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A REVIEW OF THE EXPERIMENTAL RESEARCH ON HIGH TEMPERATURE SUPERCONDUCTORS

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ABSTRACT

The recent discovery of 'new' high T_c superconductors has caused uncertainities as to which features of the crystal structure the experimentalist should be looking at. To assist Thai experimentalists who are interested or are beginning to do research in this field, a review of the experimental work done prior to March 1988 is presented.

I. INTRODUCTION

The 1987 Nobel Prize in Physics was awarded to J.G. Bednorz and K.A. Müller for their discovery of high temperature superconductivity in the cupric oxide ceramics (with T_c of 35 K). Their first paper,[1] entitled, "Possible High T_c Superconductivity in the Ba-La-Cu-O System", did not attract much interest at the time nor was its significance recognized by most physicists. For example, nobody paid much attention to a remark made by Professor Dr. H. Kamimura (University of Tokyo) in his talk at the First Regional Workshop on TOPICS IN SEMICONDUCTOR PHYSICS held at Chulalongkorn University, Bangkok, Thailand, Jan. 5-8, 1987, before the news reports of Chu's discovery of 90 K superconductivity in the popular press in February. In a side remark, Prof. Kamimura mentioned that the people at the University of Toyko were working on a high temperature superconductor which had a layered structure. The present author remembers Prof. Kamimura putting one finger to his lips saying that this was a secret. His remarks were quickly forgotten and do not appear anywhere in the minutes of this workshop. Only three other groups became actively interested in what had been done by Bednorz and Müller, the University of Tokyo team of Tanaka, the Chinese team of Zhao, and Chu and the Chinese expatriate team in the United States.

The almost simultaneous announcements of 90 K superconductivity in the Y-Ba-Cu-O ceramic compounds by Chu *et al.*[2] by Hikami *et al.*[3] and by Zhao *et al.*[4] changed this lack of appreciation of Bednorz and Müller's discovery. In the frenetic period between the February news report in the New York Times newspaper[5] and publication of Chu's paper in Physical Review Letters,[2] almost every experimental superconductivity laboratory in the world sought to duplicate the results. Since Chu had not given the composition of the superconductor in the newspaper, everyone had to essentially discover the composition for themselves. By mentioning only one minor thing (the need for internal pressure) in the news article, Chu had provided enough information for those who knew something about the field to fabricate their own high T_c superconductors. By the time of the March 1987 meeting of the American Physics Society in New York, enough work had been done to justify a special session devoted to high temperature superconductors. News reports[6] of this session mentioned that several thousand scientist packed the meeting room and that the discussions lasted until three o'clock in the morning. Since then, an unenumerable number of meetings and articles in the popular press have been devoted to the subject. It is estimated that over 20,000 scientists are working in the field. These include physicists, chemists, material scientists and engineers. There are even high school students working in the field.

In all of this excitement, a lot of things have been said in both the popular press[7] and in the scientific journals. Much of what has been said is "hype" and some is just plain nonsense. It has been suggested that the new high temperature superconductors will shortly lead to the use of magnetically levitated trains, loss-less transmission of electricity, superconducting wiring in one-water supercomputers and superconducting power generation. Most of these applications will occur only after many problems associated with the new materials are solved. In a report of the US Department of Energy,[8] it was concluded that it would take at least twelve years to overcome the "formidable material science and engineering problems" of the new materials.

Recently (within the last three months, to be specific), a menagerie of new high temperature superconductors have been discovered. Many of these new systems do not have the features of the 'old' high T_c superconductors which were thought to be important to the physics of the superconductivity in the materials. This has caused a re-thinking in the field. The editors of the Journal of Science Society of Thailand have chosen this opportunity to present a review of the present (experimental) state of the physics of the high temperature superconductors (as of March 1988).

II. 2-1-4 COMPOUNDS

A. Composition and Structure

In the paper,[1] "Possible High T_c Superconductivity in the Ba-La-Cu-O System", Bednorz and Müller reported that the resistivity of a multiphase ceramic $Ba_x La_{5-x} Cu_5 O_{8-y}$ started to decrease drastically at about 35 K. Since perfect diamagnetism and not perfect conductivity is the true signature of superconductivity, they could only point to the possibility of superconductivity in their compound. In a later paper,[9] they showed that the observed phenomenoma was in fact superconductivity. Subsequently, Uchida *et al.*[10] and Takagi *et al.*[11] showed that the layered perovskite K_2NiF_4 structure phase of the three phases seen in ref. 1 was the superconducting phase. Later, Chu *et al.*[12] found that the T_c of these superconductors could be increased to 52 K by applying pressures above 1.2 GPa. Most of the data in these reports indicated that the onset of superconductvity in the ceramics was granular in nature.

Transition temperatures above 35 K could also be achieved by replacing the barium by strontium. Cava *et al.*[13] reported that the highest transition temperature in the $La_{2-x} Sr_x CuO_{4-y}$ series was 36 K for $x = 0.2$ and that superconductivity in these ceramics was bulk in nature. Politis *et al.*[14] was able to achieve a T_c of 40 K in a single phase $La_{1.8} Sr_{0.2} CuO_4$ ceramic. Politis *et al.* showed that superconducting oxides have a tetragonal structure belonging to the space group I 4/mmm similar to the $K_2 NiF_4$. Replacement of strontium (barium) by calcium resulted in the lowering of the transition temperature.[15] Replacement of some of the copper ions in this compound also caused a lowering of the transition temperature.[16]

As we have mentioned, Cava *et al.*[13] found the structure of the La-Sr-Cu-O systems to be tetragonal ($K_2 NiF_4$ type) at room temperature. This structure can be thought of as alternation along the c-axis of layers of perovskite (CuO_3) and rocksalt (La or Sr-O) structure types. The perovskite layers consist of corner sharing CuO_6 octahedra that are slightly elongated along the c-axis. Each perovskite layer is shifted relative to the next so that the copper sites in one CuO_3 layer are aligned with the oxygens in the next. More detailed structural analysis based on neutron diffraction studies[17] and single crystal X-ray diffractometer studies[18] reveal that a tetragonal-to-orthorhombic phase transition occurs at 180 K. Current thinking is that the orthorhombic distortion results from a Peierls $2k_F$ instability or a soft zone-boundary phonon mode.

B. Measured Properties

i. Energy Gap

As in "conventional" superconductors, one of the most important characteristic of the high T_c superconductors is its energy gap (which should not be confused with the order parameter). A gap arises in the density of states of the quasi particles involved in the normal-to-superconducting phase transition when the normal phase particles within the gap undergo a Bose Einstein condensation. This occurs regardless of the mechanism responsible for the pairing. Gough *et al.*[19] has shown that the condensate pair contains two electronic charges (note that we have not said that condensate pair contains two electrons).

Since the states within the energy gap are not available for absorbing energy via the normal interaction mechanisms, gaps in the infrared absorption and tunneling spectrums should reveal the size of the energy gaps in the La-Ba (Sr, Ca)-Cu-O superconductors. By fitting the far infrared reflectance to the Bardeen-Mattis expression for the FIR (derived for "conventional" superconductors), several investigators have found a range of values for the ratio $2\Delta / k_B T_c$ (Δ being the energy gap at T = 0 K) which depends on several extrinsic properties of the 2-1-4 superconductors such as the grain geometry. Sulewski *et al.*[20] found the ratio to be 2.6 ; Bonn *et al*[21] to be 3.2 ; while Schlesinger *et al.*[22] obtained a distribution of values having an average of 3.6 which is close to the conventional Bardeen-Cooper-Schrieffer (BCS) prediction. The tunneling data of Kirtley *et al.*[23] gave a ratio of 4.5, while the data of Pan *et al.*[24] gives a ratio of 7. Walter *et al.*[25] and Sherwin *et al.*[26] have pointed out that temperature dependence of the energy gap obtained by fit of the data to the BCS expressions is similar to that predicted by the BCS theory, and van Bentum *et al.*[27] found that the measured I-V curves of a tunneling junction containing the La-Sr-Cu-O superconductor is described 'neatly' by a simple tunneling expression using the BCS expression for the density of states for the super-conductor.

Measurement of the specific heat of a "conventional" superconductor also gives the size of the energy gap. In addition, the conventional BCS theory makes predictions about the size of the specific heat jump at T_c, which can be used to differentiate between weak coupling superconductors and strong coupling superconductors. (To be able to discuss superconductivity meaningfullly, one must also know about the Elaishberg formulation of superconductivity.[28]) Complicating the task of measuring the specific heat jump in the high T_c superconductor is the need to remove the lattice vibration contribution to the specific heat. At the transition temperatures of the "conventional" superconductors, the lattice contribution is almost negligible and so the measured specific heat is the electronic specific heat which is of interest to the theory of superconductivity. In the high temperature superconductors, the lattice contribution to the measured specific heat is the dominant one. Assumptions about the lattice specific heat must be made so that it can be substracted to obtain the electronic component of the specific heat. Difficulties can arise if wrong assumptions are made. Wenger *et al.*[29] report that there is no specific heat jump at T_c of a $La_{1.8}\,Ba_{0.2}\,CuO_{4-y}$ superconductor. In a sample with the same composition, Nieva *et al.*[30] find that $\delta C(T_c)/T_c$ = 33 mJ/mol K and that C(T) exhibits a linear temperature dependence at low temperatures. Reeves *et al.*[31] obtain a value of 39 mJ/mol K^2 for this compound and a value of 71 mJ/mol K^2 for a $La_{1.85}\,Ba_{0.15}\,CuO_4$ compound. Dunlap *et al.*[32] has also measured the specific heat of the latter compound. They find the jump to be 20 mJ/mol K^2. Estimating the value of the normal phase electronic heat capacity γ, they find that the ratio $\delta C(T_c)/T_c$ places their sample into the strong coupling category of superconductors.

As we have mentioned already, assumptions about the lattice specific heat have to be made. The usual assumption is that the ceramic is a Debye solid. Ultrasonic studies done on these superconductors indicate that there are complications to this picture. Bourne *et al.*[33] and others[34] find that a soft phonon mode opens up near 200 K. Below 100 K, Fossheim *et al.*[35] see a stiffening of the lattice. This is reflected in the observation of a decrease in the sound velocity between 20 K and 100 K.[36]

Before we leave the topic of the specific heat, it should be mentioned that Nieva *et al.*[30] observed a linear temperature dependence in the specific heat of the La-Sr-Cu-O superconductor at low temperature. This linear dependence was also seen in La-Ba-Cu-O superconductors by Kumagai *et al.*[37] Since a linear temperature dependence is counter to the prediction of the conventional BCS theory and is predicated by the RVB (resonant valence bond) theory of high T_c superconductivity of Anderson,[38] Zou and Anderson[39] quote the existence of the linear T dependence of Cp as proof of their theory. Alternative explanations exist however, the most convincing being the existence of two level systems in ceramic compounds.[40]

ii. Magnetic Properties

The next most characteristic property of any superconductor is its response to a magnetic field. The classification of any superconductor as a Type I or II superconductor is based on its magnetic behavior. Aeppli *et al.*[41] and Wappling *et al.*[42] found that the penetration depth in $La_{1.85}$ $Sr_{0.15}$ CuO_4 is around 2500 °A, which leads to a carrier density of the order 10^{22} cm^{-3}. The above penetration depth along with the values of coherence lengths of these superconductors (30-50 °A[43]) place the high T_c superconductors into the extreme Type II category.

This allows the physicists to use the Ginzberg-Laudau theory[44] to treat the possible presence of N-S interfaces in these ceramic compounds. As was pointed out earlier, the initial measurements had indicated that the onset of superconductivity in the La-Ba(Sr)-Cu-O ceramics was granular in nature. This has led to the modelling of the superconducting phase as an array of Josephson junction with special interface conditions. Magnetization studies[45,46a] have indicated that the flux pinning for fields above 20 mT (milli Telsa) is very low, which makes these superconductors useful for microelectronic application.

Since La-Ba(Sr)-Cu-O is a Type II superconductor, it has two critical fields B_{c1} (T) and B_{c2} (T). (A third critical field also exists, the field at which surface superconductivity vanishes.) Renker *et al.*[46b] find that the upper critical field B_{c2} at T = 0 K is 50 T while Orlando *et al.*[47] obtain a value of 58 T. The lower critical field B_{c1}, the field at which the magnetic field lines begin to penetrate into the superconductor, is 20 mT. The highest critical current measured is 10^5-10^6 °A/cm^2 .[48] All of the measurements indicate that these properties are highly anisotropic.

iii. Properties which Elucidate the Mechanicisms Responsible for Superconductivity

In addition to the measurements of properties which characterize the materials, other measurements have to be done to elucidate the mechanisms responsible for superconductivity in the ceramics. Foremost of these measurements is the measure of the isotope effect. A dependence of the transition temperatures of the conventional superconductors on the mass of the nucleus ($T_c \sim M^{-0.5}$) would point to the electron-phonon interaction being the mechanism responsible for superconductivity in the conventional systems. Many people have taken the existence or non-existence of the isotope effect in the La-Ba(Sr)-Cu-O superconductor as proof that the electron-phonon interaction is or is not the responsible mechanism. Batlogg *et al.*[49] and Faltens *et al.*[50] have observed the isotope effect in $La_{1.85}Sr_{0.15}CuO_4$ superconductor. The transition temperatures were observed to vary as $M^{-0.16}$ when ^{16}O was replaced by ^{18}O. Bourne *et al.*[51] have pointed out that the absence of the isotope effect or a value of α (in $M^{-\alpha}$) much lower than 0.5 does not necessarily indicate a dominant role for the phonon mediated pairing mechanism. The isotope effect could be masked by the strong coupling effects or other interaction mechanisms which might be present.

