,Bi)O_3$ and, more recently, the physics of CuO-based high temperature superconductors.

Robert Cava is a distinguished member of the technical staff in the Solid State Chemistry Research Department at AT&T Bell Laboratories. He received his PhD in ceramics at Massachusetts Institute of Technology after undergraduate degrees in metallurgy and materials science at the same school. He was a National Research Council postdoctoral fellow with R.S. Roth at the National Bureau of Standards for one year before joining AT&T in 1979.

Sang-Wook Cheong is a graduate student at the University of California, Los Angeles, a guest scientist at Los Alamos National Laboratory, and a consultant to the Department of Physics at the University of Florida, Gainesville. His research interests include superstring theory (as a 2D supergravity with a few scalar fields) and experiments on high T_c superconductors involving single-crystal growth and transport measurements.

B.D. Dunlap is director of the Materials Science Division at Argonne National Laboratory. He received his PhD in physics from the University of Washington in 1966, and joined Argonne at that time. His research has focused on the electronic and magnetic properties of rare-earth and actinide materials, most recently dealing with magnetic superconductors, heavy-fermion systems, and oxide superconductors.

Victor J. Emery is a senior scientist at Brookhaven National Laboratory. He received his PhD from Manchester University in England and is a Fellow of the American Physical Society. His research interests are in theoretical physics (particularly condensed matter physics) and statistical mechanics.

Zachary Fisk, who is on the staff at Los Alamos National Laboratory, received his PhD from the University of California, San Diego. His work has concentrated on single-crystal growth of heavy fermion materials, and also on layered cuprates related to high T_c superconductors.

David C. Johnston holds joint appointments as senior physicist with Ames Laboratory and professor in the Department of Physics at Iowa State University. Formerly, he served in the Corporate Research Laboratories of Exxon Research and Engineering Company, Annandale, New Jersey. He obtained his PhD in solid state physics and superconductivity at the University of California, San Diego, where his thesis advisor was the late Bernd T. Matthias. His current research centers on the high T_c oxide superconductors. His group and collaborations have contributed to the understanding of magnetic interactions and magnetic ordering, superconducting fluctuation diamagnetism, magnetic susceptibility scaling, magnetic field penetration depth, and other properties of the high T_c cuprates.

James D. Jorgensen is a physicist and group leader of the Neutron and X-ray Scattering Group in the Materials Science Division at Argonne National Laboratory, where he has worked for 14 years. He also directs the Powder Diffraction Program at Argonne's Intense Pulsed Neutron Source. Prior to his work on high T_c oxide superconductors, his research interests included ternary superconductors, fast ion conductors, and structural phenomena at high pressure. He has played a leading role in the development of instrumentation and data analysis techniques for time-of-flight powder diffraction at pulsed neutron sources. Jorgensen, who received his PhD in solid state physics from Brigham Young University, is a member of the American Physical Society, the American Crystallographic Association, and the Materials Research Society.

Robert B. Laibowitz is a research staff member at the IBM Research Center, Yorktown Heights, New York. He received BA, BS, and MS degrees from Columbia University and a PhD in applied physics from Cornell University. His research interests encompass many areas of superconductivity, including applications and mesoscopic phenomena in ultrasmall structures. He is a Fellow of the American Physical Society and a member of the American Vacuum Society and the Materials Research Society.

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William J. Nellis is head of the High-Pressure Shock-Compression Group at Lawrence Livermore National Laboratory. His research interests include the shock compaction and synthesis of superconductors and the measurement of properties of condensed matter at high dynamic pressures and temperatures. This work is directed at developing techniques for fabricating novel materials, understanding the nature of condensed matter at extreme conditions, and characterizing the nature of materials in deep planetary interiors. Nellis received a PhD in physics from Iowa State University and held a postdoctoral appointment in the Materials Science Division of Argonne National Laboratory.

Ivan K. Schuller is professor of physics at the University of California, San Diego and a special term appointee at Argonne National Laboratory. He received his Licenciado of Ciencias from the University of Chile and his MS and PhD from Northwestern University. Schuller is co-author of more than 175 publications and patents and has given numerous invited talks. A Fellow of the American Physical Society and the recipient of many awards, Schuller has focused his research on the physics and applications of layered and thin film materials, including high temperature superconductors. He has been involved in a variety of activities geared toward popularizing condensed matter physics among nonspecialists and, in his role as secretary/treasurer of the International Physics Group of the American Physical Society, is especially interested in promoting international scientific relations.

Arthur W. Sleight is currently a visiting professor at the University of California, Santa Barbara and a research leader at E.I. du Pont de Nemours & Company, Wilmington, Delaware. In 1975, he discovered superconductivity in the $(Ba,K)(Bi,Pb)O_3$ system at 13 K; the T_c in this system has now been pushed to 34 K and thus rivals $La_{2-x}A_xCuO_4$ superconductors. His research activities have spanned many aspects of the solid state chemistry of oxides, including surface chemistry and catalysis, magnetic properties, metal-insulator transitions, and superconductivity. Sleight served on the recent National Academy Panel on Superconductivity and is a member of the Materials Research Society.

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