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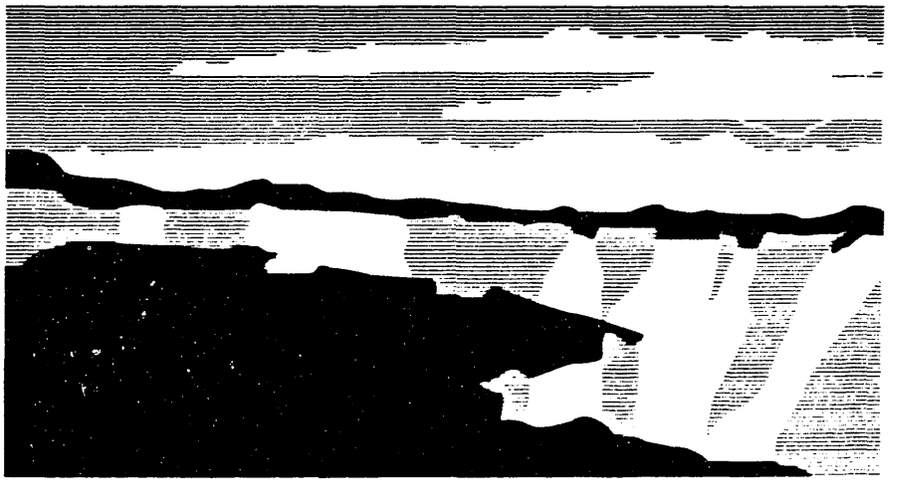

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Experimental Evidence for Lattice Effects in High Temperature Superconductors

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Abstract

We present an overview of the experimental evidence for a role of the lattice in the mechanism of high temperature superconductivity. It appears unlikely that a solely conventional electron-phonon interaction produces the pairing. However, there is ample evidence of strong electron and spin to lattice coupling and observations of a response of the lattice to the electronic state. We draw attention to the importance of the local structure in discussions of lattice effects in high-T_c superconductivity.

I. INTRODUCTION

In all materials the structure plays a critical role in determining physical properties and a detailed knowledge of the structure is a prerequisite to understanding these properties. Furthermore, in the case of conventional superconductivity structure plays an active role in the electronic pairing mechanism: an attractive electron-electron interaction is produced by an exchange of phonons. The pairing mechanism which gives rise to high temperature superconductivity still has not been established and this remains one of the primary goals of research in this field. The extraordinarily high T_c's suggest against a solely conventional electron-phonon mechanism for the pairing in these materials. However, since their discovery, a large number of experiments have been reported which indicate a response of

the lattice to the superconducting transition. It is important to establish to what extent these observations indicate a direct involvement of the lattice in the pairing mechanism and to what extent they are a benign response of the lattice to the change in the electronic ground state. We give an overview of a number of these observations.

Regardless of whether or not the lattice is involved in the pairing, it is very important to study the structure of these materials: accurate bond lengths are required for quantitative analysis using electronic structure calculations; correlations have been proposed between structural phase transitions and the disappearance of superconductivity; chemical substitutions have been shown to destroy superconductivity; and repeated observations have been made of structural distortions which appear to be generic in these structures. Before we can understand the importance of these effects it is necessary to characterize in detail all aspects of the structural phase transitions, local distortions and impurity-ion defects.

A number of factors should be taken into account when considering lattice effects in these materials. The first, obvious, fact is that the superconductivity derives from holes (or electrons) which are doped into the CuO_2 plane. T_c is a strong function of the carrier density in the planes. Thus, when evaluating correlations between the superconductivity and external factors, such as pressure or impurity concentration, it is important to separate the intrinsic response of the superconductivity to the perturbation from the "chemical" effect of variable doping.

Another important factor is less widely appreciated. The superconducting coherence length, ξ, in these materials is estimated to be of the order 10-80 Å in the plane and $\xi < 10$ Å perpendicular to the plane. Thus, it is the structure *on this short length scale* which is probed by the pairing interaction. The high-T_c materials are multi-component compounds with complicated crystal structures. The structures must accommodate the competing bonding demands of all the ions present. This cannot be accomplished perfectly and gives rise to bonding mismatches which are frequently relaxed by the introduction of defects, such as local structural distortions, cation or anion vacancies, oxygen interstitials

and long wavelength structural modulations. On the length scale pertinent to superconductivity, the atomic structure can deviate significantly from that described by the "crystal structure" which gives the average global structure. It is notoriously difficult to determine the structure directly on short length scales. A number of techniques show promise in this regard. Nuclear magnetic/quadrupole resonance (NMR/NQR), muon spin relaxation (μSR), Mössbauer spectroscopy, and x-ray absorption fine structure (XAFS) analysis are all being used to extract very short range structural information. The pair distribution function (PDF) analysis of diffraction data yields short range order up to ~ 20 Å and lattice imaging by transmission-electron microscopy reveals extended defects such as stacking faults. Results from these techniques should be considered as complementary to the more conventional and well-trusted crystallographic results. The crystal structures provide the basis for understanding the structures. However, a detailed knowledge of actual bond lengths and symmetry of the structure on the length scale of the superconducting coherence length requires additional information from local structural techniques. Given the complexity of these materials, defects and local structural distortions are the norm rather than the exception. We also note that these distortions might be expected to couple strongly to the electrons since, in highly ionic materials such as high-T_c superconductors, they introduce electric field gradients into the sample.

This paper is intended as an overview of the experimental evidence for lattice effects in high-T_c superconductors. It does not contain a comprehensive review of all work in this area and we apologize to authors whose work is omitted. In Section II we discuss phonon-mediated electron pairing and the predictions for lattice effects of conventional strong coupling theory. These are compared to measurements of these parameters in high-T_c materials. Section III contains experimental evidence for deviations of the short length scale structure from the average structure. In Section IV we review evidence of structural effects observed at T_c and discuss the implications of these observations. Recently, great interest has been expressed in the correlation between structural phase transitions and superconductivity in $La_{2-x}A_xCuO_4$ (A=Ba,Sr,Ca) (La214) materials. In Section V we focus on

this issue, drawing attention to our own recent results on the local structure. These show that our understanding of the microscopic mechanism for these transitions is inadequate. One implication of this is that, at least in the Ba-doped compound, a structural coherence length exists which is similar in magnitude to the superconducting coherence length, electronic mean-free-path and antiferromagnetic spin-fluctuation correlation length.