Mattheiss[52] has calculated the band structure of the $La_{2-y}X_yCuO_4$ compounds. He finds the half filled Cu(3d)-O(2p) band to be two dimensional in nature with a nearly square Fermi surface. His calculations predict the Peierls instability seen by Stavola *et al.*[53] There is good agreement between his calculations and those calculated by others.[54] The calculated band structure agrees with those determined from XPS measurements[55] and from inverse photoemission spectroscopy studies.[56] However, the agreement between the calculations and the x-ray absorption near edge structure studies[57] are bad. We have mentioned the agreements and disagreements because Matthias' results have been used by Weber[58] to calculate the electron-phonon interaction in these ceramics. Using first principle calculations based on the Eliashberg formulation,[28] Weber calculates T_c of the La-Ba-Cu-O ceramics to be in the range of 30-40 K.

The discovery of an antiferromagnetic phase transition in the parent La_2CuO_{4-x} ceramic at 220 K,[59] has led many to believe that superconductivity in the La-(Ba,Sr)-Cu-O ceramics is due to some mechanism other than the electron-phonon interaction. Anderson[60] argues that the same mechanism responsible for the antiferromagnetic transition is responsible for the superconducting transition. This has led many scientists to describe the Cu-O layer in these ceramics as a two dimensional Hubbard layer[61] since the Hamiltonain for the two dimensional Hubbard model will lead to antiferromagnetism under certain conditions. Furthermore, it can be shown that this Hamiltonian can give rise to an attractive interaction.[62]

Since the Hubbard Hamiltonian cannot determine a priori the nature of the excitations present, i.e., the dependence of the density of states on the presence of Cu^{2+} and Cu^{3+} ions in the layers, the role of the oxygen vacancies, the strength of the Cu-O bond or what the carriers are, these inputs to the theory must be determined experimentally. Xanes studies[63] point to the presence of both Cu^{2+} and Cu^{3+} ions in $La_{2-x}(Sr,Ba)_xCuO_4$. Photoemission studies[64] indicate that the carriers are the oxygen p holes. Other studies[65] point to the oxygen vacancies being determined by the Sr^{2+} concentration. In turn many of the properties of the ceramics show a dependence on the oxygen vacancies.[66]

III. 1-2-3 COMPOUNDS

A. Composition and Structure

The real excitement about high T_c superconductivity began with the almost simultaneous announcement of 90 K superconductivity in Y-Ba-Cu-O ceramics by Chu *et al.*,[2] Hikami *et al.*[3] and Zhao *et al.*[4] Unlike the low key announcement by Bednorz and Müller,the discovery of the 90 K superconductor was heralded in the popular press as one of the discovery of the centuries which would cause a technological revolution. Notwithstanding the 'hype' surrounding the discovery of the 90 K superconductors, the importance of this discovery is due to the fact that liquid nitrogen can be used to achieve the temperatures required for the ceramic to go superconducting. The La-(Ba,Sr)-Cu-O superconductors discovered by Bednorz and Müller still required the use of liquid helium to achieve the necessary operating temperatures. Most of the early press reports emphasized the savings that would occur when liquid nitrogen is used instead of liquid helium. Now, it is reported that the savings obtained would only be a few percent.[67] Furthermore, the need to have better vacuums for operation at 77 K would offset the above savings.

The real importance of the discovery of high T_c superconducting ceramics lies in the fact that 'new physics' is needed. It appears that the structure of the superconducting phase (the original Y-Ba-Cu-O ceramic obtained by Chu *et al.*[2] contained several phases: a black phase which is the superconducting one, and a green phase which does not occur in Nature. The phase which became superconducting was identified by Muromachi *et al.*[68] Using a Rietveld analysis of the X-ray powder diffraction patterns, Izumi *et al.*[69] identified the crystal structure of the superconducting phase to be orthorhombic (with a = 3.8857 °A, b = 3.8267 °A and c = 11.681 °A) belonging to the space group Pmmm. Similar analyses[70] of single-crystal X-ray diffraction patterns have yielded values for the bond lengths and angles. An alternative structure has been suggested by Reller *et al.*[71] The relative merits of the two proposed structures have been discussed by Gupta *et al.*[72] and Katano and Matsumoto.[73] Katano and Matsumoto have pointed out that while the structure proposed by Reller *et al.* would reproduce the observed X-ray diffraction patterns, the structure would not yield the single crystal neutron diffraction patterns seen by them and by Yan *et al.*[74] You *et al.*[75] also pointed out that their single crystal neutron diffraction patterns are not consistent with Reller's structure. The powder neutron diffraction patterns observed by Francois *et al.*[76], by Cox *et al.*[77] and others [78-80] are consistent with the structure proposed by Izumi *et al.*[78]

The structure of $YBa_2 Cu_3 O_{7-x}$ is based on a triple perovskite structure obtained if ion atoms also surround the Yttrium ions (along the axis connecting the copper ions). The resulting chemical compound would be $YBa_2 Cu_3O_9$ and we would have three layers of distorted CuO octahedron in each unit cell. Since these oxygen ions are missing, we would have $YBa_2 Cu_3 O_8$ (each one of these ions are shared by four unit cells and so we get a minus 1/4th from each of these missing ions). The absence of these ions leads to the formation of two layers of pyramidal structures whose basal planes sandwich the layer of yttrium ions. Combined thermogravimetric and X-ray studies[81] show that the oxygen ions on the 'a' axis (the differentiation of the 'a' and 'b' axis occurs after the removal of the oxygen ion) between the Cu ions in the middle copper layer are the first to leave as the ceramic is being heated. The absence of these O ions causes the distortion[82] which leads to the orthorhombic structure occurring in these ceramics. Since each of these oxygen ions are shared by two unit cells, their absence leads to the chemical composition $YBa_2Cu_3 O_7$. In these composition compounds, one has a layer containing linear chains of Cu-O occurring along the 'b' axis sandwiched between two 2-dimensional Cu-O layers. Removal of additional oxygen ions from the 'b' axis linking the Cu ions on the middle copper layer results in the composition $YBa_2 Cu_3 O_{7-x}$. If enough oxygen ions are removed from these sites, a structural transition in a tetragonal phase occurs and superconductivity disappears.[83-85] The positions of the oxygen vacancies have been determined by neutron diffraction[86] and by X-ray diffraction[87].

The importance of the oxygen vacancies to superconductivity has been emphasized by several groups[88,89] and so the rate and means by which the oxygen atoms enter or leave the ceramic while it is being fabricated are extremely important to the achievement of good quality superconductors. Using thermogravimetric analysis (TGA) at a heating rate of 1 °C/min, Steinfink *et al.*[90] finds that $YBa_2 Cu_3 O_{7-x}$ initially absorbs oxygen for T between 220 °C and 325 °C (no evolution of gas is seen for T below 220 °C). It then loses oxygen at a nearly constant rate as T is increased to 900 °C. Upon cooling, the oxygen content increases monotonically from 900 °C down to room temperature. Additional TGA studies [87,91,92] indicate that the rate of oxygen absorption depends on the partial pressure of the oxygen surrounding the ceramic as it is being annealed and as it is being cooled down to room temperature. A slow rate of cooling is necessary to insure that the oxygen atoms, once they are absorbed into the superstructure, have enough time to diffuse uniformly into the structure. Otherwise, the tetragonal-orthorhombic structural transition, which usually takes place around 750 °C, will not occur and we would be left with a non superconducting tetragonal specimen.[93,94]

The tetragonal-orthorhombic transition is accomplished by a shear.[95] If the transition is not uniform, strains are created in the ceramic. These strains may give rise to the twin-boundaries seen.[96-98] The twinning planes are along the ^{110} direction and are 90 °C twins with the 'a' axis becoming 'b' axis and vice versa across the boundary. The thickness of the twin layers appear to be different for each sample. Van Tendeloo *et al.*[96] find the thickness to be 600 °A while Pande *et al.*[97] see an average thickness of 1000 °A in their sample. Pande *et al.* also finds that the twin layers disappear when the sample is heated up to 400 °C but reappears upon cooling. It has been suggested by many that these twin boundaries are responsible for the granular nature of the superconductivity. Garcia *et al.*[98] and others [99-101] believe that these boundaries act as weak links, leading to a network of Josephsen junctions. Fang *et al.*[102] have suggested that 'localized' superconductivity nucleates at the grain boundaries at temperatures close to T_c.

In addition to the tetragonal-orthorhombic transition at 750 °C and the transition to twin boundary phase at 400 K, it is believed that other structural transitions occur in the Y-Ba-Cu-O ceramics. Ultrasonic attenuation data[103,104] indicate possible structural changes near 250 K, 160 K and just above T_c. Evidence of these structural transitions was also seen in thermal analysis studies by He *et al.*[104] Zhang *et al.*[105] have identified a change in the symmetry (Pmmm-to-Pmm2) at 234 K. This transition is thought to involve a rotation of the oxygen octahedron and the consequent loss of a mirror plane. The nature of the possible transition at 160 K has not been identified but it may be connected to the onset of granular superconductivity at 160 K seen by Cai *et al.*[101] Some confusion about a possible structural transition close to or at T_c exists. Horn *et al.*[106] report that there is an anomaly in the orthorhombic splitting, b-a, near the superconducting transition. It would appear that a and b unit cell lengths respond differently to the superconducting transition. David *et al.*[107] report that their neutron powder diffraction data do not indicate the presence of the large anomaly in the orthorhombic strain at T_c seen by Horn *et al.*[106] Khachaturyan *et al.*[108,109] have developed a theory which predicts that at low temperatures the orthorhombic structure undergoes a phase transition into a state in which both the tetragonal and orthorhombic structures coexist. In ref. 109, some experimental evidence for this predicted transition is given.

B. Dimensionality

There has been much discussion on the role of dimensionality in the superconductivity of the high T_c ceramics. Kresin[110] and Kresin and Wolf[111] argue that many of the properties of the high T_c superconductors can be understood on the basis of the low dimensionality of these ceramics. It was argued that the two dimensional integrations of the integral expressions for many superconductive properties yield numerical values close to those observed. Also it was argued that the use of two dimensional phasmoms modes in the equations for T_c yield results which could account for the high T_cs observed. However, Freitas *et al.*[112] believe that their resistivity measurements indicate that superconductivity in the high T_c superconductors are 3-D in nature. This is opposite to the conclusion of Ausloos and Laurent.[113] The latter believe that the superconductivity in the high T_c superconductors are 2-D in nature. Better measurements[114] even indicate that in some temperature regions, 1-D superconductivity occurs.

As is evident from the Sections on the structures of the 2-1-4 and 1-2-3 compounds, the structure of the 2-1-4 compounds is built up from two layers of CuO_6 octahedron while that of the 1-2-3 compounds is built up from one layer of CuO_6 octahedron sandwiched between two layers of CuO_4 pyramid, whose basal plane is adjacent to the yttrium layer. The basal CuO plane in the 1-2-3 compounds and the CuO planes formed by the copper ions and oxygen ions in between the copper ions in a single octahedron layer form a two dimensional array of copper and oxygen ions. The absence of the oxygen ions along the 'a' axis connecting the copper ions in the middle (octahedron) layer of the 1-2-3 leads to the appearance of one dimensional Cu-O chains in the 'b' direction.

The presence of the one dimensional chain was thought at one time as being crucial to the phenomenon of high T_c s. It was believed that the main reason for the difference in the T_c s of the 1-2-3 superconductors (90 K superconductors) and the 2-1-4 superconductors (30-40 K superconductors) was the presence of the one-dimensional chain. By quenching the Y-Ba-Cu-O pellets after they have been heat annealed at temperatures above 600 °C, several groups[93,94,115-117] found that the tetragonal phase of the ceramic would remain at the lower temperatures. Since this phase is non superconducting and since the main difference between this phase and the orthorhombic (superconducting) phase is the presence of the linear Cu-O chain along the 'b' axis in the middle Cu-O plane, they believed that the existence of superconductivity in the orthorhombic phase is due to the presence of the linear chain. This belief was reinforced by the observation that, as random vacancies were introduced into the chain, the transition temperature T_c dropped drastically. Cava *et al.*[118] and Werder *et al.*[119] found that when the oxygen vacancies along the linear chain in $YBa_2 Cu_3 O_{7-x}$ ($0.3 < x < 0.4$) is ordered, the sample has a T_c of 60 K. Evidence for the one dimensional chain being responsible for the superconductivity in $YBa_2 Cu_3 O_{7-x}$ was seen in the behavior of the normal state resistivity by Park *et al.*[120]

Bates and Eldridge[121] have calculated the frequencies of the 36 vibrational modes of the thirteen atoms of the orthorhombic unit cell of the $YBa_2 Cu_3 O_{6.7}$ compound. A simple valence bond force field was used to calculate the 16 force constants used in their calculations and so their results are not very accurate. Of the 36 vibrational modes present, 21 of them are infrared active and 15 are Raman active. The Raman active modes are of species Ag, B_{2g} and B_{3g}. All the modes above 500 cm^{-1} are assigned to the stretching of the Cu-O bonds. The modes in the frequency range 400 to 550 cm^{-1} are due to the stretching of either the Ba-O or Y-O bonds. Simultaneous motion of two ions bonded to a common ion would result in a higher frequency mode. The vibration of the O(2)-Cu(1)-O(2) group against the Cu(2) layers would give rise to a mode at 254 cm^{-1}. Experimentally, however, this mode appears at 310 cm^{-1} and shows that calculations are very rough.

