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CERAMIC SUPERCONDUCTORS

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F O R E W O R D

This volume contains the Proceedings of the XI Winter Meeting on Low Temperature Physics. It has been a privilege for the Instituto de Investigaciones en Materiales, of the Universidad Nacional Autónoma de México, to pursue with this yearly event which brings together outstanding scientists from Mexico and several other countries of the world to talk and discuss the most relevant advances and problems in the field of Low Temperature Physics.

The interest in the field of high-T_c superconductors has been, in recent years, the driving power for intense theoretical and experimental research. For this reason, we have devoted the XI Winter Meeting to a review of recent theoretical developments, advances in the experimental search for the possible mechanisms involved in this phenomenon, in the characterization of these ceramic materials and aspects related with the search for new materials with even higher critical temperatures. Panel sessions and informal discussions were important and provided an excellent opportunity to discuss theory, experiment and some possible solutions to existing problems.

Thanks are given to all participants for the rich and fruitful academic atmosphere. We acknowledge the administrative support from Reuniones de Invierno A.C., which made possible the organization of this meeting.

The Editors

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HIGH TEMPERATURE SUPERCONDUCTIVITY: CHALLENGES FOR THE 1990'S

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ABSTRACT: We will review events leading to the discovery of high temperature superconductivity almost four years ago this month, discuss progress in synthesis, applications, and understanding of basic physical properties dating from that time, and finally address areas which are likely to present major challenges in the decade of the 1990's. With respect to the latter, we point to the necessity for thorough materials characterization as requisite for all attempts to build theoretical models for both the microscopic and macroscopic mechanisms of high temperature superconductivity.

Introduction

The science of superconductivity began, of course, with its discovery in 1911 by Kamerlingh Onnes,[1] and ushered in a new era of successive exciting discoveries in low temperature physics which continues to this day. It arose as a consequence of the steady improvement in gas liquifaction machinery during the 19th century, stressing the always important recurring interplay between science and technology as each progresses. Since Onnes' seminal measurement on mercury, literally hundreds of superconducting materials have been found. In fact, superconductivity is a rather pervasive phenomena in metallic compounds -- the number of metals and alloys that superconduct far outnumber those that do not. Whenever a new non-ferromagnetic metal is discovered, the odds that it will be a superconductor are very high. However, history also teaches that the transition temperature could be expected to be low, and, until recently, require liquid helium refrigeration.

For many years, workers in the field speculated and dreamt about the possibility that higher transition temperatures could be eventually achieved. One of the great triumphs of the Bardeen-Cooper-Schrieffer theory had been the identification of the electron-phonon interaction as the "bosonic-glue" by which electrons paired to give the superconducting state. Yet this same mechanism seemed to constrain the upper limits of accessible transition temperatures to a few percent of the lattice Debye temperature or else the material would suffer the consequence of inevitable structural instabilities arising from ever stronger electron-phonon coupling. On the other hand, the mathematical framework of the BCS theory did not restrict the boson field to phonons -- in principle, any well-behaved boson would do. Therefore, in the 1960's Bill Little[2] at Stanford and Vasily Ginzburg[3] in the Soviet Union proposed structural models whereby the pairing bosons were excitons whose characteristic energies were 10-20 times that of phonons. A period of intense activity followed in the 70's searching for appropriate material embodiments, concentrating mostly on organic and/or low dimensional systems (none have been found with $T_c > 13$ K...yet!). Most importantly, the initiatives of Little and Ginzburg encouraged the exploration of all sorts of "exotic" compounds in pursuit of higher transition temperatures, leading eventually to the discovery of superconductivity at greater than 10 K in lithium titanate by Dave Johnston[4] and Pb-doped barium bismuth oxide by Art Sleight.[5] This proof that significant transition temperatures could occur in metal oxides paved the way for the breakthrough of Georg Bednorz and Alex Mueller.[6]

It is interesting -- perhaps ironic -- that Berndt Matthias, who uncovered more superconducting materials than any other researcher of his time, yet remained a vocal skeptic of the possibility of T_c's much above 30 K, and Alex Mueller, eventual co-discoverer of just such a compound, were contemporaries from the same European institute and worked initially with ferroelectric oxides. Matthias went on to concentrate on superconductivity in metal alloy systems (I am told he intended to begin a search for superconductivity in ferroelectrics and transition metal oxides shortly before his untimely death in 1980), whereas