II. LATTICE EFFECTS FROM STRONG ELECTRON-PHONON COUPLING

Our historical view of phonon-mediated superconductivity has encouraged the belief that to raise T_c we should increase the electron-phonon coupling reflected in the parameter $\lambda = N(0)\langle I^2\rangle/M\langle\omega^2\rangle$, where $N(0)$ is the electronic state density at the Fermi energy, $\langle I^2\rangle$ is the Fermi-surface average of the electron-phonon matrix element, M is the ionic mass and $\langle\omega^2\rangle^{\frac{1}{2}}$ reflects some characteristic phonon energy of the system. McMillan's [1] early model of electron-phonon coupling gave a maximum T_c for $\lambda \approx 2$. Although this subsequently was shown [2] to be a spurious limit, the gain in T_c with increasing λ and prospects for raising T_c much above 30 K by the conventional mechanism were doubtful. Of course, the discovery of high temperature superconductivity in the cuprates, with bona fide T_c's near 150 K [3], has questioned whether electron-phonon coupling by itself can account for the very high T_c's.

Because of various experimental difficulties, no definitive values of λ for the cuprates have been established; however, it appears from several different types of experiments, e.g. optical and photoemission spectroscopy, neutron scattering, specific heat, etc. that electron-phonon coupling in cuprates is at least modestly strong, with values of λ roughly ranging between 1 and 3 [4]. Frozen phonon calculations [5] for $La_{1.85}Sr_{0.15}CuO_4$ find an average value for $\lambda = 1.37$, which from the Allen-Dynes [2] relation gives $T_c = 39$ K, a value close to that actually measured. The largest contribution to this average λ comes from the Γ-point axial oxygen breathing mode which has $\lambda = 11.7$. In a similar vein, Zeyher and Zwicknagl [6] have calculated the shift in Raman-active phonon lines [7] in

$YBa_2Cu_3O_7$ (Y123) caused by the appearance of superconductivity. They find reasonably good agreement with experiment if they take $\lambda = 2.9$. Cardona [8] has discussed similar observations in some detail. In particular, he notes that analysis of phonon-frequency shifts and changes in linewidths upon cooling $REBa_2Cu_3O_7$ (RE = rare earth) below T_c leads to an estimate of $\lambda = 0.8$ if all phonons couple as B_{1g} modes. However, as Cardona has emphasized, these $q = 0$ phonon effects depend strongly on sample quality, i.e. oxygen stoichiometry, purity, etc., and, therefore, one must be cautious in drawing conclusions about the strength of electron-phonon coupling.

Experimental evidence for (strong) electron-phonon coupling to $q \neq 0$ modes comes from inelastic neutron scattering in $Bi_2Sr_2CaCu_2O_8$ (Bi2212) [9]. Figure 1 gives plots of two high-energy oxygen-phonon linewidths as a function of temperature. Below $T_c \approx 80$ K, the linewidths increase substantially, between 1.5 and 2%. Such broadening is expected because phonons having an energy greater than the superconducting gap energy Δ break Cooper pairs and, therefore, have additional decay channels. In contrast, the phonon mode at 5 meV has a linewidth that may decrease upon cooling below T_c, which is expected if the energy of this mode is less than the gap frequency since in this case decay channels are removed by the opening of the gap. As with $q = 0$ phonons, changes in $q > 0$ phonon linewidth due to superconductivity are, in general, expected to be very small [6]; therefore, the large increases found in the high energy phonon linewidths of Bi2212 imply strong electron-phonon coupling for these modes. A further aspect of the data in Fig. 1 is the rapid decrease in linewidth above T_c in the high energy modes. Such a strong decrease is consistent [9] with anharmonicity that also appears to be related to superconductivity, as evidenced by the abrupt arrest of linewidth narrowing upon approaching T_c.

A softer lattice, inferred from the measured phonon density-of-states, has been associated with higher-T_c's in $(Y, Pr)Ba_2(Cu, Zn)_3O_{6+\delta}$, $Bi_2Sr_2(Ca, Y)Cu_2O_8$ [10] and $La_{1.85}Sr_{0.15}(Cu, Zn)O_4$ [11]. This is similar to observations made in conventional superconductors and might suggest the importance of electron-phonon coupling for superconductivity. However, it is difficult quantitatively to explain this T_c enhancement with a

conventional electron-phonon interaction. Nonetheless, these multiple observations of a correlation between lattice softening and T_c in the high-T_c materials are evidence of a strong electron-lattice interaction, possibly associated with local modes, and should not be dismissed necessarily as coincidental.

Of course, the hallmark of electron-phonon coupling within BCS theory is the existence of an isotope effect, i.e. $T_c \propto M^{-\alpha}$. For harmonic phonons, mean-field theory gives $\alpha = 0.5$. A summary of α-values for several different cuprate superconductors is shown in Fig. 2 [12]. There are two observations to note here. One is that in the single-cuprate-layer series α actually exceeds the BCS value. The second is that the maximum T_c within a given series is associated with the smallest, or nearly so, value of α, which is less than 0.1. If electron-phonon coupling plays a role in superconductivity, as suggested by the optical and neutron scattering results discussed above, then the small α for optimal T_c may arise if anharmonic phonons dominate in this coupling.

Not shown in Fig. 2 are the results of a systematic study of α vs. x in the $La_{2-x}Ba_xCuO_4$ system [13]. In this case, α follows quantitatively the systematics of the $La_{2-x}Sr_xCuO_4$ series. In both cases, α is a maximum for $x = 0.12$ and drops rapidly to a small value for $x = 0.15$, where T_c is a maximum. Structural studies of $La_{2-x}Ba_xCuO_4$ [14] find a low-temperature orthorhombic (LTO) to low-temperature tetragonal (LTT) transition that occurs over a range of x near $x = 0.12$, implying a connection between the very large value of α and phonons involved in the LTO-LTT transition. It is also at this composition where T_c is depressed to near zero in the Ba-doped system and exhibits a dip in the otherwise smooth variation of $T_c(x)$ in Sr-doped La214. This has led to the speculation that the LTT phase does not support superconductivity and that the Sr-doped material is close to an LTO-LTT transition near $x = 0.12$. However, as will be discussed more fully in Sec. V, close inspection of the local structure of Ba-doped La214 shows that the LTT does support bulk superconductivity and that, instead of the structural change, it is the appearance of an electronic transition that is responsible for depressing T_c.

III. LOCAL DEVIATIONS FROM LONG RANGE STRUCTURE

Significant structural distortions are widespread in HTS materials, in part because of the presence of defects such as substitutional "dopant" ions and oxygen vacancies. Lattice mismatches, which give rise to distortions, also exist between the CuO_2 and the intergrowth charge reservoir layers. For example, buckling of the CuO_2 plane in La214 is generally thought to originate from a compressive stress that the La_2O_2 layer places on the CuO_2 layer at low temperature [15]. Thus, distortions are expected due to the relaxation of the lattice to accommodate steric incompatibilities in the structure. However, there is mounting evidence that structural distortions exist in these materials which are *intrinsic* and which cannot be explained by simple static lattice relaxations.