Experimentally, ten Raman active phonon modes are seen[122] at 153, 217, 291, 309, 335, 441, 493, 506, 601 and 640 cm^{-1}. The mode at 335 cm^{-1} exhibits anomalous behavior. Above T_c, it increases in frequency as the temperature is lowered while below T_c, the frequency shift changes sign as the mode begins to soften. The mode at 644 cm^{-1} (the 640 cm^{-1} mode of ref. 121) disappears at T = 234 K.[105] This mode is also interesting in that it is missing in the tetragonal phase of ytterium compounds.[123] For this phase, Burns *et al.*[124] have identified all the modes seen with those predicted by group theory arguments. The mode at 644 cm^{-1} is therefore thought to arise from the Cu-O vibrations in the one dimensional chain. It is expected that additional Raman active modes should appear as oxygen vacancies are created and that Raman spectroscopy can be used to characterize the oxygen stoichiometry of high T_c superconductors.[125]

C. Measured Properties

i. Energy Gap

The value of the superconducting energy gap as determined from tunneling studies varies greatly. Crommie *et al.*[126] measured the gap at 4.2 K and 77 K. Extrapolating the value of the gap to T = 0 K, they obtained $2 \Delta (0)/k_B T = 3.9$ with a temperature dependence consistent with the Bardeen-Cooper-Schrieffer theory. Kirk *et al.*[127] however, obtained a value of 13 with the gap having a value of 50 meV. Moreland *et al.*[128] obtained a gap value of 19.5 ± 1 meV, leading to a ratio value of 4.8. This latter figure was also obtained by Hohn *et al.*[129] and Barone *et al.*[130] This value is within the range expected of a strong coupling superconductor.[28]

As with the La-(Ba,Sr)-Cu-O superconductors, the value of the energy gap can also be obtained from the infrared reflectivity measurements. Fitting the reflectivity data on polycrystalline samples of $YBa_2 Cu_3 O_{7-x}$ to the Bardeen-Mattis formula, values of between 2.5 to 4.5[131-134] were obtained for $2\Delta (0)/k_B T_c$. In spite of the warning[135] of experimentalists that the differences in the values of the energy gap determined by different means were probably due to artifacts in the experimental situations, several theorists[136,137] have attempted to explain the differences as being a natural consequence of their theories. Further measurements performed on epitaxial films[138] and on single crystal specimens[139] have clearly shown that the lower values of the energy gap determined from the reflectivity data are indeed experimental artifacts. Collins *et al.*[138] obtained a value $2 \Delta(0) = (4.7 \pm 1.2) k_B T_c$ for an epitaxial film in which the c-axis is primarily aligned perpendicular to the film surface. Reflectivity measurements performed on single crystal specimens with the electric field in the a-b plane gave a ratio value of 8.[139] Schlesinger *et al.*[139] attributes the difference between the epitaxial film result and the single crystal results to the presence of c-axis reflectivity in the measured reflectivity from the epitaxial film (the slight misalignment of the c-axis in the epitaxial film causing some c-axis reflection).

ii. Magnetic Properties

As is well known, the Meissner effect is the exclusion of the component of the magnetic field normal to the surface of the superconductor. When the magnetic field is tangent to the surface however, there are magnetic field lines (parallel to the surface) lying inside the superconducting region. The depth to which the magnetic field lines penetrate into the superconductor helps to determine whether the superconductor is a type I or II superconductor. When some of the magnetic field lines normal to the surface bunch up, the magnetic flux created by them can be high enough to destroy the superconductivity in the region below. In type I superconductors, the regions which go normal are in the form of layers and so we have a S-N-S-.....S-N-S laminar structure. In a type II superconductor, the normal regions are tubular and are called vortices. In the "conventional" superconductors, these vortices form into a triangular array. Many of the useful magnetic properties depend on how the normal regions respond to external perturbations.

Felici *et al.*[140] was the first to determine directly the penetration depths of the high T_c superconductors. By looking at the reflection of spin-polarized slow neutrons, they found for $YBa_2 Cu_3 O_{7-x}$, a penetration depth of 225 ± 75 °A at 4.8 K with an applied field of 350 Oe. This value is much lower than the values obtained by applying "conventional" interpretation to the behavior of the magnetization and other properties of the high T_c superconductors. Perez-Ramirez *et al.*[141] obtained a value of 485 °A by looking at the slope of the magnetization curves; Cooper *et al.*[142] obtained a range of values between 600 °A and 730 °A ; while Harshman *et al.*[143] obtained a value of 1400 °A. This latter value is the most quoted value.[144] Combining any of these values with the values of the coherence length (12 °A - 10 °A), we will find that the Ginzburg-Landau criterion places the high T_c superconductor, $YBa_2 Cu_3 O_{7-x}$, into the extreme type II category. One should expect to see a vortex structure when these superconductors are in the mixed state. Gammel *et al.*[145] have seen a hexagonally correlated vortex structure. The flux enclosed within the vortices was determined to be hc/2e (h being the Planck constant) and is the same as in "conventional" type II superconductors.

Lest one thinks that the high T_c superconductors behave magnetically the same as the "conventional" superconductors, it should be mentioned that the temperature dependence of penetration depths is not exactly BCS-like. While Harshman *et al.*[143] report that the penetration depths follow the prediction of the BCS theory, Cooper *et al.*[142] report that at low temperatures, the temperature dependence deviates from the BCS prediction and follows instead a T^2 dependence. This deviation from the BCS predicted behavior at low temperatures is also seen in many other properties[146] and may or may not be important.

Perez-Ramirez *et al.*[141] found that the field lines begin to penetrate into a single phase specimen at a field strength of 750 Gauss (thus H_{cl} = 750 G) and that bulk superconductivity disappeared at H_{c2} = 880 kG. The thermodynamic critical field H_c was determined to be 23.4 kG. For their specimen, Felici *et al.*[140] found that H_{cl} = 600 ± 100 Oe. Other values have been reported. Bezinge *et al.*[147] obtained H_{cl} = 20 mT and H_{c2} = 300 T ; Drumbeller *et al.*[148] obtained H_{cl} = 300 Oe. Sun *et al.*[149] obtained H_{c2} = 750 kOe. The wide range of reported values for the critical fields has been shown to be due to the multi crystalline nature of the specimens studied.

Measurements carried out on single crystal specimens have shown that these properties are highly anisotropic. It has been shown[150-152] that the critical fields for the fields applied parallel to the orthorhombic c axis are at least 20 times larger than the critical fields with the applied field in the a-b plane. McGuire *et al.*[150] found that H_{cl} = 4000 Oe for H parallel to the 'c' axis and was 200 Oe for H perpendicular to 'c'. Worthington *et al.*[151] have measured the lower critical field at 4.5 K and found that H_{cl} (parallel) = 0.5 T and H_{cl} (perpendicular) < 0.005 T. They have calculated H_{c2} (parallel) to be 140 T and H_{c2} (perpendicular) to be 29 T. Moodera *et al.*[152] have found that H_{c2} (parallel) = 62 T and H_{c2} (perpendicular) = 256 T. Many other measurements[153-155] of the slopes of the critical fields versus temperature show the strongly anisotropic nature of the ceramic superconductors.

In the mixed state of any type II superconductor, movement of the fluxiods (the tubes of normal phase material) would lead to energy dissipation and possible destruction of the superconductivity. Since the fluxiods are formed at low field strengths (20 mT), measurements of the critical current density (the current density strength which causes the movement of the fluxiods) have been carried out. Like the critical fields, the critical current densities are highly anisotropic, with the larger current densities for flows in the a-b plane. Dinger *et al.*[156] found that at 4.5 K and low fields, J_c (para) = 3.2 x 10^6 °A/cm^2 and J_c (per) = 1.6 x 10^5 °A/cm^2. As the temperature or field strength is increased, the critical currents decrease with the anisotropy still present. At T = 40 K, the larger current density dropped to 1.7 × 10^6 °A/cm^2 while at 60 K, J_c dropped to 4.2 × 10^4 °A/cm^2. Similar values were also reported by Schneemeyer *et al.*[157] and by Crabtree *et al.*[158] for their single crystal specimens. Chaudhari *et al.*[159] reported that the critical current densities in epitaxial films of YBa_2 Cu_3 O_{7-x} are similar in value to those of the single crystal specimens. At 77 K, they obtained a maximum J_c of 10^5 °A/cm^2 for flow perpendicular to the 'c' axis.

These large values of the critical currents should be contrasted with the low values reported for polycrystalline specimens. Laborde *et al.*[160] obtained J_c = 1100 °A/cm^2 at 77 K ; Leider and Feile[161] obtained J_c = 250 °A/cm^2 at 77 K while Ji *et al.*[162] obtained J_c = 336 °A/cm^2 at 78 K. Since many of the commerical applications of superconductors require high current densities (superconducting magnets require high currents in order to obtain the strong fields and the interconnections between devices on computer chips require current densities of the order 10^6 °A/cm^2[67]), several studies have been made on ways to increase the critical current value in the polycrystalline specimens. By melt textured growth of the ceramic, specimens having J_c = 7.5 x 10^3 °A/cm^2 have been obtained.[163] The value of J_c given by Ji *et al.*[162] was for a sample which had undergone some additional heat treatment. The starting specimens had a J_c of 23-32 °A/cm^2. The most promising method for increasing J_c is by neutron irradiation. By irradiating a specimen with 8.16 x 10^{17} n/cm^2 (fast neutrons), the critical current density has been increased by a factor of 2.4.[164] A similar increase of J_c was also observed by Cost *et al.*[165] who also found that the critical current density increased monotonically with increased fluence up to some limiting fluence. For fluences above 10^{18} n/cm^2, the critical current densities begin to drop.[166] This drop is accompanied by a decrease in the critical temperature. Several of these studies report that the resistivity of the ceramic superconductors increases with increase in fluence.

iii. Properties which might Elucidate the Mechanisms Responsible for Superconductivity in the Ceramic Superconductors

The existence of the isotope effect in YBa_2 Cu_3 O_{7-x} is a matter of controversy.[167-169] Bourne *et al.*[170] and Batlogg *et al.*[171] were not able to detect any shift of the transition temperature T_c when ^{16}O was replaced by ^{18}O. Bourne's study differed from that of Batlogg's study in that the exchange of the oxygen in the former's study was carried out at 950 °C, while the exchange of oxygen in the latter's study was done at 500 °C. This meant that the oxygen exchange was occurring in the tetragonal phase in Bourne's experiment, while the exchange was occurring in the orthorhombic phase in Batlogg's study. Grimsditch's argument[167] that the preferential substitution of the oxygen atoms on to certain sites may leave the O4 sites still occupied by the ^{16}O atoms is not applicable to Bourne's experiment, since neither the O4 nor O5 sites are occupied at 950 °C. The O4 sites become occupied as the temperature decreases as diffusion of oxygen ions from the sites on the Cu-O layers (occupied by ^{18}O atoms) occur. We would thus expect the O4 sites in the orthorhombic phase to be occupied by the ^{18}O atoms.

When the copper atoms in the ceramic were replaced by ^{63}Cu or ^{65}Cu atoms, no shift in T_c was seen either.[51,172] No isotope effect was seen when barium isotopes were substituted. It would appear that the isotope effect does not exist in the high T_c $YBa_2Cu_3O_{7-x}$ superconductors and that the electron-phonon interaction has no role in the superconductivity of these systems. Bourne *et al.*[51] has pointed out that it would still be possible for the electron-phonon interaction to have a role since the coulomb repulsion effects might mask the dependence of T_c on the mass dependent electron-phonon interaction. This could explain why the isotope effect[50] in the La-(Sr,Ba)-Cu-O is much less than that predicted by the BCS theory.

Leary *et al.*[173] mentioned that Bourne *et al.*[170] had expected an isotope shift of several degrees and so they compared the value of T_c s of specimens which had undergone different processing conditions. To truly test for the existence of the isotope effect, Leary *et al.* compared the T_c s of specimens which had been subjected to almost identical processing. In this way, they were able to establish an isotope shift of $M^{-0.004}$. However, the existence of such a small isotope effect can not be taken as proof that the electron-phonon interaction is primarily responsible for superconductivity since several other theories[174,175] also predict a small isotope effect.

In the absence of a clear indication of what mechanism is responsible for the superconductivity in the $YBa_2Cu_3O_{7-x}$ and related compounds, investigations of the vibrational modes occurring in these compounds and of the electronic structures of the compounds have been carried out. Using positron annihilation measurements, far infrared conductivity measurements, Raman and other spectroscopic techniques, investigators have looked for changes in the intensities of the excitation modes, and in the electronic structure as the compound undergoes the superconducting transition. Positron life time studies[176,177] indicate that the electron density at the oxygen vacancies increases as the compound goes superconducting. Zhu *et al.*[178] interpret this as an enhancement of the covalent character of the electrons while Wang *et al.*[179] interpret the results in terms of localization of the positron in the lattice distortions. Smedskjaer *et al.*[180] have pointed out that the behavior would be consistent with the BCS theory if the energy band had a small dispersion which crosses the Fermi surface.