Mueller proceeded to build his career on research in ferroelectricity. This background opened his thinking to the possibility that unusually strong carrier-lattice interactions, like those which might occur in mixed-valent transition metal oxide Jahn-Teller configurations, could provide a path to higher transition temperatures. Around 1984, along with Bednorz, he began such a search, initially in nickelate compounds, which led to the discovery of high temperature superconductivity in barium-doped La_2CuO_{4-y} in early 1986, almost four years ago this month. It remains to be seen whether Mueller's intuition was right or if some other pairing mechanism is responsible for high-T_C. Nonetheless, the principal lesson of the copper oxide perovskite discoveries is that unusual superconductivity is most likely to occur in unusual materials beyond the scope of the conventional current wisdom. It is important to understand that high temperature superconductivity could have been discovered much earlier than 1986. It is actually hard to make La_2CuO_{4-y} without small regions of excess oxygen which give rise to trace superconductivity...and the compound has been around since the 50's! Nobody, until Bednorz and Mueller, was motivated to look for superconductivity in this seemingly most unpromising class of materials.

Progress in New Materials

Layered copper oxide perovskites remain the paradigm for high temperature superconductivity. Since early 1988, no new copper oxide materials have been discovered with T_C higher than the thallium 2223 125 K compound.[7] Two of the major challenges for the decade of the 1990's will be to both reach out for higher transition temperatures and to search for non-CuO-based high temperature superconductors, perhaps expanding on the "medium-T_C" $Ba_{0.6}K_{0.4}BiO_{3-y}$ compound discovered in 1988 by Bob Cava and his colleagues at AT&T.[8]

Although no new T_C records have been recently set in planar copper oxides, interesting and important variations still continue to be found. In 1989 the first materials exhibiting n-type behavior in the normal state with T_C = 21-24 K were synthesized using Nd_2CuO_{4-y} as the host structure,[9] and I will devote my discussion on new materials exclusively to these. Unlike La_2CuO_{4-y}, where divalent alkaline earth cations are substituted on the lanthanide site, the neodymium cations are replaced by tetravalent cerium and charge conservation implies the production of carriers with negative sign as indeed supported by the results of Hall and Seebeck effect measurements. Figure 1 compares the structures of the two compounds and the respective doping sites. The key difference is the location of the oxygens coordinated to the lanthanide position within each structure, resulting in the presence of a Cu-O plane apical oxygen in La_2CuO_{4-y} and its absence in Nd_2CuO_{4-y}. I believe this is the critical factor which permits delocalized holes in the former and delocalized electrons in the latter, and not vice versa, as confirmed by many unsuccessful attempts at cross-doping. If true, then the host structure choice for n-type superconductivity is restricted to the Nd_2CuO_{4-y} T′ class, at least for the present, inasmuch as all other Cu-O planar perovskite structures have at least