Typical of crystal-structure refinements in these materials are the presence of rather large, often quite anisotropic, and weakly temperature-dependent thermal factors [e.g. see?] [16]. This is generally an indication that static (or quasi-static, meaning much slower than typical phonon frequencies) displacive disorder exists in the material. Large thermal factors are characteristically found on oxygen sites suggesting, for example, inhomogeneous lateral buckling of the chains in Y123 and of the planes in the HTS materials in general.

As we mentioned, extrinsic disorder is expected due to substitutional defects. However, a recent careful crystallographic study [17] of $La_{2-x}Sr_xCuO_4$ as a function of doping indicated that the large thermal factors on apical and in-plane oxygen sites do not increase significantly over the entire doping range from $x = 0$ to $x = 0.375$, indicating that the underlying disorder is dominated by *intrinsic* inhomogeneous atom displacements. Our own PDF studies also indicate that the local structure, even in undoped $La_2CuO_{4.00}$, is significantly distorted from the average crystal structure [18].

The PDF also indicates similar effects in other systems. The lattice mismatch in $Tl_2Ba_2CaCu_2O_8$ (Tl2212) produces large displacements of Tl and O in the Tl_2O_2 layers which are not ordered over long range. These were seen in the PDF to be locally ordered [19]. This result has been confirmed by other techniques [20]. However, in this material,

significant inhomogeneous buckling of the CuO_2 plane (including apical oxygen ions) also was observed in the PDF with no obvious steric origin. Furthermore, this buckling appears to be sensitive to the electronic state as we mention later (Section IV).

In a similar vein, plane buckling has been seen [21] in $Nd_{2-x}Ce_xCuO_4$ (Nd214) which, again, is too extensive to be a lattice relaxation around the Ce ions. This, and related RE_2CuO_4 materials which assume the T' structure, present a special case since atomic mismatch arguments indicate that the CuO_2 plane is in *tension* in these materials and, therefore, is expected to be flat and undistorted. However, there is compelling evidence that this is not the case. Weak ferromagnetism is observed in Gd_2CuO_4 which is forbidden by the symmetry of the T' crystal structure [22]. Group theoretical arguments indicate a finite number of allowed local structural distortions which could give rise to the observed magnetic behavior [23]. Further evidence for local distortions in this material comes from ^{155}Gd Mössbauer measurements. A large asymmetry parameter is observed which is a clear indication that the local symmetry at the Gd sites is orthorhombic (or lower), rather than the tetragonal symmetry of the average structure [24]. However, this is qualitatively consistent with the group-theoretical predictions and also the PDF observations in the (Nd,Ce)214 compound. These results also are consistent with the observation of phonon modes in Raman spectroscopy which are disallowed by the average crystallographic symmetry but which could be explained if the center of symmetry is destroyed by local distortions [25]. In these cases there is no doubt that the average crystal structure is missing some of the important physics which can be explained by locally correlated but inhomogeneous atom displacements. Again, we point out that, in these materials, the CuO_2 plane is in tension and distortions are not expected from lattice mismatch considerations.

Like the Nd214 system [25], the crystallographic structure of superconducting $La_{2-x}Sr_xCuO_4$ in either HTT or LTO phases also has inversion symmetry and, therefore, Raman activity and IR activity are again mutually exclusive. Using polarized Raman spectroscopy, Sugai [26] found Raman active modes at 145, 282, 367 and 670 cm^{-1} only for superconducting samples with $x = 0.12$ and 0.20 (but with T_c's of only 10 K), which

are not seen in nonsuperconducting samples with $x = 0$ and 0.34. The modes at 145, 367 and 670 cm^{-1} coincide with infrared-active transverse optical modes which have polarization vectors parallel to the CuO_2 plane. This clearly indicates that inversion symmetry is lost on a local scale, contrary to the predictions from the crystallographic structure. Further, the Raman spectra for the $x = 0.34$ sample show local orthorhombic symmetry despite the sample having the crystallographically tetragonal HTT structure.

Further evidence for deviations of the local structure from the crystallographic structure has been found by Hammel *et al.* [27] from Cu nuclear quadrupole resonance (NQR) measurements on a single crystal of superoxygenated $La_2CuO_{4+\delta}$ with $\delta = 0.03$. This material phase separates into a nearly stoichiometric antiferromagnetic phase ($\delta \approx 0.01$ and an oxygen-rich metallic superconducting phase ($\delta \approx 0.06$) at T = 265 K. Peaks in the Cu NQR spectrum of the superconducting phase indicate at least two distinct copper environments in contrast to the single site expected from crystallography. Further, for equivalent hole doping levels, the NQR frequency of these peaks agrees (to within 2%) with similar peaks observed in *strontium* doped $La_{2-x}Sr_xCuO_4$, although this material also should have only a single copper site. Therefore, this effect is independent of the type of dopant (interstitial O vs. substitutional Sr) and indicates a change in local structure that results from the crystal response to the presence of doped holes [27].

A number of x-ray absorption fine structure (XAFS) experiments have shown deviations in the local structure as well, but for the more complex cuprates. Data from polarized Cu K-edge XAFS measurements on aligned Y123 powder show temperature dependent beat pattern near $k = 12$ $Å^{-1}$ [28]. The presence of the beat in the XAFS indicates a double peak in the Cu – O(4) axial bond distance distribution. This could indicate the presence of a double-well structure in the crystal potential [?]; however, it is also possible that the two bond lengths are associated with distinct sites in the structure. The existence of the double-peak feature has been confirmed by Stern et al. [29,30]. These authors studied samples prepared in different ways with a range of oxygen content, T_c and grain size [30]. They question the importance of the double-peak feature for superconductivity

since the separation of the peaks does not correlate with T_c, since the double-peak feature is least pronounced in their highest T_c materials and since no temperature dependence of this feature is seen near T_c in any of their samples.

Bianconi *et al.* [31] have determined the XAFS at a number of temperatures for Bi2212 and also find two-site behavior for the axial oxygens. However, this behavior could result from either axial oxygen instabilities resulting from a double well or from an inhomogeneous distribution of Cu sites, which results in both short and long Cu-O distances. They find that the latter interpretation agrees with the crystallographic structures where the Cu-O distances are modulated over 4.75 or 5 crystalline unit cells with a period of 26-27 Å.