Another reason for investigating the electronic structure of the $YBa_2Cu_3O_{7-x}$ compounds was to determine the ratio between the number of Cu^{2+} and Cu^{3+} ions. In initial investigations of the La-Ba-Cu-O superconductors, much attention was paid to this ratio[181] since it was believed that charge fluctuation on the copper ions was necessary for superconductivity to occur.[1,38,182] However, evidences for the presence of both Cu^{2+} and Cu^{3+} are somewhat conflicting.

Lyte *et al.*[183] propose evidence for both types of copper ions in his x-ray-absorption near-edge structure (XANES) data. Crozier *et al.*,[184] however, believe that the peak in the XANES data taken to be evidence for the Cu^{3+} ion is due to interference effects and should not taken as evidence for the presence of this ion in the system. X-ray photoemission spectra (XPS) studies[185-187] also indicate that Cu^{3+} ions are not present in the yttrium compounds. There is however evidence in the XPS data for oxygen dimerization and the presence of Cu^{1+} ions[186-189] as the compound goes superconducting. The valence (charge) fluctuations which are believed to be important to the superconductivity in the ceramic superconductors are between the Cu d^{10} O p^5 and the Cu d^9 O p^5 states.

D. Atomic Substitution

i. Rare Earth Substitution

Ever since Abrikosov and Gorkov[190] showed that the spin flip scattering by well localized magnetic impurities could suppress the superconducting state, physicists have been interested in the interplay between magnetism and superconductivity. In the late 60s and early 70s when the physicists thought that almost everything about superconductivity had been uncovered, Müller-Hartmann and Zittartz[191] published their seminal paper showing that if the spin flip interaction was treated beyond second order perturbation correction, the Kondo effect[192] would show up in the superconducting state. Under certain conditions, the Kondo scattering led to reentrant behavior, i.e., in addition to the normal-to-superconducting phase transition at T_c, a second phase transition, a superconducting-to-normal transition, took place at a much lower temperature. The Müller-Hartmann and Zittartz paper stimulated an enormous amount of experimental work to discover Kondo superconductors and to clarify the nature of magnetic interaction. This, in turn, led to a great amount of theoretical work on the effects of local magnetic moments whose life times were very short. A review of this facet of superconductivity has previously appeared in this journal.[193]

In all the cases considered, magnetism and superconductivity did not coexist, i.e., long range magnetic ordering and the superconducting ordering do not exist at the same time. In the late 70s and early 80s the ternary rare-earth superconductors such as $ErRh_4B_4$ and $SmRh_4B_4$ were discovered.[194] Evidences indicate that in some of these superconductors, antiferromagnetic ordering and superconductivity are both present in some temperature ranges. More recently, a new set of superconductors called the heavy fermion superconductors has been discovered. In these superconductors, the electrons behave as though they had masses of several hundred free electron masses. Much effort was devoted to the study of these novel superconductors prior to the discovery of the high T_c superconductors. At least one of the heavy fermion superconductors contains a rare earth element. As is with the case of the high T_c superconductors, it is believed that something more than the 'conventional' BCS theory is needed to explain the phenomenon of the heavy fermion superconductors. People working in this field are, however, well versed in the field of conventional superconductivity.

The reason for mentioning the previous classes of 'exotic' superconductors containing magnetic rare earth ions is that, shortly after the discovery of the $YBa_2 Cu_3 O_{7-x}$ superconductor, it was realized that the replacement of the ytterium ions by other rare earth ions would not destroy the '123' structure. It was somewhat surprising to find that, in most cases, the replacement of the ytterium ions by other rare earth ions did not lead to any appreciable changes in the transition temperatures.[196-200] Except for R = La, Ce, Tb and Pr, all compounds $RBa_2 Cu_3 O_{7-x}$ were superconducting[197] with T_c, above 90 K. An explanation for the non formation of a superconducting phase by the four mentioned rare earths was that,(1) the La ions have the largest ionic radius of the rare earths and therefore the '123' structure would be distorted beyond recognition, and (2), the Ce, Tb and Pr form into 4+ valence states. Of the rare earths in the $RBa_2 Cu_3 O_{7-x}$ superconductors, only Y, Lu and Yb do not have magnetic moments; all the others have, ranging from 0.85 to 10.65 Bohr magnetons. These are calculated values based on Hund's rule and in most cases correspond with the values measured.

Orlando *et al.*[200] found the extrapolated upper critical fields at T = 0 K of the $RBa_2 Cu_3 O_{7-x}$ (R = Nd, Eu, Gd, Dy, Ho, Er, and Tm) clustered around 160 $\pm$ 20 Telsa and the midpoints of the slope of the critical field vs. temperature curve clustered around 2.8 $\pm$ 0.2 Telsa/degree K. Heremans *et al.*[201] found that the molar specific heats of the rare earth '123' superconductors, (R = Y, Eu, Gd, Dy and Er) are identical to within $\pm$ 2 %. Infrared and Raman studies of the compounds (R = Y, Sm, Eu, Gd, Ho, and Nd, Dy, Er, Tm[203]) indicate an anomalous temperature behavior of the 310 cm^{-1} and 280 cm^{-1} lines associated with the bond bending vibrations of the Cu2-O2and Cu2-O3bonds in all of the compounds. This would indicate that the opening up of a gap below T_c was a universal feature of the '123' compounds.

The low temperature specific heats[204] of these compounds (R = Y, Eu, Ho, Tm and Yb) reveal, in several cases, Schottky anomalies associated with crystalline electric field splitting of the Hund's rule ground state multiplet of the R^{3+} ions. The magnetic susceptibility of these superconductors (R = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb) in the temperature range between 3 K and 400 K all exhibit Curie Weiss behavior.[205] A few of them show indications of possible antiferromagnetic ordering at very low temperatures, below 3 K. Based on specific heat data, Ramirez *et al.*[206] found that the interactions between the rare earth ions in these systems (R = Pr, Nd, Sm, Gd and Dy) are more of the spin-spin exchange type than of the dipole type. The insensitivity of the transition temperature to the replacement of Y by magnetic rare earth ions in the '123' superconductors and the common magnetic behaviors of magnetic rare earth ions have reinforced the idea that superconductivity in the '123' compounds is confined to the Cu-O/Ba-O/Cu-O/Ba-O/Cu-O layer and that no interaction takes place between the R layer and the superconducting layers.

More detailed studies of specific rare earth '123' superconductors have been done. Addition has been paid to mostly the Gd ceramic superconductor since Gd^{3+} has the largest J value of all the rare earths (J = 7/2). Specific heat data[207] indicates that an antiferromagnetic ordering of these ions is occurring at 2.24 K. Neutron diffraction studies[208] show the ordering of the Gd ions to occur at 2.22 ± 0.07 T. Like Ramirez *et al.*, Paul *et al.*[208] believe that the ordering is not due to dipolar interactions. ^{155}Gd Mossbauer studies[209] show that there are no conduction electrons at the Gd sites and so no exchange interactions between the Gd ion (or any other rare earth ions in the R layer) and conduction electrons occur. The orientation of the ordered Gd moments is parallel to the c axis[210] and shows that the ordering is due to anisotropic super-exchange interactions. In the tetragonal phase (semiconducting phase) of the $GdBa_2\ Cu_3\ O_{7-x}$ ceramic,[211] a magnetic transition at 2.24 K is still seen. The antiferromagnetic ordering is seen to have a strong 2-dimensional Ising character.

The $EuBa_2\ Cu_3\ O_{7-x}$ ceramic is also a well studied compound. Both polycrystalline and single crystal specimens have been studied. Hikita *et al.*[212] found the slope of upper critical field H_{c2} vs T curve for the c axis to be four times that of the slope for the a-b plane. The extrapolated upper critical field at T = 0 K is 190 Telsa, close to the values for the polycrystalline specimen studied by Orlando *et al.* No evidence for Eu^{2+} between 4.2 K and 400 K is seen in the ^{151}Eu Mossbauer studies.[213, 214] These studies indicate that the Eu^{3+} layer vibrates as a Debye solid with a Debye temperature of 280 ± 5 K. No evidence is seen for any anomaly around 240 K or at T_c. Wortmann *et al.*[215] find evidence in their Mossbauer studies for slight electronic modifications of Eu^{3+} ion induced by the neighbouring Cu-O layers. Magnetization measurements[214] indicate that the lower critical field H_{c1} is about 500 G. Properties dependent on phonon transport in the ceramics indicate that, at low temperatures, the $EuBa_2\ Cu_3\ O_{7-x}$ compound can be described as a tunneling system.[40] No studies have reported that the Eu ions become ordered below any temperature.

Some interest has been shown in the $ErBa_2\ Cu_3\ O_7$ superconductors since the Er^{3+} ions undergo a magnetic transition at 0.87 °K.[216,217] Spins within the chains are coupled ferromagnetically with the spins on adjacent chains being anti-parallel. Also interesting is that, above T_c, a magnetic interaction between the 4f electrons of the Eu ions and the conduction electrons exists,[217] while below T_c, the interaction disappears. The lower critical field for this superconductor is about 600 G which is close to those of the other rare earth '123' superconductors.

Individual studies of the other rare earth superconductors have also been made[218-223] but they do not point to any surprises.

ii. Transition Metal Substitution

As mentioned above, the insensitivity of the superconductive properties to the replacement of the ytterium ion by any other trivalent rare earth ion, be it magnetic or nonmagnetic, leads to the conclusion that superconductivity exists only in the CuO_2-Ba-CuO_2 layer. The local density of states at the Fermi surface should be small around Ba^{2+} and R^{3+} sites because of the stable Xe and Kr core electron structure of these ions. The main contributions to the DOS (E_F) come from the Cu *d* band and the *spd* hybridization states due to the Cu and O ions (see band calculations in refs. 224 and 225). Substitution of Cu by other transition metals should produce a large change in the superconducting properties which, in turn, should shed light on the mechanisms responsible for the superconductivity.

Xiao *et al.*[226] and Strobel *et al.*[227] have been able to fabricate the ceramics $YBa_2 (Cu_{0.9} M_{0.1})_3 O_{6+y}$ (M = Ti, Cr, Mn, Fe, Co, Ni, Cu and Ni) and $YBa_2 Cu_{3(1-x)}M_{3x} O_{7-z}$ (x = .05, 0.1, M = Ag, Li, Pt, Zn, Cr, Mn, Fe, Co and Ni). Both types show a sizeable drop of the transition temperature, e.g. T_c of the Zn doped ceramic dropped to less than 3 °K, while T_c of the Cr doped ceramic dropped to 84.5 K. Strobel *et al.* found that most substitutions, except for Fe and Co, caused only a slight change in the $YBa_2 Cu_3 O_7$ unit cell parameter. Xiao *et al.* also measured the magnetic susceptibilities of the compounds and found the property to be well described by the Curie Weiss law. As expected, Fe and Co had the largest magnetic moments, followed by Mn and Ni. The magnetic moments of the Ti and Cr ions were negligible. In general, the drop in T_c correlates with the size of the paramagnetic moments of the impurities except in the case of Zn. Fe and Co, which have the largest magnetic moments, produced the largest drops in T_c, T_c for the Fe doped ceramic being 38.0 K, and for the Co-doped ceramic, 21.2 K. Xiao *et al.* attributes the drop in T_c to pair breaking by conduction and *d*-electron exchange scattering at a paramagnetic site. The drop in T_c caused by Zn substitution is due to the filling of the anti-bonding *d* band. Dharma-Wardana[228] points out that the T_cs obtained by Xiao *et al.* strongly correlate with the difference in the crystal field stabilization energies for Cu2 sites and Cu1 sites in the 2D layer and 1D chain, respectively. This led Dharma-Wardana to hypothesize that superconductivity is depressed because of the changes in the 1D chain.

Mehbod *et al.*[229] found that for low Fe concentrations, the transition temperature T_c decreased linearly as a function of the Fe concentration until the latter reached 10.7% of the Cu concentration, at which point, the transition temperature dropped drastically. At a concentration of 12%, the Fe ions no longer substituted into the Cu sites. Instead, a new phase (semiconducting) appeared. Mossbauer studies[230,231] showed that Fe substituted into both Cu1 and Cu2 sites. Substitution of the Fe ions (above a concentration of 1.5%) led to an orthorhombic-to-tetragonal phase transition.[232] Below a Fe concentration of 1%, no magnetic ordering occured (even at 0 K). Other

Mossbauer studies of $YBa_2(Cu_{.985}Fe_{.015})_3O_{7-x}$ (T_c = 59 K)[233] and $YBa_2(Cu_{.95}Fe_5)_3O_{7-x}$ (T_c = 57 K)[234] showed that long range magnetic ordering is established at 7 K and 12 K, respectively. The Fe ions appear to be aligned with the c-axis. Fe substitution into the $GdBa_2Cu_3O_y$ ceramics has a more steep linear drop in T_c and earlier transition into the tetragonal phase.[235]

Aluminum substitution in the high T_c superconductors is of special interest since it can be substituted for either the Cu or the Y ions. Siegrist *et al.*[236] looked at substitution of the Al ions into Cu1 sites in the linear chain, while Franck *et al.*[237] looked at the substitution of the Al ions into the Y sites. Siegrist *et al.* found the drop in T_c with increasing Al substitution to be gradual. For $YBa_2Cu_{2.9}Al_{.1}O_7$, T_c dropped only to 80 K. Past this concentration, the drop was drastic. Replacing ytterium ions by Al ions also produced a drop in T_c.[237] This is attributed to the crystal structure change resulting from the fact that the ionic radius of Al (0.51 °A) is much smaller than the ionic radius of Y (0.97 °A). Complete substitution of the Y ions by Al produced an insulator at 77 K.