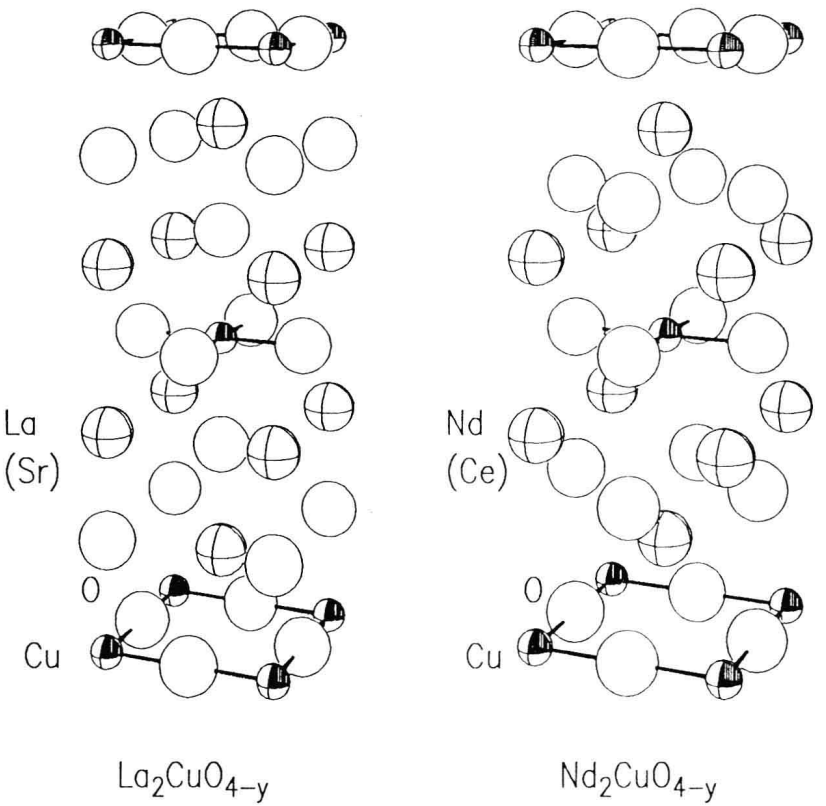

Fig. 1. Unit cells of La_2CuO_{4-y} and Nd_2CuO_{4-y}. Note the absence of apical oxygens in the latter structure.

one apically coordinated plane and appear p-type, with any accompanying non-apical planes "dead" with regard to transport; e. g., the middle Cu-O layer in the 2223 structure. The only structural exception that I know is $Ca_{0.86}Sr_{0.14}CuO_2$; however, there is no obvious location for tetravalent cationic substitution. One of the synthetic challenges for the 90's will be for chemists to discover other n-type systems with hopefully higher T_C's, but right now the outlook seems bleak.

Regarding the nature of electrical conduction in the Cu-O planes, the present picture is that hole transport occurs on the network of oxygen ligands in p-type compounds. On chemical grounds, it would be difficult to argue that electrons move in the same band -- their more natural level would be derived from Cu^{+1} states. To explain the experimental existence of charge symmetry in high temperature superconductors, we may have to rethink the location of hole transport in the p-type materials. The Cu-O bond is clearly a hybridization of O 2p and Cu 3d states, and it may be overly simplistic to identify transport in either case as occurring on a specific ionic level.

There are several important differences in the chemical and physical properties of the p- and n-type compounds. First of all, the "apparent" carrier concentration range over which superconductivity appears is much narrower for the n-type systems[11] ($0.15 < x < 0.18$ in $Nd_{2-x}Ce_xCuO_{4-y}$) than for the analogous p-type materials[12] ($0.10 < x < 0.23$ in $La_{2-x}Sr_xCuO_{4-y}$). I say "apparent" because it is not clear to what extent doping fractions can be translated to carrier concentrations. In addition, achieving homogeneous doping by diffusing tetravalent cations in the Nd_2CuO_{4-y} host is quite difficult compared to the p-type materials. Doping alone does not lead to superconducting samples -- a tricky and mysterious oxygen reduction process must be undergone, and a variety of transition temperatures running from 21-29 K can be obtained depending on reduction conditions. The paper given by Maria Lopez-Morales[13] at this conference addresses some of these issues. One might expect to be able to obtain superconductivity by oxygen reduction of undoped Nd_2CuO_{4-y} in analogy to oxygen-rich La_2CuO_{4+y}. However, efforts to find superconductivity in Nd_2CuO_{4-y} this way by ourselves and others we have heard from have to date have failed -- another mystery. Understanding the details of oxygen processing in the 2-1-4 compounds presents an interesting challenge to materials scientists to start the decade of the 90's.

One very intriguing feature about Nd_2CuO_{4-y} is that it is the first structure to be successfully (i. e., "beneficially") doped with fluorine or any other anion for that matter. First accomplished at AT&T,[14] our confirming work done at IBM Almaden[15] is summarized in Figs. 2 and 3. We have strong indirect evidence, derived from testing several chemical synthetic routes, that fluorine substitutes as shown in Fig. 2 -- on an oxygen site attached to Nd. Attempts to fluorinate the Cu-O plane did not yield superconducting samples. It appears that a necessary requirement for anion doping is that an ancillary oxygen site, not coordinated in or to the Cu-O plane, be available for substitution. As in the cation case, the potential candidate host structures seem limited right now