However, not all axial oxygen systems show two-site behavior. Yamaguchi *et al.* [32] have measured XAFS from $Tl_2Ba_2CuO_6$ (Tl2201) which has only a single CuO_2 layer. In this case, the Cu XAFS shows that there is a substantial change with temperature at a radial distance of $\sim$ 1.5Å, which corresponds roughly to the in-plane Cu-O bond length. The radial distribution function shows that there are two closely spaced in-plane Cu-O bonds, which coalesce as T_c is approached. The existence of two such in-plane oxygen positions is expected if there is a local static or dynamic orthorhombic distortion of the O atoms away from tetragonal symmetry. No detectable changes with temperature were observed for the axial oxygens in the CuO_6 octahedra or for the in-plane Cu-O bonds when the Tl2201 is not superconducting.

Several diffraction studies of Y123 have attempted searches for postulated split axial oxygen sites near T_c. Possible site disorder or anharmonic motion cannot be distinguished in diffraction experiments, but the existence of either should lead to elongated electron/nuclear density Fourier maps or to anisotropic thermal parameters. An earlier study using neutron-powder diffraction did not show any anomalies around T_c [33]. The nuclear density for the axial oxygen along the c-axis had the same widths as those for the Cu atoms and its thermal parameters appeared to be nearly isotropic. Recently, a room-temperature single-crystal x-ray diffraction study was used to map the electron density

along the c-axis of a $YBa_2Cu_3O_{6.9}$ crystal [34]. Again, the electron density for the axial oxygen was found to be nearly spherical. At present, it is difficult to reconcile the results from XAFS and diffraction and further experiments are required to resolve this issue.

In summary, there is extensive evidence that the local structure deviates from the average long-range structure in a wide variety (and probably all) the high-T_c superconductors. These deviations are apparently dominated by disorder which is intrinsic to the structure and not simply a relaxation of the lattice around defects. These intrinsic atom displacements involve CuO_2 plane ions; they are inhomogeneous but appear to be locally correlated. There is evidence that they are sensitive to the electronic state and a number of authors have speculated that they have an electronic origin [21,27,35].

IV. STRUCTURAL RESPONSES SEEN AT T_c

An unprecedented amount of effort has been devoted to studying the cuprate superconductors using a battery of techniques and a rather confusing picture emerges. Although there is ample evidence that the structure *is* sensitive to the electronic state, there is no obvious way to interpret all the various results using established theoretical approaches. Often the observed effects are small and techniques are close to the limits of their detection capabilities. In order to draw concrete conclusions from the observations, a more systematic picture needs to emerge from the experiments. For example, comparisons need to be made of lattice effects between different systems of compounds and a consensus reached on why some techniques see what looks like lattice softening while other observations are interpreted as the lattice hardening at T_c. In light of this confusion, we keep our discussion of the results to a minimum.

Clear evidence for coupling of a lattice instability to the electronic system has come from elastic constant measurements on single crystal $La_{1.86}Sr_{0.14}CuO_4$ by Nohara *et al.* [36] using a high-resolution ultrasound technique. The evolution of the $C_{11} - C_{12}$ mode with temperature is shown in Fig. 3. This mode corresponds to an in-plane shear which

is the same as that responsible for the HTT to LTO orthorhombic distortion ($C_{11} - C_{12}$ corresponds to C_{66} in the high temperature tetragonal space group). The temperature range shown in the figure is far from this structural transition which occurred at 210 K in this sample. The mode initially hardens with decreasing temperature due to thermal contraction of the sample. At $\sim$ 50 K it softens, indicating the approach to a structural instability; however, the instability is quenched by the appearance of superconductivity. The correlation of this quenching with T_c was demonstrated by applying magnetic fields. With H parallel to the *c*-axis T_c is shifted to lower temperature and the lattice hardening follows as can be seen in Fig. 3(c). None of the other modes that were studied showed this anomalous softening and hardening. This is a very clear demonstration of the lattice coupling to the superconductivity. It draws to mind very similar observations in the A-15 class of compounds [37]. Testardi and Bateman showed that in V_3Si the softening of a shear mode, which ultimately leads to a martensitic transformation, is arrested by the appearance of superconductivity. Similar behavior also was found in Nb_3Sn and ultimately in all of the A-15's which had high-T_c's, whereas similar behavior was not observed in the low-T_c A-15's [37]. This led to the belief that phonon softening associated with the instability was instrumental to T_c enhancement. It is interesting, however, that a lattice softening strong enough to produce a structural transition in these materials enhances T_c to a whopping 17 K. The observation of this behavior in $La_{1.86}Sr_{0.14}CuO_4$ apparently cannot explain the high T_c of this material. Indeed, Lang *et al.* [38], based on careful thermal expansion measurements, claim that a lattice instability is limiting T_c to below 36 K in all the La214 materials. Nonetheless, the ultrasound results provide a nice demonstration of a strong electron-lattice coupling in these materials.

A further piece of evidence that a lattice instability is coupling to superconductivity may be suggested by the inelastic neutron scattering results of Arai *et al.* [39]. Using the time-of-flight method, these authors see a change in the phonon density-of-states above and below T_c in fully oxygenated Y123. The change is small but is larger than the experimental errors and was reproduced in two runs carried out with different incident neutron

energies, as shown in Fig. 4. From an analysis of the Q-dependence (Q is the momentum transfer), the authors interpret the changes as coming from short range vibrations whose dynamical correlation length diverges right at T_c. The importance of this interpretation is that it appears to be a *local* mode which couples strongly to the electrons, presumably associated with the local lattice distortions which have already been discussed. Localized lattice distortions allow for the possibility that a very strong and nonlinear electron-lattice coupling can exist without inducing a macroscopic phase transition. We wish, merely, to point out that local lattice distortions might be expected to couple strongly to the electrons in a rather complicated way.

Most observations of a lattice response at T_c have been associated with the local structure. Changes in the local structure at T_c have been reported from PDF analysis of neutron diffraction data from Tl2212 [40] and Nd214 [41]. Data from Tl2212 are shown in Fig. 5. The peak height (minus the adjacent valley) of the 3.4 Å peak is plotted as a function of temperature and indicates a fluctuation right at T_c. The solid line shows the expected dependence of the peak-height parameter due to thermal motion. From their analysis, the authors inferred that the effect was dynamical in origin and involved a change in the degree of correlation (static or dynamic) of in-plane and apical oxygen ions associated with approximately half the copper sites.