Substitution of Ag or Pd into the Cu sites are also of special interest. Nishi *et al.*[238] found that a small amount of Pd substitution could increase the transition temperature. Increasing the Pd substitution led to a decrease of T_c. Substitution of Ag in place of Cu is interesting since Ag is a monovalent ion while Cu is a mixed valent ion. Tomy *et al.*[239] saw an increase in the Cu^{3+}/Cu^{2+} m ratio in the normal phase. They observed, however, a decrease in the transition temperature as the concentration of Ag was increased. Complete replacement of the Cu ions was accomplished by Pan *et al.*[240] The resulting multiphase ceramic had an onset temperature of 50 K with a transition width of about 30 K. The interesting things about this superconductor are the absence of localized moments or valence fluctuations present in the Cu-based ceramics. The existence of high temperature superconductivity in this ceramic should cause a reconsideration of all the theories which are based on the presence of localized moments or valence fluctuations in the high T_c superconductors.

iii. Anion Substitution

In the hope of achieving higher temperature superconductors, several groups have attempted to modify the $YBa_2Cu_3O_{7-x}$ ceramics by replacing the oxygen anion by some other anion. Felner *et al.*[241] have succeeded in substituting a S ion into one of the O sites. While the resulting $YBa_2Cu_3O_6S$ ceramic has the same T_c as the $YBa_2Cu_3O_7$ superconductor, its phase transition is sharper and it displays the full Meissner effect and has a larger upper critical field. In the presence of an external 20 kOe field, the S-rich ceramic exhibits full diamagnetism, while the normal ceramic exhibits only paramagnetic behaviour.

Substitution of Cl or F into the ceramic leads to a decrease in T_c. For the Cl substitution ($YBa_2Cu_3O_6Cl$), the transition temperature drops to 72 K.[241] Substitution of F into O sites has been reported to lead to a drop of T_c into the range 80-89 °K.[242] Two other groups report that their F-doped ceramics exhibit superconductive properties at 148.5 K[243] and 155 K.[244] These results however, have not been reproducible by other laboratories and so it is believed that the evidences presented for the presence of superconductivity were due to some artifacts of the experimental method used by the two groups.

IV. "NEW" HIGH T_C SUPERCONDUCTOR

In the euphoria following the announcement of the 90 K superconductor by Chu on Feb. 16, 1987,[5] the public was led to think that room temperature superconductors was just around the corner.[7] After one year of intensive effort, it appeared that T_c was stuck at 90 °K. The reports of superconductivity at 155 K,[244] 159 K,[245] 240 K,[246] 260 K[247] and at 500 K[248] proved to be somewhat illusory. They were either not reproducible or the evidence for superconductivity could be attributed to some other phenomenon. In January of this year, almost one year after Chu's announcement, rumours about "new" high T_c superconductors began to circulate. The rumours were confirmed with the appearance of a paper by Maeda *et al.*[249] of 105 K superconductivity in a Bi-Sr-Ca-Cu oxide sample prepared on 23 December, 1987. This was followed by Chu's announcement on 25 January, 1988 of 120 K superconductivity in a Bi-Sr-Ca-Cu-Al-O ceramic. A different class of "new" high T_c superconductors was announced on 22 January, 1988 (the same day Maeda made his announcement to the Japanese press). Sheng and Hermann reported 85 K superconductivity in Tl-Ba-Cu oxides. This was followed by their announcement of 115 K superconductivity in a Tl-Ba-Ca-Cu oxide.

Before the appearances of the papers in the scientific journals, many people had guessed at the composition and sought to make the "new" superconductors themselves. Within weeks of Maeda's announcement, Liu *et al.*[250] had grown a single crystal of a $BiSrCuCa_{.5}O_x$ compound having a T_c of 85 K while Kang *et al.*[251] had made a superconducting film of Bi-Sr-Ca-Cu-O having a T_c between 90-110 K. Enough work had been done so that at a conference held in Interlake six weeks after Maeda's announcement, over thirty papers on the "new" high T_c superconductors were presented. The chemical composition of Maeda's superconductor is reported to be $BiCaSrCu_2O_X$. The Bi-ceramic made by Chu *et al.*[252] has the chemical composition $Bi_2CaSr_2Cu_2O_9$.[253]

That the "new" superconductors are truly "new" high T_c superconductors can be seen in two articles in the News and Views section of Nature. In an article by Forgan and Greaves in the March 3rd issue,[254] they stated that : "it is fairly certain that similar structural features (refering to 1D and 2D Cu-O layers) are present in the new materials." In the March 24th issue,[255] when results of X-ray and neutron-diffraction studies of the crystal structure became known, they pointed out the presence of two 2D copper-oxygen layers adjacent to each other with no copper-oxygen chains present. They pointed out that a structural similarity does exist between the "new" high T_c superconductors and the 'old' $YBa_2Cu_3O_7$ superconductors. The similarity to which they referred is how the basal Cu-O planes of the pyramidal CuO_4 units sandwich a bridging cation (Y^{3+} for the 'old' superconductor and Ca^{2+} for the 'new' superconductor). These 'new' bismuth superconductors were foreshadowed by a paper by Michel *et al.*[256] which reported 22 K superconductivity in a $Bi_2\ Sr_2\ Cu_2\ O_x$ ceramic.

While the papers describing the structure of the thallium compounds have not reached Thailand, Hermann and Sheng are reported to have said that patterns of three adjacent copper-oxygen layers are seen.[257] In their paper which describes how they initially fabricated the thallium compounds,[258] they give the reasons which motivated them to consider thallium. First, thallium has a valence state of 3+. Next, its ionic radius is 0.95 °A which is close to those of the rare earths. Based on experience with the rare earth substitution in $YBa_2\ Cu_3\ O_7$, they thought this was the best candidate. The chemistry of thallium compounds required that the fabrication processes be modified. It turns out that the fabrication becomes very easy as long as one remembers that thallium compounds are very toxic. In the issue of Nature that announced the discovery, this toxicity was pointed out as a separate warning.

We would like to end this review with the mention that Cava has reported finding high temperature (20-30 K) superconductivity in a perovskite structure compound $Ba_{.6}\ K_{.4}\ Bi_{.4}$. Like the Ag-compound fabricated by Pan *et al.*,[240] there is no copper ions in this 'new' high T_c superconductor.

REFERENCES

1. Bednorz, J.G. and Müller K.A. (1986). *Z. Phys. B* **64,** 189.
2. Chu, C.W., Hor, P.H., Meng, R.L., Gao, L., Huang, Z.J. and Wang, Y.Q. (1987). *Phys. Rev. Lett.* **58,** 405.
3. Hikami, S., Hirai, T. and Kagoshima, S. (1987). *Jpn. J. Appl. Phys.* **26,** L314.
4. Zhao, Z.X., Chen, L.Q., Cui, C.G., Huang, Y.Z., Liu, J.X., Chen, G.H., Li, S.L., Guo, S.Q. and He, Y.Y. (1987). *Kexue Tongbao* **3,** 177.
5. New York Times, Feb. 16, 1987.
6. New York Times, Mar. 19, 1987.
7. Time Magazine, May 4, 1987.
8. *Report of the Basic Energy Sciences Advisory Committe panel on high T_c Superconducting Magnetic Applications in Particle Physics* (1987). US Department of Energy, Office of Energy Research, Washington, D.C.
9. Nednorz, J.G., Takashige, M. and Müller, K.A. (1987). *Europhys. Lett.* **3,** 379.
10. Uchida, S., Takagi, H., Kitazawa, K. and Tanaka, S. (1987). *Jpn. J. Appl. Phys.* **26,** L1.
11. Takagi, H., Uchida, S., Kitazawa K. and Tanaka, S. (1987). *Jpn. J. Appl. Phys.* **26,** L123.
12. Chu, C.W., Hor, P.H., Meng, R.L., Gao, L., Huang, Z.J. and Wu, Y.Q. (1987). *Phys. Rev. Lett.* **58,** 405.
13. Cava, R.J., van Dover, R.B., Batlogg, B. and Rietman, E.A. (1987). *Phys. Rev. Lett.* **58,** 408.
14. Politis, C., Geerk, J., Dietrich, M. and Obst, B. (1987). *Z. Phys. B* **66,**141.
15. Grover, A.K., Dhar, S.K., Paulose, P.L., Nagarajan, V., Sampathkumaran, E.V. and Nagarajan, R. (1987). *Sol. State Commun.* **63,** 1003.
16. Muraleedharan, K. and Rambabu, D. (1987). *Phys. Rev. B* **36,** 8918.

17. Jorgensen, J.D., Schuttler, H.B., Hinks, D.G., Capone II, D.W., Zhang, K., Brodsky, M.B. and Scalapino, D.J. (1987). *Phys. Rev. Lett.* **58**, 1024.
18. Geiser, U., Beno, M.A., Schultz, A.J., Wang H.H., Allen, T.J., Monaghan, M.R. and Williams, J.M. (1987). *Phys. Rev. B* **35**, 6721.
19. Gough, C.E., Colclough, M.S., Forgan, E.M., Jordan, R.G., Keene, M., Muirhead, C.M., Rae, A.I.M., Thomas, N., Abell J.S. and Sutton, S. (1987). *Nature* **360**, 855.
20. Sulewski, P.E., Noh, TW., McWhirter, J.T. and Sievers, A.J. (1987). *Phys. Rev. B* **36**, 5735.
21. Bonn, D.A., Greedan, J.E., Stager, C.V. and Timusk, T. (1987). *Sol. State Commun.* **62**, 383.
22. Schlesinger, Z., Greene, R.L., Bednorz, J.G. and Müller, K.A. (1987). *Phys. Rev. B* **35**, 5334.
23. Kirtley, J.R., Tsuei, C.C., Park S.I., Cji, C.C., Rozen, J. and Shafer, M.W. (1987). *Phys. Rev. B* **35**, 7216.
24. Pan, S., Ng, K.W., de Lozanne, A.L., Tarascon, J.M. and Greene, L.H. (1987). *Phys. Rev. B* **35**, 7220.
25. Walter, U., Sherwin, M.S., Stacy, A., Richards, P.L. and Zettl, A. (1987). *Phys. Rev. B* **35**, 5327.
26. Sherwin, M.S., Richards, P.L. and Zettl, A. (1987). *Phys. Rev. B* **37**, 1587.
27. van Bentum, P.J.M., van de Leeput, L.E.C., Schreurs, L.W.M., Teunissen, P.A.A. and van Kempen, H. (1987). *Phys. Rev. B* **36**, 843.
28. Eliashberg, G.M. (1963). *Sov. Phys. JETP* **11**, 780.
29. Wenger, L.E., Chen, J.T., Hunter, G.W. and Logothetis, E.M. (1987). *Phys. Rev. B* **35**, 7213.
30. Nieva, G., Martinez, E.N., de la Cruz, F., Esparza, D.A. and D'Ovidio, C.A. (1987). *Phys. Rev. B* **36**, 8781.
31. Reeves, M.E., Friedmann, T.A. and Ginsberg, D.M. (1987). *Phys. Rev. B* **35**, 7207.
32. Dunlap, B.D., Nevitt, M.V., Slaski, M., Klippert, T.E., Sungaila, Z., McKale, A.G., Capone, D.W., Poeppel, R.B. and Flandermeyer, B.K. (1987). *Phys. Rev. B* **35**, 7210.
33. Bourne, L.C., Zettl, A., Chang, K.J., Cohen, M.L., Stacy, A.M. and Ham, W.K. (1987). *Phys. Rev. B* **35**, 8785.
34. Horie, Y., Fukami, T. and Mase, S. (1987). *Sol. State Commun.* **63**, 653.
35. Fossheim, K., Laegreid, T., Sandvoid, E., Vassenden, F., Müller, K.A. and Bednorz. J.G. (1987). *Sol. State Commun.* **63**, 531.
36. Esquinazi, P., Luzuriaga, J., Duran, C., Exparza, D.A. and D'Ovicio, C. (1987). *Phys. Rev. B* **36**, 2316.
37. Kumagai, K., Nakamichi, Y., Watanabe, I., Nakamura, Y., Nakajima, H., Wada, N. and Lederer, P. (1988). *Phys. Rev. Lett.* **60**, 724.
38. Anderson, P.W. (1987). *Science* **235**, 1196.
39. Zou, Z. and Anderson, P.W. (1987). *Phys. Rev. B* **37**, 627.
40. Walker, F.J. and Anerson, A.C. (1984). *Phys. Rev. B* **29**, 5881.
41. Aeppli, G., Cava, R.J., Ansaldo, E.J., Brewer, J.H., Kreitzman, S.R., Luke, G.M., Noakes, D.R. and Kiefl, R.F. (1987). *Phys. Rev. B* **35**, 7129.
42. Wappling, R.,Hartmann, O., Senateur, J.P., Madar, R., Rouault, A. and Yaouanc, A. (1987). *Phys. Lett.* **122A**, 209.
44. Kwok, W.K., Crabtree, G.W., Hinks, D.G., Capone, D.W., Jorgensen, J.D. and Zhang, K. (1987). *Phys. Rev. B* **35**, 5343.
45. Finnemore, D.K., Shelton, R.N., Clem, J.R., McCallum, R.W., Ku, H.C., McCarley, R.E., Chen, S.C., Klavins, P. and Kogan, V. (1987). *Phys. Rev. B* **35**, 5319.
46. (a) Razavi, F.S., Koffyberg, F.P. and Mitrovic B. (1987). *Phys. Rev. B* **35**, 5323. (b) Renker, B., Apfelstedt, I., Kupfer, H., Politis, C., Rietschel, H., Gottwick, U., Kneissel, H., Rauchschwalbe, U., Spille, H. and Steglich, F. (1987). *Z. Phys. B* **67**, 1.
47. Orlando, T.P., Delin, K.A., Foner, S., McNiff, E.J., Jr., Tarascon, J.M., Greene, L.H., McKinnon, W.R. and Hull, G.W. (1987). *Phys. Rev. B* **35**, 5347.
48. Senoussi, S., Oussena, M. and Ribault, M. (1987). *Phys. Rev. B* **36**, 4003.
49. Batlogg, B., Kourouklis, G., Weber, W., Cava, R.J., Jayaraman, A., White, A.E., Short, K.T., Rupp, L.W. and Rietman, E.A. (1987). *Phys. Rev. Lett.* **59**, 912.