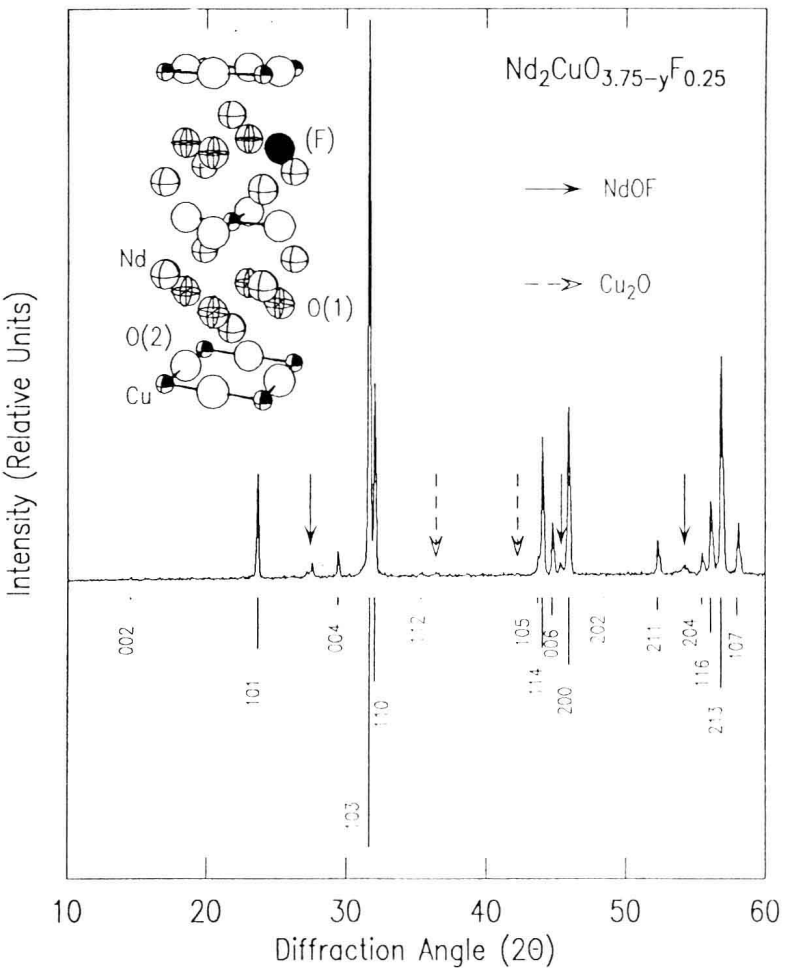

Fig. 2. X-ray diffraction pattern and structure for $Nd_2CuO_{3.75-y}F_{0.25}$. Impurity phases and pattern simulation are indicated.

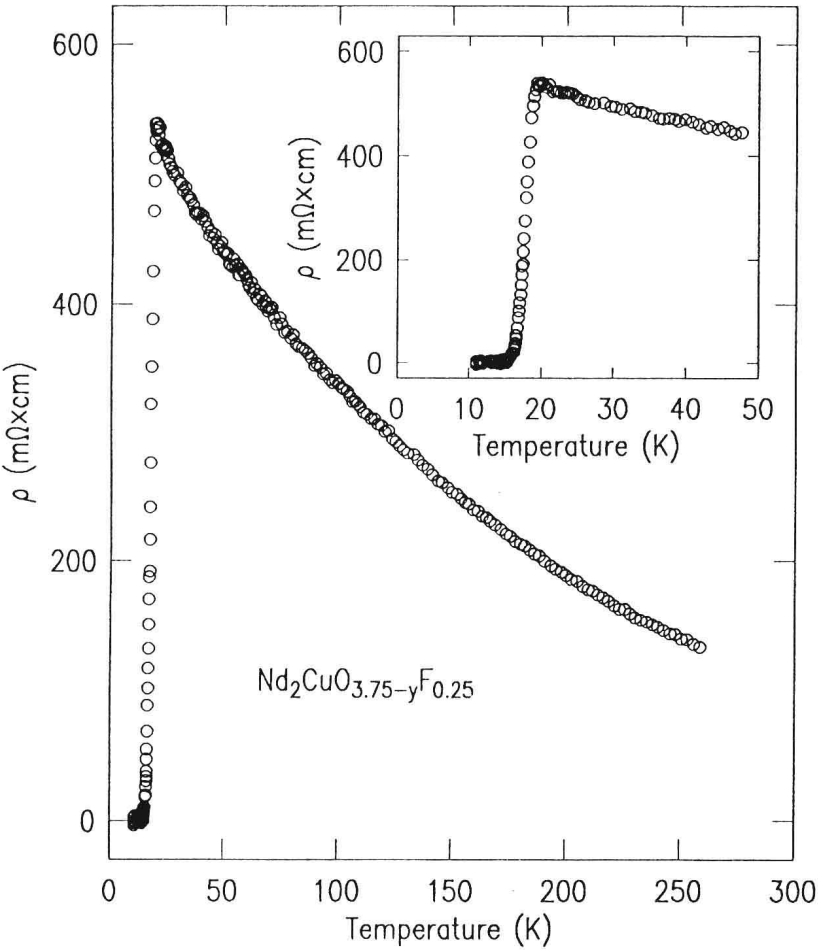

Fig. 3. Resistivity vs. temperature for $Nd_2CuO_{3.75-y}F_{0.25}$

to the Nd_2CuO_{4-y} class and another challenge of the 90's for chemists would be to discover other materials amenable to anion doping.