The ion-channeling results of Sharma *et al.* [42] can be interpreted in a similar way, though they were observed in the Y/Er123 system where no fluctuations have been reported at T_c in PDF measurements. The FWHM of the channeling angle (measured with respect to the c-axis) is plotted in Fig. 6. A discontinuous jump is observed at T_c in the data which include the Cu signal but is not seen when the data are gated to exclude the Cu signal. This suggests that displacements (either static or dynamic) of Cu ions perpendicular to the c-axis are getting smaller, or more highly correlated, or both. This result is in qualitative agreement with those from PDF; although, in the latter case the observed atom displacements are predominantly of oxygen rather than copper ions and parallel, rather than perpendicular, to the c-axis. Unfortunately, the signal from oxygen

could not be reliably measured in the ion-channeling experiment. It is interesting to note that the chain-copper ions have much more structural freedom in directions perpendicular to the c-axis than do the plane ions. We might speculate that the largest component of the structural response at T_c is coming from the chains. Attempts to find changes in the channeling behaviour of Bi2212 at T_c failed [43] and it is difficult to establish the broader importance of this result to the cuprates in general.

Both the PDF and ion-channeling results suggest a change in dynamics at T_c. This should not be interpreted necessarily as renormalization of conventional phonons (although these are observed, see Section II) since we know that significant local structural distortions exist. The lattice response at T_c may originate from localized modes associated with these regions. One technique that measures the total dynamic response of ions in the lattice, including localized and extended phonons, is neutron resonance absorption spectroscopy (NRAS). In this technique, the Doppler broadening of resonant absorption peaks gives the total kinetic energy $\langle E \rangle$ associated with a particular ion. By studying aligned samples it is also possible to extract directional information. The kinetic energy of Cu in a sample of Bi2212 is shown in Fig. 7 as the open circles [44]. In (a) the c-axis vibrations are shown and in (b) vibrations parallel to the CuO_2 plane. In each case the expected temperature dependence of based on a shell-model calculation of copper vibrations in La_2CuO_4. The c-axis Cu vibrations in Bi2212 follow this curve very nicely; however, there is a distinct and large (20%) softening of the in-plane vibrations at T_c. The experimental uncertainty in $\langle E \rangle$ is ~ 5 K and so this softening corresponds to 6σ.

The observations of lattice effects at T_c are widespread and give powerful evidence that a strong electron-lattice interaction exists in these materials. However, details of the results give an unsatisfactory and confusing picture. There is no compelling evidence of systematic behavior from system to system which might indicate that the lattice is involved in the pairing mechanism in some simple way.

The greatest consensus seems to be that *local*, rather than global, lattice parameters are most sensitive to the electronic state. This is not surprising on two counts. First,

as we have already pointed out, local lattice distortions in these materials are expected and widely observed. A strong electron-lattice interaction should have a large effect on such distortions. Also, there is speculation [21,27,35] that the distortions themselves may be stabilized by the electronic system in which case they should be very sensitive to the electronic state. Second, the superconductivity will couple most strongly to the lattice on length-scales comparable to the superconducting coherence length ξ which is ($\sim 10 - 80$ Å) and so the largest effects should be seen in the local structure.

There is certainly no conclusive evidence that the lattice is involved directly in the pairing mechanism. However, the lattice *is* strongly coupled to the electronic and magnetic systems and this should be taken into account in theories for superconductivity. The local structure is quite inhomogeneous and it is the local structural parameters that are coupling most strongly to the superconducting transition. This fact may contribute to the confusing results because there is no established theoretical framework for understanding these phenomena. However, a more systematic picture from the experimental results is probably required before a big advance in understanding is possible.

V. PHASE TRANSITIONS AND SUPERCONDUCTIVITY

Much attention has been focussed recently on determining whether superconductivity is lost when a doped La214 sample transforms *out* of the low temperature orthorhombic phase (LTO, space group *Abma*) into nearby tetragonal phases. Such an observation would give valuable information about the conditions required to support superconductivity. However, close examination indicates it not to be the case: the tetragonal phases of this material exhibit bulk superconductivity. Nonetheless, our experimental effort has brought to light new information about the *local* structure which has important implications for understanding the properties. In addition, it raises again the important question of exactly which variables *do* destroy the superconductivity in this system.

The structural phase diagram for the Ba-doped material is shown in Fig. 8. At high

temperature and/or high Ba concentration, the sample is in the high temperature tetragonal (HTT, space group $I4/mmm$) phase [45] and the CuO_2 planes are crystallographically flat. On cooling, it undergoes a second order transition into the LTO phase [46]. Finally, over a restricted composition range the sample undergoes a further transition to the low temperature tetragonal (LTT, space group $P4_2/ncm$) phase [14,47]. These transitions have been understood [48] as arising primarily from rigid tilts of the CuO_6 octahedra accompanied by small strains which distort the octahedra. In the LTO phase the octahedra tilt about [010] axes, referred to the *Abma* space group. At the LTO-LTT transition the average octahedral tilts reorient through 45°, the tilt axes now being about [110] directions.

In this section we discuss how these phase transitions couple to the electronic system. Mounting evidence indicates that the electronic transitions observed in these materials, which destroy superconductivity, are not a result of the structural transitions.

A. LTT phase

As shown in Fig. 9, in the Ba-doped La214 material at a hole doping concentration, p, of exactly $p = \frac{1}{8}$ ($x = 0.125$) superconductivity is suppressed [49]; whereas, at compositions on either side of this magic fraction, samples show almost optimal bulk superconductivity with T_c's of $\sim$ 27 K (Fig. 9). This observation has been correlated with the appearance of the LTT phase which occurs in the same region of the phase diagram [47,14]. The LTO-LTT transition is first order and samples do not transform fully into the LTT phase. Axe *et al.* [14] postulated that the LTT phase is not superconducting. In this picture, at compositions on either side of $x = 0.125$, the superconductivity comes from residual LTO material; whereas, at exactly $x = 0.125$ the sample fully transforms and superconductivity is annihilated. Further credibility was lent to this view by measurements of the normal state properties [47,50]. An *electronic* transition was evident in $x = 0.125$ samples at a temperature of $\sim$ 60 K, very close to the LTO-LTT structural transition temperature: thermopower changes from positive to negative, resistivity shows an abrupt upturn and