50. Faltens, T.A., Ham, W.K., Keller, S.W., Leary, K.J., Michaels, J.N., Stacy, A.M., zur Loye, H.C., Morris, D.E., Barbee, III, T.W., Bourne, L.C., Cohen, M.L., Hoen, S. and Zettl, A. (1987). *Phys. Rev. Lett.* **59**, 915.
51. Bourne, L.C., Zettl, A., Barbee III, T.W., and Cohen, M.L. (1987). *Phys. Rev. B* **36**, 3990.
52. Mattheiss, L.F. (1987). *Phys. Rev. Lett.* **58**, 1028.
53. Stavola, M., Cava, R.J. and Rietman, E.A. (1987). *Phys. Rev. Lett.* **58**, 1571.
54. Freeman, A.J., Yu, J. and Fu, C.L. (1987). *Phys. Rev. B* **36**, 7111.
55. Redinger, J., Yu, J.J., Freeman, A.J. and Weinberger, P. (1987). *Phys. Lett.* **124A**, 463.
56. Reighl, B., Riesterer, T., Bednorz, J.R. and Müller, K.A. (1987). *Phys. Rev. B* **35**, 8804.
57. Tranquada, J.M., Heald, S.M. and Moodenbaugh, A.R. (1987). *Phys. Rev. B* **36**, 5263.
58. Weber, W. (1987). *Phys. Rev. Lett.* **58**, 1371.
59. Vaknin, D., Sinha, S.K., Moncton, D.E., Johnston, D.C., Newsam, J.M., Safinya, C.R. and King, Jr., H.E. (1987). *Phys. Rev. Lett.* **58**, 2802.
60. Anderson, P.W. (1987). quoted in *Nature* **329**, 481.
61. Hubbard, J. (1963). *Proc. Roy. Soc. London A* **276**, 283.
62. Hirsch, J.E. (1987). *Phys. Rev. Lett.* **59**, 228.
63. Alp, E.E., Shenoy, G.K., Hinks, D.G., Capone II, D.W., Soderholm, L., Schuttler, H.B., Guo, J., Ellis, D.E., Montano, P.A. and Ramanathan, M. (1987). *Phys. Rev. B* **35**, 7199.
64. Fujimori, A., Takayama-Muromachi, E. and Uchida, Y. (1987). *Sol. State Commun.* **63**, 657.
65. Smedskjaer, L.C., Routbort, J.L., Flandermeyer, B.K., Rothhman, S.J., Legnini, D.G. and Baker, J.E. (1987). *Phys. Rev. B* **36**, 3903.
66. Johnston, D.C., Stokes, J.P., Goshorn, D.P. and Lewandowski, J.T. (1987). *Phys. Rev. B* **36**, 4007.
67. Quoted in *Nature* **330**, 611 (1987).
68. Murouchi, E.T., Uchida, Y., Matsui, Y. and Kato, K. (1987). *Jpn. J. of Appl. Phys.* **26**, L476.
69. Izumi, F., Asano, H., Ishigaki, T., Ono, A. and Okamura, F.P. (1967). *Jpn. J. Appl. Phys.* **26**, L611.
70. Calestani, G. and Rizzoli, C. (1987). *Nature* **328**, **606**. ; Siegrist, T., Sunshine, S., Murphy, D.W., Cava, R.J. and Zahurak, S.M. (1987). *Phys. Rev. B* **35**, 7137. ; Hazen, R.M., Finger, L.W., Angel, R.J., Prewitt, C.T., Ross, N.L., Mao, H.K., Hadidiacos, C.G., Hor, P.H., Meng, R.L. and Chu, C.W. (1987). *Phys. Rev. B* **35**, 7238.
71. Reller, A., Bednorz, J.G. and Müller, K.A. (1987). *Z. Phys. B* **67**, 285.
72. Gupta, R.P. and Gupta, M. (1987). *J. Phys. C* **20**, L1021.
73. Katano, S. and Matsumoto, T. (1988). *Z. Phys. B* **70**, 15.
74. Yan, Q.W., Zhang, P.L., Jin, L., Shen, Z.G., Zhao, J.K., Ren, Y., Wei, Y.N., Mao, T.D., Liu, C.X., Ning, T.S., Sun, K. and Yang, Q.S. (1987). *Phys. Rev. B* **36**, 8810.
75. You, H., McMullan, R.K., Axe, J.D., Cox, D.E., Liu, J.L., Crabtree, G.W. and Lam, D.J. (1987). *Sol. State Commun,* **64**, 739.
76. Francois, M., Walker, E., Jorda, J.L., Yvon, K. and Fischer, P. (1987). *Sol. Stat Commun.* **63**, 1149.
77. Cox, D.E., Moodenbaugh, A.R., Hurst, J.J. and Jones, R.H. (1988). *J. Phys. Chem. Solids* **49**, 47.
78. Izumi, F., Asano, H., Ishigaki, T., Muromachi, E.T., Uchida, Y., Watanabe, N. and Nishikawa, T. (1987). *Jpn. J. Appl. Phys.* **26**, L649.
79. Greedan, J.E., O'Reilly, A.H. and Stager, C.V. (1987). *Phys. Rev. B* **35**, 8770.
80. Katano, S., Funahashi, S., Hatano, T., Matsushita, A., Nakamura, K., Matsumoto, T. and Ogawa, K. (1987). *Jpn. J. Appl. Phys.* **26**, L1046.
81. Dharwadkar, S.R., Jakkal, V.S., Yakhmi, J.V., Gopalakrishnan, L.K. and Iyer, R.M. (1987). *Sol. State Commun.* **64**, 1429.
82. Gabelica, Z., Derouane, E.G., Vigneron, J.P., Lambin, Ph., Renier, M., Lucas, A.A., Deconninck, G., Bodart, F. and Demortier, G. (1987). *Sol. State Commun.* **64**, 1221.
83. Jorgensen, J.D., Veal, B.W., Kwok, W.K., Crabtree, G.W., Umezawa, A., Nowicki, L.J. and Paulikas, A.P. (1987). *Phys. Rev. B* **36**, 5731.

84. Hatano, T., Matsushita, A., Nakamura, K., Sakka, Y.,Matsumoto, T. and Ogawa, K. (1987). *Jpn. J. Appl. Phys.* **26**, L721.
85. Derouane, E.G., Gabelica, Z., Andre, J.L., Lambin, P., Lucas, A.A. and Vigneron, J.P. (1987). *Sol. State Commun.* **64**, 1091.
86. Greedan, J.E., O'Reilly, A.H. and Stager, C.V. (1987). *Phys. Rev. B* **35**, 8770.
87. Hauck, J., Bickmann, K. and Zucht, F. (1987). *Z. Phys. B* **67**, 299.
88. Jorgsen, J.D., Beno, M.A., Hinks, D.G., Soderholm, L., Volin, K.J., Hitterman, R.L., Grace, J.D., Schuller, I.K., Segre, C.U., Zhang, K. and Kleefisch, M.S. (1987). *Phys. Rev. B* **36**, 3608.
89. Steiner, P., Hufner, S., Kinsinger, V., Sander, L., Siegwart, B., Schmitt, H., Schulz, B., Junk, S., Schwitzgebel, G., Gold, A., Politis, C., Müller, H.P., Hoppe, R., Kemmler-Sack, S. and Kunz, C. (1988). *Z. Phys. B* **69**, 449.
90. Steinfink, H., Swinnea, J.S., Manthiman, A., Sui, Z.T. and Goodenough, J.B. (1987). In *Proceedings of the International Workshop on Novel Mechanisms of Superconductivity, Berkeley,* edited by S.A. Wolf and V.Z. Kresin (Plenum, New York, 1987) p. 1067.
91. Strobel, P., Capponi, J.J., Marezio, M. and Monod, P. (1987). *Sol. State Commun.* **64**, 513.
92. Karpinski, J. and Kaldis, E. (1988). *Nature* **331**, 242.
93. Kwok, W.K., Crabtree, G.W., Umezawa, A., Veal, B.W., Jorgensen, J.D., Malik, S.K., Nowicki, L.J., Paulikas, A.P. and Numez, L. (1988). *Phys. Rev. B* **37**, 106.
94. Ng, H.K., Mathias, H., Moulton, W.G., Pan, K.K., Pan, S.J., Rey, C.M. and Testardi, L.R. (1988). *Sol. State Commun.* **65**, 63.
95. Brokman, A. (1987). *Sol. State Commun.* **64**, 257.
96. van Tendeloo, C., Zandbergen, H.W. and Amelinckx, S. (1987). *Sol. State Commun.* **63**, 389.
97. Pande, C.S., Singh, A.K., Toth, L., Gubser, D.U. and Wolf, S. (1987). *Phys. Rev. B* **36**, 5669.
98. Garcia, N., Vieira, S., Baro, A.M., Tornero, J., Pazos, M., Vazquez, L., Gomez, J., Aguilo, A., Bourgeal, S., Buendia, A., Hortal, M., Lopez de la Torre, M.A., Ramos, M.A., Villar, R., Rao, K.V., Chen, D.X., Noques, J. and Karpe, N. (1988). *Z. Phys. B* **70**, 9.
99. Deutscher, G. and Müller, K.A. (1987). *Phys. Rev. Lett.* **59**, 1745.
100. Morgenstern, I., Müller, K.A. and Bednorz, J.G. (1987). *Z. Phys. B* **69**, 33.
101. Cai, X., Joynt, R. and Larbalestier, D.C. (1987). *Phys. Rev. Lett.* **58**, 2798.
102. Fang, M.M., Kogan, V.G., Finnemore, D.K., Clem, J.R., Chumbley, L.S. and Farrell, D.E. (1988). *Phys. Rev. B* **37**, 2334.
103. Horie, Y., Fukuda, H., Fukami, T. and Mase, S. (1987). *Sol. State Commun.* **64**, 501.
104. He, Y.S., Zhang, B.W., Lin, S.H., Xiang, J.O., Lou, Y.M. and Chen, H.M. (1987). *J. Phys. F* **17**, L243.
105. Zhang, M.S., Chen, Q.A., Sun, D.K., Ji, R.F., Qin, Z.H., Yu, Z. and Scott, J.F. (1988). *Sol. State Commun.* **65**, 487.
106. Horn, P.M., Keane, D.T., Held, G.A., Jordan-Sweet, J.L., Kaiser, D.L., Holtzberg, F. and Rice, T.M. (1987). *Phys. Rev. Lett.* **59**, 2772.
107. David, W.I.F., Edwards, P.P., Harrison, M.R., Jones, R. and Wilson, C.C. (1988). *Nature* **331**, 245.
108. Khachaturyan, A.G. and Morris, Jr., J.W. (1987). *Phys. Rev. Lett.* **59**, 2776.
109. Khachaturyan, A.G., Semenovskaya, S.V. and Morris, Jr. (1988). *Phys. Rev. B* **37**, 2243.
110. Kresin, V.Z. (1987). *Phys. Rev. B* **35**, 8716.
111. Kresin, V.Z. and Wolf, S.A. (1987). *Sol. State Commun.* **63**, 1161.
112. Freitas, P.P., Tsuei, C.C. and Plaskett, T.S. (1987). *Phys. Rev. B* **36**, 833.
113. Ausloos, M. and Laurent, Ch. (1988). *Phys. Rev. B* **37**, 611.
114. Laurent, Ch., Laguess, M., Patapis, S.K., Vanderschueren, H.W., Lecomte, G.V., Rulmont, A., Tarte, P. and Ausloos, M. (1988). *Z. Phys. B* **69**, 435.
115. Parkin, S.S.P., Engler, E.M., Lee, V.Y. and Beyers, R.B. (1988). *Phys. Rev. B* **37**, 131.
116. Sugai, S. (1987). *Phys. Rev. B* **36**, 7133.