Finally, we note the activated dependence of the normal state resistivity on temperature of the $Nd_2CuO_{4-y-x}F_x$ sample as shown in Fig. 3. This behavior was characteristic of all initial reports on n-type samples, and, in my opinion, is an indication of the presence of a considerable amount of insulating phase even in more recently reported data where, although the overall slope of ρ vs. T is positive, the temperature dependence is not linear, especially in the region just above T_C.

Recent Experimental Results

The normal state properties of all previously known superconductors has been well described by Fermi liquid theory; i.e., that the ground and low lying excited states of a correlated many-body ensemble of electrons can be approximated in a single particle picture embodied by a Fermi surface with a singular boundary at zero temperature. Whether this is also true for high temperature superconductors has become a major theoretical issue. Many of the traditional magneto-oscillatory experiments used to probe Fermi surface structure are inaccessible to the new materials due to their exceedingly large upper critical fields. One generally accepted way of detecting the presence of a Fermi surface in metals is to use angle-resolve photoemission (ARPES) to look for conduction band dispersion in the vicinity of the Fermi energy and associated increases in photoemissive yield as the band crosses E_F. ARPES studies on single crystal Bi 2212, recently done by Olson[16] and colleagues at Ames-Los Alamos-Argonne, indeed reveal such behavior thus providing the strongest evidence yet that the high-T_C normal state is Fermi liquid-like. In one important respect, however, the data depart from classical Fermi liquid models in that the lifetime broadening of photoemissive yield peak varies as $E - E_F$ rather than the $(E - E_F)^2$ required by the conventional theory. More ARPES studies need to be done on other high-T_C compounds to firmly establish the nature of the normal state and its relationship to the Fermi liquid model -- another challenge for the 90's.

An additional signature of classical BCS-like superconductors is the presence of an optical gap in the superconducting state whose energy has a prescribed temperature dependence in the range $0 < T < T_C$. A large literature has developed on optical experiments in high-T_C materials, containing controversial data and interpretations as to whether a gap exists, or can be seen, its temperature dependence, and its magnitude, $2\Delta(T = 0)/kT_C$, the latter a measure of the strength of the carrier-boson coupling in the BCS-Eliashberg framework. Recently, Zack Schlesinger and Reuben Collins,[17] and their co-workers at IBM and Argonne, performed polarized reflectance experiments on untwinned single crystals of $YBa_2Cu_3O_{7-y}$ in which they were able to look exclusively at optical excitations normal to the chain system and thus characteristic only of the Cu-O planes. They found a distinctive gap-like feature with no residual structure below T_C. This residual structure, seen by both the IBM group and others

in previous twinned single crystal studies, is ascribed by Schlesinger and Collins to contributions from chain conductivity projected onto all directions of polarization in the a-b plane. However, their gap-like structure has an exceedingly weak, non-BCS-like, temperature dependence of its energy, quite unlike that found in low-T_c compounds. Moreover, the magnitude of the gap is around $7 - 8\ kT_c$, consistent with their earlier results and also with more recent tunneling data, yet enormously high compared to low-T_c superconductors. The optical data now appears quite definitive and a theory of the pairing mechanism must accommodate it -- one more future challenge.

Before going on to theoretical matters, I want to mention one experimental issue that seems to have been definitively settled in 1989 -- that is the matter of the pair wave function symmetry. Bill Little[18] and his students at Stanford, and independently Praveen Chaudhari[19] at IBM, have demonstrated the existence of persistent currents in composite rings of $YBa_2Cu_3O_{7-y}$ in series with a conventional superconductor like Nb or Pb. Persistent current in such a structure could not be maintained unless the pair wave function possessed the same symmetry for each superconductor in series, and, since that symmetry is known to be s-wave in Nb and Pb, it must be the same in $YBa_2Cu_3O_{7-y}$ (more precisely, the highest symmetry allowed by its space group), otherwise the loop current would decay rapidly due to mismatch of pair functions of unlike symmetry. This conclusion is reinforced by the results of Chaudhari which were obtained on epitaxial thin films where the contact direction to the Pb bridge was along the c-axis.