Hall resistance a sharp drop at this temperature. Much theoretical effort has been applied to explain why the LTT structure does not superconduct whereas the LTO structure does [51–55]; indeed some theories postulate that the LTT structure itself is stabilized by the electronic transition [51]. However, subsequent experiments show [56,57] beyond doubt that the *electronic* and *structural* transitions are not uniquely coupled. First, it was demonstrated in closely related doubly doped materials that the LTT structure does support superconductivity [56,58]. In these materials the average dopant ion size (which controls the structural phase transitions [58]) can be varied independently of the hole concentration (which controls the electronic transition [59]) by controlled doping of, for example, strontium *and* neodymium instead of Sr or Ba alone. Superconductivity is observed in the LTT phase in these materials [56,58]. Furthermore, in pure $La_{2-x}Ba_xCuO_4$ it also has been shown recently that the LTT phase can superconduct perfectly well. This has been demonstrated quantitatively by comparing the phase composition of a bulk superconducting sample with $x = 0.15$ with that of a non-superconducting $x = 0.125$ sample. The phase composition was determined by curve fitting to high-resolution x-ray diffraction data collected at a synchrotron source, shown in Figs. 10(a) and (b). Within the errors of the measurement both samples are 95% transformed into the LTT phase at low temperature although the samples had very different superconducting properties [57] [Fig. 10(c) and (d)]. The LTT structure supports bulk superconductivity with a T_c of 27 K in this system. Finally, in recent careful work by Nagano *et al.* [60], a sharp superconducting anomaly was induced in Sr-doped samples with $p = \frac{1}{8}$. A structural transition to the LTT phase has not been seen in this system suggesting that the electronic transition can occur in the LTO phase.

These experimental results together indicate that the structural and electronic transitions are not coupled directly. This new understanding is placed in a new light by our studies of the local structure of LBCO which are described below. The superconducting anomaly at $p = \frac{1}{8}$ in the La214 materials still begs for a satisfactory explanation. It is interesting that μSR measurements indicate that the Cu spins develop static (on a mi-

crosecond time scale) antiferromagnetic order at low temperature at this hole concentration [61], though no evidence of this has been seen in neutron diffraction experiments.

The local structure of the LTO and LTT phases has been studied using PDF analysis of neutron powder diffraction data. This technique utilizes data over a very wide range of momentum transfers (approximately twice the range used in a crystallographic analysis) as well as diffuse scattering intensity. These extra data contain information predominantly about short-range order in the material. The intention was to study the change in local structure at the LTO-LTT transition. Two Ba-doped samples were studied with $x = 0.125$ and $x = 0.15$. These were the same samples used in the synchrotron x-ray experiment to establish phase composition which was described above. Part of the x-ray diffraction patterns from the $x = 0.125$ sample at 80 K and 10 K can be seen in the Fig. 10(a). The phase transition is very clear in the diffraction data.

In the average crystal-structure model, the tilt axes of the CuO_6 octahedra are rotated through 45° at this LTO-LTT transition. This results in a significant rearrangement of atoms within the unit cell, especially of the out-of-plane O2 ion, and should be clearly visible in the PDF. This is illustrated in the upper panels (a-c) of Fig. 11 [18] where PDFs *calculated from the crystal structure models* of the LTO and LTT structures are compared to each other. The difference curves in Figs. 11(a-c) indicate that large changes are expected for certain PDF peaks. For example, the peak at 0.26 nm, which originates from a La-O2 near-neighbor pair correlation, is very sensitive to the local tilt orientation. The data are shown in the lower panels [Fig. 11(d-f)]. It is clear that the changes predicted by the crystal structure model do not occur. In particular, there is no change, within the errors, to the indicator peak at 0.26 nm, although the crystal-structure models predict changes to this peak many times the experimental errors. It is clear that *the octahedra do not change their local tilt direction at this transition.*

Small changes are observed to certain peaks at higher r values, as can be demonstrated by considering the variation of peak heights through the LTO-LTT transition [18]. This suggests that a change in the intermediate range pattern of tilt ordering occurs at this

transition. In any case, the PDF demonstrates dramatically that, on the length scale of the superconducting coherence length, changes to the structure at this transition are very small.

The fact that the direction of local tilting does not change at this transition implies that the crystal-structure models do not describe correctly the direction of local tilting in one of the two phases. We have modelled the local tilts by refining structure models to the PDFs using a least squares regression code. The fully converged refinements are shown in Fig. 12. The data are from the $x = 0.125$ sample measured at 80 K (LTO phase). In the low-r region, the LTT model fits best, indicating that, even in the LTO phase, the tilts are in the [110] (LTT) directions. However, the best fit to the intermediate range data come from a model in which two local LTT variants, rotated by 90° with respect to each other, are superposed. This model retains the local LTT tilt directions, consistent with the PDF results, but recovers the LTO tilt pattern *on the average*, thus reconciling the observed average crystal structure. This model is not unique, but in unbiased refinements it gives the best agreement for PDFs from samples in the LTO phase. The model also predicts the LTO-HTT phase transition as being a continuous disordering of correlated tilts. Details will be published elsewhere [18].

This result indicates that, in the LTO phase, a structural correlation length exists which is of the order of the superconducting coherence, the electronic mean-free-path and antiferromagnetic correlation lengths. The local tilts are always in the LTT directions in this material. Below the structural coherence length the tilts are ordered in the LTT sense. However, the locally ordered domains are interleaved with domains whose tilts are rotated by 90°. The tilt magnitudes and directions obtained from crystal structure analysis are the *average* values only.

It is known that spins couple to the octahedral tilts [54]. Therefore, it is interesting that a highly inhomogeneous background of octahedral tilts is observed in these materials. This will tend to frustrate spin ordering. It is also likely that the tilts fluctuate significantly, even at low temperature, since the transverse tilt mode (the mode which rocks the tilts

from one tilt variant to the other) is very low in energy ($\sim$ 45 K) [62]. Thus, spins which are pinned to local tilts will fluctuate in direction as the local tilts fluctuate. At very low temperature these tilt fluctuations will gradually freeze out. If the structure transforms to the LTT phase, the tilt domains line up and presumably spins can order over longer range, as is suggested by μSR measurements. When the structure remains in the LTO phase at low temperature, a frozen "tilt glass" will result. Long range spin ordering will be frustrated and a spin-glass state might result with frozen disordered spins. In this case, the inhomogeneous potential seen by the spins comes from the spin-lattice coupling which must dominate over the exchange interaction that is attempting to line up the spins over longer range. It is known that the exchange interaction falls off quickly with increasing hole doping in these materials [63].

These PDF results suggest that we may have to modify the way we understand the structures and transitions in the La214 materials. Resonant ultrasound measurements [64,65] at the HTT-LTO transition also indicate that the canonical soft-mode picture [48] may not give the complete picture. However, much more work is required to establish the generality and wider importance of these results.