117. Hangyo, M., Nakashima, S., Mizoguchi, K., Fujii, A., Mitsuishi, A. and Yotsuya, Y. (1988). *Sol. State Commun.* **65,** 835.
118. Cava, R.J., Batlogg, B., Chen, C.H., Pietman, E.A., Zahurak, S.M. and Werder, D. (1987). *Phys. Rev. B* **36,** 5719.
119. Werder, D.J., Chen, C.H., Cava, R.J. and Batlogg, B. (1988). *Phys. Rev. B* **37,** 2317.
120. Park, S.I., Tsuei, C.C. and Tu, K.N. (1988). *Phys. Rev. B* **37,** 2305.
121. Bates, F.E. and Eldridge, J.E. (1987). *Sol. State Commun.* **64,** 1435.
122. Macfarland, R.M., Rosen, H. and Seki, H. (1987). *Sol. State Commun.* **63,** 831.
123. Blumenroder, S., Zirngiebl, E., Schmdt, H., Guntherodt, G. and Brenten, H. (1987). *Sol. State Commun.* **64,** 1229.
124. Burns, G., Dacol, F.H., Freitias, P., Plaskett, T.S. and Koning, W. (1987). *Sol. State Commun.* **64,** 471.
125. Kourouklis, G.A., Jayaraman, A., Batlogg, B., Cava, R.J., Stavola, M., Krol, D.M., Rietman, E.A. and Schneemeyer, L.F. (1987). *Phys. Rev. B* **36,** 8320.
126. Crommie, M.F., Bourne, L.C., Zettl, A., Cohen, M.L. and Stacy, A.(1987). *Phys. Rev. B* **35,** 8853.
127. Kirk, M.D., Smith, D.P.E., Mitzi, D.B., Sun, J.Z., Webb, D.J., Char, K., Hahn, M.R., Naito, M., Oh, B., Beasley, M.R., Geballe, T.H.,Hammond, R.H., Kapitulnik, A. and Quate, C.F. (1987). *Phys. Rev. B* **35,** 8850.
128. Moreland, J., Ekin, J.W., Goodrich, L.F., Capobianco, T.E., Clark, A.F., Kwo, J., Hong, M. and Liou, S.H. (1987). *Phys. Rev. B* **35,** 8856.
129. Hohn, N., Koltun, R., Schmidt, H., Blumenröder, S., General, H., Guntherodt, G. and Wohlleben, D. (1987). *Z. Phys. B* **69,** 173.
130. Barone, A., Di Chiara, A., Peluso, G., Scotti di Uccio, U., Cucolo, A.M., Vaglio, R., Matacotta, F.C. and Olzi, E. (1987). *Phys. Rev. B* **36,** 7121.
131. Noh, T.W., Sulewski, P.E. and Sievers, A.J. (1987). *Phys. Rev. B* **36,** 8866.
132. Bonn, D.A., Greedan, J.E., Stager, C.V., Timusk, T., Doss, M.G., Herr, S.L., Kamaras, K. and Tanner, D.B. (1987). *Phys. Rev. Lett.* **58,** 2249.
133. Ye, H.J.,Lu, W., Yu, Z.Y., Shen, X.C., Miao, B.C.,Cai, Y.M. and Qian, Y.J. (1987). *Phys. Rev. B* **36,** 8802.
134. Wrobel, J.M., Wang, S., Gygax, S., Clayman, B.P. and Peterson, L.K. (1987). *Phys. Rev. B* **36,** 2368.
135. Ng et al., K.W. quoted in ref. 131.
136. Kivelson, S. (1987). *Phys. Rev. B* **36,** 7237.
137. Xu, J.H. (1987). *Sol State Commun.* **64,** 1425.
138. Collins, R.T., Schlesinger, Z., Koch, R.H., Laibowitz, R.B., Plaskett, T.S., Freitas, P., Gallagher, W.J., Sandstrom, R.L. and Dinger, T.R. (1987). *Phys. Rev. Lett.* **59,** 704.
139. Schlesinger, Z., Collins, R.T., Kaiser, D.L. and Holtzberg, F. (1987). *Phys. Rev. Lett.* **59,** 1958.
140. Felici, R., Penfold, J., Ward, R.C., Olsi E. and Matacotta, C. (1987). *Nature* **329,** 523.
141. Perez-Ramirez, J.G., Baberschke, K. and Clark, W.G. (1988). *Sol. State Commun.* **65,** 845.
142. Cooper, J.R., Chu, C.T., Zhou, L.W., Dunn, B. and Gruner, G. (1988). *Phys. Rev. B* **37,** 638.
143. Harshman, D.R., Aeppli, G., Ansaldo, E.J., Batlogg, B., Brewer, J.H., Carolan, J.F., Cava, R.J., Celio, M., Chaklader, A.C.D., Hardy, W.N., Kreitzman, S.R., Luke, G.M.,Noakes, D.R. and Senba, M. (1987). *Phys. Rev. B* **36,** 2386.
144. Salamon, M.B. and Bardeen, J. (1987). *Phys. Rev. Lett.* **59,** 2615.
145. Gammel, P.L., Bishop, D.J., Dolan,G.J., Kwo, J.R.,Murray, C.A., Schneemeyer, L.F. and Waszczal, J.V. (1987). *Phys. Rev. Lett.* **59,** 2592.
146. Lang, B., Lechner, T., Riegel, S., Steglich, F., Weber, G., Kim, T.J., Luthi, B., Wolf, B., Rietschel, H. and Wilhelm, M. (1988). *Z. Phys. B* **69,** 459.
147. Bezinge, A., Jorda, J.L., Junod, A. and Müller, J. (1987). *Sol. State Commun.* **64,** 79.
148. Drumbeller, J.E., Rubenacker, G.V., Ford, V.K., Anderson, J., Hong, M., Liou, S.H., Kwo, J. and Chen, C.T. (1987). *Sol. State Commun.* **64,** 509.

149. Sun, J.Z., Webb, D.J., Naito, M., Char, K., Hahn, M.R., Hsu, J.W., Kent, A.D., Mitzi, D.B., Oh, B., Beasley, M.R., Geballe, T.H., Hammond, R.H. and Kapitulnik, A. (1987). *Phys. Rev. Lett.* **58**, 1574.
150. McGuire, T.R., Dinger, T.R., Freitas, P.J.P., Gallagher, W.J., Plaskett, T.S., Sandstrom, R.L. and Shaw, T.M. (1987). *Phys. Rev. B* **36**, 4032.
151. Worthington, T.K., Gallagher, W.J. and Dinger, T.R. (1987). *Phys. Rev. Lett.* **59**, 1160.
152. Moodera, J.S., Meservey, R., Tkaczyk, J.E., Hao, C.X., Gibson, G.A. and Tedrow, P.M. (1988). *Phys. Rev. B* **37**, 619.
153. Orlando, T.P., Delin, K.A., Foner, S., McNiff, Jr., E.J., Tarascon, J.M., Greene, L.H., McKinnon, W.R. and Hull, G.W. (1987). *Phys. Rev. B* **35**, 7249.
154. Forro, L., Henry, J.Y., Ayache, C. and Stamp, P. (1988). *Phys. Lett. A* **128**, 283.
155. Welch, D.O., Suenaga, M. and Asano, T. (1987). *Phys. Rev. B* **36**, 2390.
156. Dinger, T.R., Worthington, T.K., Gallagher, W.J. and Sandstrom, R.L. (1987). *Phys. Rev. Lett.* **58**, 2687.
157. Schneemeyer, L.F., Gyorgy, E.M. and Waszczak, J.V. (1987). *Phys. Rev. B* **36**, 8804.
158. Crabtree, G.W., Liu, J.Z., Umezawa, A., Kwok, W.K., Sowers, C.H., Malik, S.K., Veal, B.W., Lam, D.J., Brodsky, M.B. and Downey, J.W. (1987). *Phys. Rev. B* **36**, 4021.
159. Chaudhari, P., Koch, R.H., Laibowitz, R.B., McGuire, T.R. and Gambino, R.J. (1987). *Phys. Rev. Lett.* **58**, 2684.
160. Laborde, O., Tholence, J.L., Lejay, P., Sulpice, S., Tournier, R., Capponi, J.J., Michel, C. and Provost, J. (1987). *Sol. State Commun.* **63**, 877.
161. Leiderer, P. and Feile, R. (1988). *Z. Phys. B* **70**, 141.
162. Ji, C.L.,Wang, K.H., Fan, Z.G., Liu, S.L., Cui, C.M., Zhang, G.F., Zeng, G.Y., Qian, C.F. and Wang, S.L. (1988). *Sol. State Commun.* **65**, 863.
163. Mentioned in *Superconductor Week I* **19**, (1987).
164. Umezawa, A., Crabtree, G.W., Liu, J.Z., Weber, H.W., Kwok, W.K., Numez, L.H., Moran, T.J., Sowers, C.H. and Claus, H. (1987). *Phys. Rev. B* **36**, 7151.
165. Cost, J.R., Willis, J.O., Thompson, J.D. and Peterson, D.E. (1988). *Phys. Rev. B* **37**, 1563.
166. Kupfer, H., Apfelstedt, I., Schauer, W., Flukiger, R., Meier-Hirmer, R., Wuhl, H. and Scheurer, H. (1987). *Z. Phys. B* **69**, 167.
167. Grimsditch, M., Brun, T.O., Bhadra, R., Dabrowski, B., Hinks. D.G., Jorgensen, J.D., Beno, M.A., Liu, J.Z., Schuttler, H.B., Segre, C.U., Soderholm. L., Veal, B.W. and Schuller, I.K. (1988). *Phys. Rev. Lett.* **60**, 752.
168. Zettl, A. and Kinney, J. (1988). *Phys. Rev. Lett.* **60**, 753.
169. Batlogg, B., Cava, R.J. and Stavola, M. (1988). *Phys. Rev. Lett.* **60**, 754.
170. Bourne, L.C., Crommie, M.F., Zettl, A., zur Loye, H., Keller, S.W., Leary, K.L., Stacy, A.M., Chang, K.J., Cohen, M.L. and Morris, D.E. (1987). *Phys. Rev. Lett.* **58**, 2337.
171. Batlogg, B., Cava, R.J., Jayaraman, A., van Dover, R.B., Kourpuklis, G.A., Sunshine, S., Murphy, D.W., Rupp, L.W., Chen, H.S., White, A., Short, K.T., Mujsce, A.M. and Rietman, E.A. (1987). *Phys. Rev. Lett.* **58**, 2333.
172. Lin, C., Wei, Y.N., Yan, Q.W., Chen, C.H., Zhang, P.L., Shen, Z.G., Ni, Y.M., Yang, Q.S., Liu, C.X., Ning, T.S., Zhao, J.K., Shao, Y.Y., Han, S.H. and Li, J.Y. (1988). *Sol. State Commun.* **65**, 869.
173. Leary, K.J., zur Loye, H., Keller, S.W., Faltens, T.A., Ham, W.K., Michaels, J.N. and Stacy, A.M. (1987). *Phys. Rev. Lett.* **59**, 1236.
174. Mattis, D.C. and Mattis, M.P. (1987) *Phys. Rev. Lett.* **59**, 2780.
175. Gersten, J.I. (1988). *Phys. Rev. B* **37**, 1616.
176. Ishibashi, S., Suzuki, Y., Yamamoto, R., Hatano, T., Ogawa, K. and Doyama, M. (1988). *Phys. Lett. A* **128**, 387.
177. Usmar, S.G., Sferlazzo, P., Lynn, K.G. and Moodenbaugh, A.R. (1987). *Phys. Rev. B* **36**, 8854.