Current Theoretical Issues

There is as yet no generally accepted theory of high-T_c. I made this remark at last year's Low Temperature Physics conference and it is even more appropriate today. One of the most actively discussed new ideas to emerge last year is the so-called "marginal" Fermi liquid picture proposed by Varma, Littlewood and Schmitt-Rink (AT&T), and Abrahams and Ruckenstein (Rutgers),[20] known collectively as the "five friends." Essentially they replace the energy scaling parameter (the Fermi energy) of conventional Fermi liquid theory by temperature and cut-off this temperature dependence when it exceeds the magnitude of the frequency in the frequency dependent susceptibility. That is, $\chi'' \sim \omega/E_F$ goes over to $\chi'' \sim \omega/T$, $\omega/T < 1$, $\chi'' \sim 1$, $\omega/T > 1$. This purely empirical model yields agreement with the observed linear dependence of resistivity on temperature, with a frequency dependent Drude lifetime in the near-IR, with s-wave pairing and strong coupling and with a number of other experimental findings including the linear dependence of the photoemissive peak width with energy separation from the Fermi surface, already mentioned previously. However, what underlying physics may be behind the phenomenology remains unclear.

Some of the recent experimental results have brought about a re-thinking of RVB-related models. At a workshop in Aspen last week, Phil Anderson interpreted the ARPES results as evidence for charge-spin separation, one of the

mainstays of the theory from the beginning. However, it is the feeling of most theoreticians that the ARPES data presents the most serious experimental challenge to the RVB picture to date.

Lately, there has been a interesting renaissance of lattice vibration-type models. Alex Mueller[21] has recently made a detailed analysis of the oxygen isotope effect in a number of high-T_c compounds and by partitioning the small observed shifts among various oxygen sites, concludes there is evidence that the anharmonicity of the apical oxygen contributes to the enhancement or generation of superconductivity. Computer simulations by Morgenstern[22] on the 2D Hubbard model including an anharmonic electron-phonon interaction show that superconductivity can arise through such a channel. Recent copper x-ray absorption edge structure[23] on $YBa_2Cu_3O_{7-y}$ indicates an antiferroelectric-like softening of a double-well apical oxygen potential accompanying the superconducting transition. The very existence of superconductivity in the n-type compounds, without apical oxygens, demands that such a mode cannot be the sole underlying pairing mechanism for high-T_c, but rather provides a "pump" to higher T_c in those compounds that possess this site. Two tests of this conjecture would be the finding of a total absence of an oxygen isotope effect in the n-type compounds and whether planar Cu-O systems without apical positions but with substantially higher transition temperatures ($T_c > 60$ K) can be eventually synthesized.

Role of Microscopic Inhomogeneities

It has long been recognized that macroscopic inhomogeneity (granularity, twinning, voids, phase separation, etc.) play a significant role in many of the physical properties of the perovskite high temperature superconductors. More attention now needs to be turned to effects of microscopic inhomogeneity. First of all, on what length scale do we define the term "microscopic?" In the framework of transport and superconducting properties, this means the carrier mean free path and pair coherence length, respectively. For high-T_c materials, both these parameters are extremely small, of the order 10-20 Å, and highly anisotropic. A perspective on these extremely short distances against the background of "uniformly" doped $La_{1.8}Sr_{0.2}CuO_4$ is given in Fig. 4, where we show several unit cells of the La_2CuO_{4-y} structure repeated along the a-b plane with La sites randomly doped with Sr, compared to the extent of the pair coherence length ellipsoid. It is clear that, by no means, can the material be considered uniform with respect to the coherence volume, even at the doping level considered to give the highest T_c in this compound. For lower levels of cationic substitution, the distribution on this length scale is even more non-uniform. The same reasoning can be applied to other systems where cationic substitution or non-stoichiometry is required to produce the carriers necessary to sustain metallic behavior and superconductivity. The only exception (perhaps) is $YBa_2Cu_3O_{7-y}$ with $y = 0$. For $y \neq 0$, similar scales of inhomogeniety arise. The inescapable conclusion is that the length scale defining "granularity" in high-T_c compounds is far shorter than that dealt with in traditional low-T_c superconductors.