B. HTT phase

A number of observations have been reported which suggest that the *high temperature* phase transition in the La214 systems also couples to the carriers. There has been speculation about whether superconductivity occurs in the HTT phase or not since the superconducting and structural phase boundaries seem to coincide at high doping (compare Figs. 8 and 9 in the region $x \sim 0.2$). The existence of superconductivity is well established in the LTO phase. Some superconductivity also can be seen beyond the phase boundary on the HTT side; however, less than 100% superconducting fractions typically are reported and low T_c's are observed. Does the superconducting phase boundary fall to T = 0 as a natural consequence of overdoping as is generally observed in the HTSC

materials? In this case the coincidence of the structural and electronic phase boundaries is pure chance. On the other hand, does the transition into the HTT phase destroy superconductivity in a sample which, otherwise, would be a perfectly good superconductor? This view might be supported by the observation from NMR of a spin pseudo-gap, considered to be characteristic of an "underdoped" HTS material [66], even in the highly doped La214 materials, which suggests that these materials are not overdoped, yet T_c is falling to zero. These observations would be reconciled if the suppression of T_c were caused by the structural transition. Takagi *et al.* [67] gave support to this view by studying samples which they demonstrated were macroscopically homogeneous and which were annealed at high temperature in oxygen for 1 month. Superconductivity *was* found above the LTO-HTT transition but the authors claimed that in their well-annealed samples the superconducting fraction (as measured from the Meissner signal in a 10 Oe field) was significantly lower in the HTT phase than in the LTO phase, as can be seen in Fig. 13. The residual superconductivity in the HTT phase samples could be explained, even after these long anneals, if the samples were not fully homogenized. In principle, an ideal anneal, which would be impractically long, would homogenize the samples completely and no superconductivity would be seen in the HTT phase. However, this result has been questioned and evidence now exists that demonstrates bulk superconductivity in the HTT phase. The most convincing work is by Nagano *et al.* [60]. These authors prepared samples using a spray-dry technique which produces an intimate mixture of reagents on a microscopic scale. These samples were reacted and also given a post-anneal to enhance homogeneity. Careful susceptibility measurements were carried out in extremely low fields (0.2 Oe). These authors demonstrated a full shielding fraction (> 100%) for all samples up to $x = 0.25$, well beyond the LTO-HTT transition. Fig. 14(a) superposes the T_c and structural phase boundaries obtained from their measurements. In Fig. 14(b) and (c) the shielding and Meissner curves are shown to demonstrate that a full superconducting fraction is observed in the HTT samples as well as the LTO samples. Other corroborating evidence that the structural and superconducting transitions appear together by chance

in LSCO is provided by double doping experiments similar to those mentioned previously. By introducing Pr into Sr doped La214 samples, Schäfer *et al.* [68] were able to shift the structural phase boundary to higher Sr concentrations. However, the superconducting boundary fell to T = 0 at the same Sr (and therefore hole) doping level as in the material with no Pr. The superconducting transition temperature is a function of hole concentration and independent of the structural phase transition.

We note here that a correlation has been reported between a feature in the normal state *c*-axis resistivity in Sr-doped La214 single crystals and the HTT-LTO transition [69,70]. As can be seen in Fig. 15, a distinct upturn in ρ_c is seen at a temperature which seems to correlate with the HTT-LTO transition temperature. No such effect is seen in the in-plane resistivity. We point out that, in light of the aforementioned results where electronic effects were prematurely correlated with structural transitions, this correlation has not been established beyond doubt in the present case. It would, of course, be very interesting to make this connection. Nonetheless, it is interesting that a metal-insulator (MI) transition is seen in the *c*-axis conductivity in the region of doping where samples superconduct. The MI transition temperature decreases with increasing doping (Fig. 15) until at high doping, apparently, it merges with the superconducting transition temperature. This occurs exactly in the "overdoped" region where superconductivity disappears. It is tempting to associate the change in *c*-axis conductivity with the ability of the sample to superconduct. However, we feel that it is still an open question as to whether the *c*-axis MI transition is produced by the HTT-LTO structural transition.

An interesting corollary to this is that a crossover in the dimensionality of the conducting properties also may be associated with the ability of these samples to superconduct. In the superconducting region of the phase diagram the anisotropy parameter, ρ_c/ρ_{ab}, is highly temperature dependent [69]. Nakamura *et al.* [69] argue that this demonstrates that the scattering mechanisms for *c*-axis transport are different from the in-plane scattering mechanisms and conductivity is 2-dimensional. However, in the overdoped region, where superconductivity has been suppressed, the anisotropy parameter becomes temperature

independent. Metallic conductivity is observed along both *ab* and *c* directions, indicating the dominance of the same scattering mechanism parallel and perpendicular to the CuO_2 planes and a crossover to 3-dimensional behaviour. This tends to suggest that the 2-D nature of the crystal structure is a key component in the properties. However, we should point out that in fully doped Y123 (with a 90K T_c), the *c*-axis conductivity is metallic [71]. There are no free lunches in high-T_c research.

In summary, we have reviewed experiments which consider the electronic and structural phase transitions in La214 materials. Contrary to expectation, the electronic and structural transitions are not coupled directly to each other. This raises the important questions: what are the nature of the electronic transitions and how do they compete with the superconducting ground state? A study of the local structure shows that the octahedral tilt structure is highly inhomogeneous in these materials. We speculate on some of the consequences of this for the spin fluctuations.

VI. CONCLUDING REMARKS

The body of experimental evidence addressing lattice effects in superconductors is clear on two points. First, there *is* significant coupling of the lattice to the electronic (and spin) system. Second, on the length scale of the superconducting coherence length, the structures of high-T_c materials are quite inhomogeneous and the local symmetry and bonding can deviate significantly from that predicted by the average crystal structure.

Estimates for λ vary widely and depend on the particular phonon measured and the method used of averaging over the zone. However, a significant response to superconductivity of both $q = 0$ and $q > 0$ phonons have been observed and there is little doubt that a moderate to strong electron-phonon coupling exists. Frozen phonon local density approximation calculations indicate that coupling to different individual modes can vary by over two orders of magnitude which tends to suggest that all estimates of λ based on measurements of a few modes have an uncertainty many times their actual value. Notwithstanding

these problems, there is ample proof of significant electron-lattice coupling.

Proof that local deviations from the long range structure exist in high-T_c materials is now available from a wide variety of techniques. It is not completely established the extent to which these are a benign relaxation of the lattice around point defects and the extent to which they are, somehow, intrinsic to the structures. However, increasing evidence suggests that significant inhomogeneous distortions exist which cannot be explained by simple steric arguments. A number of authors have suggested an electronic origin for these distortions. It will be an important area of research to establish their origin beyond doubt.