178. Zhu, J.S., Song, J.X., Wang, J., Yang, Z.J., Zhang, Y.H. and Lung, C.W. (1988). *J. Phys. C* **21,** L281.
179. Wang, S.J., Naidu, S.V., Sharma, S.C., De, D.K., Jeong, D.Y., Black, T.D., Krichene, S., Reynolds, J.R. and Owens, J.M. (1988). *Phys. Rev. B* **37**, 603.
180. Smedskjaer, L.C., Veal, B.W., Legnini, D.G., Paulikas, A.P. and Nowicki, L.J. (1988). *Phys. Rev. B* **37**, 2330.
181. Sreedhar, K., Ramakrishnan, T.V. and Rao, C.V. (1987). *Sol. State Commun.* **63**, 835.
182. Pauling, L. (1987). *Phys. Rev. Lett.* **59**, 225.
183. Lyte, F.W., Greegor, R.B. and Panson, A.J. (1988). *Phys. Rev. B* **37**, 1550.
184. Crozier, E.D., Alberding, N., Bauchspiess, K.R., Seary, A.J. and Gygax, S. (1987). *Phys. Rev. B* **36**,8288.
185. Steiner, P., Kinsinger, V., Sander, I., Siegwart, B., Hufner, S., Politis, C., Hoope, R. and Müller, H.P. (1987). *Z. Phys. B* **67**, 497.
186. Yarmoff, J.A., Clarke, D.R., Drube, W., Karlsson, U.O., Taleb-lbrahimi, A. and Himpsel, F.J. (1987). *Phys. Rev. B* **36**,3967.
187. Kachel, T., Sen, P., Dauth, B. and Campagna, M. (1988). *Z. Phys. Rev. B* **70,** 137.
188. Dauth, B., Kachel, T., Sen, P., Fischer, K. and Campagna, M. (1987). *Z. Phys. B* **68**, 407.
189. Sarma, D.D., Sreedhar, K., Gauguly, P. and Rao, C.N.R. (1987). *Phys. Rev. B* **36**, 2371.
190. Arbrikosov, A.A. and Gorkov, L.P. (1961). *JETP* **12**, 1243.
191. Muller-Hartmann, E. and Zittartz, J. (1963). *Z. Physik* **254**, 234.
192. Maple, M.B. *AIP Conf. Proc.* No. 4, editor D.H. Douglass (AIP, New York, 1972) p. 175.
193. Tang, I.M. (1986). *J. Sci. Soc. Thailand* **12**, 67.
194. e.g. *Superconductivity in Ternary Compounds.* Editor M.B. Maple and ϕ Fischer (Springer, New York, 1982).
195. Stewart, G.R. (1984). *Rev. Mod. Phys.* **56**, 755.
196. Tarascon, J.M., McKinnon, W.R., Greene, L.H., Hull, G.W. and Vogel, E.M. (1987). *Phys. Rev. B* **36**, 226.
197. Yang, K.N., Dalichaouch, Y., Ferreira, J.M., Lee, B.W., Neumeier, J.J., Torikachvili, M.S., Zhou, H., Maple, M.B. and Hake, R.R. (1987). *Sol. State Commun.* **63**, 515.
198. Hulliger, F. and Ott, H.R. (1987). *Z. Phys. B* **67**, 291.
199. Lee, S.C., Lee, J.H., Suh, B.J., Moon, S.H., Lim, C.J. and Khim, Z.G. (1988). *Phys. Rev. B* **37**, 2285.
200. Orlando, T.P., Delin, K.A., Foner, S., McNiff, Jr., E.J., Tarascon, J.M., Greene, L.H., McKinnon, W.R. and Hull, G.W. (1987). *Phys. Rev. B* **36**, 2394.
201. Heremans, J., Morelli, D.T., Smith, G.W. and Strite III, S.C. (1988). *Phys. Rev. B* **37**, 1604.
202. Cardona, M., Genzel, L., Liu, R., Wittlin, A., Mattausch, Hj., Garcia-Alvarado, F. and Garcia-Alvarado, E. (1987). *Sol. State Commun.* **64**, 727.
203. Cardona, M., Liu, R., Thomson, C., Bauer, M., Genzel, L., Konig, W., Wittlin, A., Amador, U., Barahona, M., Fernandez, F., Otero, C. and Saez, R. (1988). *Sol. State Commun.* **65**, 71.
204. Ferreira, J.M., Lee, B.W., Dalichaouch, Y., Torikachvili, M.S., Yang, K.N. and Maple, M.B. (1988). *Phys. Rev. B* **37**, 1580.
205. Xiao, G., Streitz, F.H., Garvrin, A. and Chien, C.L. (1987). *Sol. State Commun.* **63**, 817.
206. Ramirez, A.P., Schneemeyer, L.F. and Waszczak, J.V. (1987). *Phys. Rev. B* **36**, 7145.
207. Reeves, M.E., Citrin, D.S., Pazol, B.G., Friedmann, T.A. and Ginzberg, D.M. (1987). *Phys. Rev. B* **36**, 6915.
208. Paul, D. Mck., Mook, H.A. and Hewat, A.W. (1988). *Phys. Rev. B* **37**, 2341.
209. Alp, E.E., Soderholm, L., Shenoy, G.K., Hinks, D.G., Capone II, D.W., Zhang, K. and Dunlap, B.D. (1987). *Phys. Rev. B* **36**, 8910.
210. Meyer, C., Bornemann, H.J., Schmidt, H., Ahrens, R., Ewert, D., Renker, B. and Czjzek, G. (1987). *J. Phys. F* **17**, L345.
211. van den Berg, J., van der Beek, C.J., Kee, P.H., Mydosh, J.A., Nieuwenhuys, G.J. and de Jongh, L.J. (1987). *Sol. State Commun.* **64**, 699.
212. Hikita, M., Tajima, Y., Katsui, A., Hidaka, Y., Iwata, T. and Tsurumi, S. (1987). *Phys. Rev. B* **36**, 7199.
213. Boolchand, P., Enzweiler, R.N., Zitkovsky, I., Meng, R.L., Hor, P.H., Chu, C.W. and Huang, C.Y. (1987). *Sol. State Commun.* **63**, 521.

214. Coey, J.M.D. and Donnelly, K. (1987). *Z. Phys. B* **67**, 513.
215. Wortmann, G., Blumenroder, S., Freimuth, A. and Riegel, D. (1988). *Phys Lett. A* **126**, 434.
216. Yang, H.D., Ku, H.C., Klavins, P. and Shelton, R.N. (1987). *Phys. Rev. B* **36**, 8791.
217. Walter, U., Fahv, S., Zettl, A., Louie, S.G., Cohen, M.L., Tejedor, P. and Stacy, A.M. (1987). *Phys. Rev. B* **36**, 8899.
218. Thompson, J.R., Christen, D.K., Sekula, S.T., Sales, B.C. and Boatner, L.A. (1987). *Phys. Rev. B* **36**, 837.
219. Dirken, M.W. and de Jongh, L.J. (1987). *Sol. State Commun.* **64**, 1201.
220. Goldman, A.I., Yang, B.X., Tranquada, J., Crow, J.E. and Jee, C.S. (1987). *Phys. Rev. B* **36**, 7243.
221. Garcia-Aivarado, F., Moran, E., Vaillet, M., Gonzaiez-Caibet, J.M., Aiario, M.A., Perez, M.T., Vicent, J.L., Ferrer, S., Garcia-Michel, E. and Asensio, M.S. (1987). *Sol. State Commun.* **63**, 507.
222. Andreeta, J.P., Basso, H.C., Castellano, E.E., Gallo, J.N.H., Martin, A.A. and Piro, O.E. (1987). *Phys. Rev. B* **36**, 5588.
223. Noel, H., Gougeon, P., Padiou, J., Levet, J.C., Potel, M., Laborde, O. and Monceau, P. (1987). *Sol. State Commun.* **63**, 915.
224. Yu, J.J., Massida, S., Freeman, A.J. and Koelling, D.D. (1987). *Phys. Lett. A* **122**, 203.
225. Mattheiss, L.F. and Hamann, D.R. (1987). *Sol. State Commun.* **63**, 395.
226. Xiao, G., Streitz, F.H., Gavrin, A., Du, Y.W. and Chien, C.L. (1987). *Phys. Rev. B* **35**, 8782.
227. Strobel, P., Paulsen, C. and Tholence, J.L. (1988). *Sol. State Commun.* **65**, 585.
228. Dharma-Wardana, M.W.C. (1987). *Phys. Lett. A* **126**, 205.
229. Mehbod, M., Wyder, P., Deltour, R., Duvigneaud, Ph. and Naessens, G. (1987). *Phys. Rev. B* **36**, 8819.
230. Tamaki, T., Komal, T., Ito, A., Maeno, Y. and Fujita, T. (1988). *Sol. State Commun.* **65**, 43.
231. Bauminger, E.R., Kowitt, M., Felner, I. and Nowik, I. (1988). *Sol. State Commun.* **65**, 123.
232. Zhou, X.Z., Raudsepp, M., Pankhurst, Q.A., Morrish, A.H., Luo, Y.L. and Maartense, I. (1987). *Phys. Rev. B* **36**, 7230.
233. Pankhurst, Q.A., Morrish, A.H. and Zhou, X.Z. (1988). *Phys. Lett. A* **127**, 231.
234. Pankhurst, Q.A., Morrish, A.H., Raudsepp, M. and Zhou, X.Z. (1988). *J. Phys. C* **21**, L7.
235. Kistenmacher, T.J., Bryden, W.A., Morgan, J.S., Moorjani, K., Du, Y.W., Qiu, Z.Q., Tang, H. and Walker, J.C. (1987). *Phys. Rev. B* **36**, 8877.
236. Siegrist, T., Schneemeyer, L.F., Waszczak, J.V., Singh, N.P., Opila, R.L., Batlogg, B., Rupp, L.W. and Murphy, D.W. (1987). *Phys. Rev. B* **36**, 8365.
237. Franck, J.P., Jung, J. and Mohamed, M.A.K. (1987). *Phys. Rev. B* **36**, 2308.
238. Nishi, Y., Moriya, S. and Tokunaga, A. (1987). *Phys. Lett. A* **126**, 55.
239. Tomy, C.V., Umarji, A.M., Adroja, D.Y., Malik, S.K., Prasad, R., Soni, N.C., Mohan, A. and Gupta, C.K. (1987). *Sol. State Commun.* **65**, 889.
240. Pan, K.K., Mathias, H., Rey, C.M., Moulton, W.G., Ng, H.K., Testardi, L.R. and Wang, Y.L. (1987). *Phys. Lett. A* **125**, 147.
241. Felner, I., Nowik, I. and Yeshurun, Y. (1987). *Phys. Rev. B* **36**, 3923.
242. Davies, P.K., Stuart, J.A., White, D., Lee, C., Chaikin, P.M., Naughton, M.J., Yu, R.C. and Ehrenkaufer, R.L. (1987). *Sol. State Commun.* **64**, 1441.
243. Meng, X.R., Ren, Y.R., Lin, M.Z., Tu, Q.Y., Lin, Z.J., Sang, L.H., Ding, W.Q., Fu, M.H., Meng, Q.Y., Li, C.J., Li, X.H., Qui, G.L. and Chen, M.Y. (1987). *Sol. State Commun,* **64**, 325.
244. Ovshinsky, S.R., Young, R.T., Allred, D.D., DeMaggio, G. and van der Leeden, G.A. (1987). *Phys. Rev. Lett.* **58**, 2579.
245. Bhargava, R.N., Herko, S.P. and Osborne, W.N. (1987). *Phys. Rev. Lett.* **59**, 1468.
246. Chen, J.T., Wenger, L.E., McEwan, C.L. and Logothetis, E.M. (1987). *Phys. Rev. Lett.* **58**, 1972.
247. Ayyub, P., Guptasarma, P., Rajarajan, A.K., Gupta, L.C., Vijayaraghavan, R. and Multani, M.S. (1987). *J. Phys. C* **20**, L673.
248. Erbil, A., Wright, A.C. and Boyd, E.P. (1988). *Phys. Rev. B* **37**, 555.

249. Maeda, H., Tanaka, Y., Fukutomi, M. and Asano, T. (1988). *Jap. J. Appl. Phys. Lett.* **27**, 2.
250. Liu, J.Z., Crabtree, G.W., Rehn, L.E., Geiser, U., Young, D.A., Kwok, W.K., Baldo, P.M., Williams, J.M. and Lam, D.J. (1988). *Phys. Lett. A* **127**, 444.
251. Kang, J.H., Kampwirth, R.T., Gray, K.E., Marsh, S. and Huff, E.A. (1988). *Phys. Lett. A* **128**, 102.
252. Chu, C.W., Bechtold, J., Gao, L., Hor, H.H., Huang, Z.J., Meng, R.L., Sun, Y.Y., Wang, Y.Q. and Xue, Y.Y. (1988). *Phys. Rev. Lett.* **60**, 941.
253. Hazen, R.M., Prewitt, C.T., Angel, R.J., Ross, N.L., Finger, L.W., Hadidiacos, C.G., Veblen, D.R., Heaney, P.J., Hor, P.H., Meng, R.L., Sun, Y.Y., Wang, Y.Q., Xue, Y.Y., Huang, Z.J., Gao, I., Bechtold, J. and Chu, C.W. (1988). *Phys. Rev. Lett.* **60**, 1174.
254. *Nature* **332**, 14 (1988).
255. *Nature* **332**, 305 (1988).
256. Michel, C., Hervieu, M., Borel, M.M., Grandlin, A., Deslandes, F., Provost, J. and Raveau, B. (1987). *Z. Phys. B* **68**, 421.
257. *Science News* **133**, 148 (1988).
258. Sheng, Z.Z. and Hermann, A.M. (1988). *Nature* **332**, 55.

บทคัดย่อ

การค้นพบสารตัวนำยิ่งยวดที่อุณหภูมิสูงชนิด "ใหม่" เมื่อไม่นานมานี้มีผลทำให้เกิดความไม่แน่ใจขึ้นในกลุ่มนักทดลองว่าสมควรพุ่งความสนใจไปที่คุณสมบัติหรือลักษณะใดของโครงสร้างของผลึกกันแน่ ดังนั้นเพื่อเป็นแนวทางแก่นักทดลองไทย ผู้ที่สนใจหรือผู้ที่เริ่มจะทำวิจัยในด้านนี้ จึงใคร่เสนอบทวิจารณ์ผลการทดลองที่รวบรวมจนถึงเดือนมีนาคม ค.ศ. 1988 ไว้ ณ ที่นี้