The experimental evidence for "anomalous" lattice effects at T_c is confusing and sometimes apparently contradictory. Care should be exercised when interpreting these observations literally. However, there does seem to be consensus on two points: lattice effects *are* seen at T_c, indicating an electron-lattice coupling; and the largest effects are seen in *local* structural parameters. This might explain, in part, the difficulty in interpreting results since no established theoretical framework exists for understanding the response of individual atoms and distorted clusters to a change in electronic groundstate.

The coupling of the electronic system to the lattice is quite subtle as indicated by the behavior of the La214 system. Structural and electronic phase transitions exist in close proximity to each other but are not each caused directly by the other. Local structural studies indicate that, on the length-scale of ξ, these long-range phase transitions can appear very subtle. The microscopic nature of these phase transitions remains to be understood in detail, as does the way that they couple to the spin and electron systems.

We have argued that the 10-100 Å length scale should be very important for superconductivity and the observation of a relationship between the local structure and superconductivity is entirely consistent with this view. The challenge, experimentally, is to extract reliable structural and lattice dynamical information on these length-scales. High-temperature superconductivity has inspired great ingenuity in this regard, such as extending the scope of age-old techniques such as NRAS and PDF analysis, and not-so-old

techniques such as NMR/NQR and XAFS, to these complicated problems. In the future, it will be important to establish the reliability and useful scope of these techniques to place them on an equal footing with established diffraction and reciprocal space scattering techniques. This process is already well advanced and, in the future, a reassessment of earlier results would quickly lead to great progress in understanding the detailed phenomenology of lattice effects in high-T_c superconductors.

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FIGURES

FIG. 1. Temperature dependence of phonon linewidths in $Bi_2Sr_2CaCu_2O_8$ determined by neutron scattering. High energy modes at 76 and 62 meV correspond to oxygen motion directed toward copper atoms at q values of 0.8 (π,π) and 0.6 (π,π), respectively. The bottom plot gives the width of the longitudinal-acoustic branch at 5 meV and 0.5 (π,π). T_c was 83 K in these crystals. Data from Ref.

FIG. 2. Isotopic mass exponent α for $^{16}O/^{18}O$ substitutions in various cuprate superconductors versus superconducting transition temperature. Arrows on the dashed and solid lines give the direction of increasing x. Plot after Ref.

FIG. 3. Temperature dependence of the $(C_{11} - C_{12})/2$ elastic constant in $La_{1.86}Sr_{0.14}CuO_4$ measured in the various magnetic fields indicated in the figure. The arrows in (c) indicate T_c. Plot after Ref.

FIG. 4. Generalised phonon density of states of $YBa_2Cu_3O_7$ measured using neutron scattering below (symbols) and above (solid line) T_c. Features in the spectrum are labelled with their energy in meV. The inset shows the integrated intensity of the 44meV feature (integration from 40 to 50 meV) as a function of temperature measured with two different incident neutron energies. After Ref.

FIG. 5. Plot of $\Delta\rho(r)$ (= PDF peak height at 3.4 Å minus adjacent valley) vs. T for Tl2212. The solid line indicates the expected temperature dependence due to phonons. T_c is indicated on the plot. After Ref.

FIG. 6. (a) shows the FWHM of ^4He ion channeling scans on $ErBa_2Cu_3O_7$. These were axial scans about the c-axis. The open circles show the signal from Er and Ba ions, the closed circles from Er, Ba and Cu ions. (b) shows average rms thermal vibration amplitude (u_1) calculated from the data in (a). As before, the closed symbols contain the copper signal. Plot after Ref.

FIG. 7. Average kinetic energy $\langle E \rangle$ vs. T of the copper ion in Bi2212 due to motions parallel to the c-axis (open symbols) measured using resonant neutron absorption spectroscopy. The dashed line is the calculated temperature dependence using a projected phonon density of states calculated using a shell model and force-constants fit from single crystal La_2CuO_4 data. (a) shows the c-axis and (b) the ab-plane vibrations. Plot after Ref.

FIG. 8. Structural phase diagram of $La_{2-x}Ba_xCuO_4$. Plot after Ref.

FIG. 9. Superconducting T_c vs. Ba concentration in $La_{2-x}Ba_xCuO_4$ (triangles and dot-dash line) showing the dip in T_c at $p = \frac{1}{8}$. Plot after Ref.

FIG. 10. (a) and (b) show the 400 and 040 diffraction peaks from LBCO samples with $x = 0.125$ and 0.15 respectively at various temperatures. The fraction of LTT phase determined from the fits is plotted in (c) for the two samples ($x = 0.125$: open squares, $x = 0.15$: filled circles). Although they are both 95% in the LTT phase, they have very different superconducting properties as shown by the magnetic susceptibility curves in (d). As before, $x = 0.125$ and $x = 0.15$ are denoted by squares and circles, respectively. Plot after Ref.

FIG. 11. PDFs from LTO and LTT structures. The upper panels (a-c) show PDFs *calculated* from the LTO and LTT crystal structure models. The lower panels (d-f) show the actual data from a sample in the LTO phase (dashed line) and the LTT phase (solid line). The changes predicted by the crystal structure models are not seen in the data.

FIG. 12. Fully converged refinements of various models (solid lines) to PDFs obtained from the $x = 0.125$ sample at 80 K (crosses). The sample was in the LTO phase, yet the LTT model for local tilting gives a much better fit at low-r. The LTOLS model is a superposition of 90° rotated LTT variants and is described in the text.

FIG. 13. Upper panel shows the orthorhombic splitting of $La_{2-x}Sr_xCuO_4$ as a function of composition. Below is a plot of Meissner fraction from the samples. Plot after Ref.

FIG. 14. (a). A plot similar to Fig. 13, although these authors demonstrate that bulk superconductivity persists beyond the orthorhombic to tetragonal transition. The filled circles show T_c, the open squares show the orthorhombic splitting. (b) and (c). Meissner and shielding curves from the same samples as used in (a). The shielding curves give a 102-110% superconducting fraction for all samples up to $x = 0.25$, (Note that in the figure, x is defined by $(La_{1-x}Sr_x)_2CuO_4$) except the composition with exactly $x = 0.125$ which has a drastically reduced shielding fraction. The numbers by the symbols in (b) and (c) denote the Sr content x as per the note above. Plot after Ref.

FIG. 15. Upper two panels give the in-plane (ρ_{ab}) and c-axis (ρ_c) resistivity curves, respectively, for samples of $La_{2-x}Sr_xCuO_4$. Anisotropy parameter in the bottom panel as a function of temperature for various samples. The samples for $0.1 < x < 0.2$ are superconducting, the $x = 0.3$ sample does not superconduct. Plot after Ref.

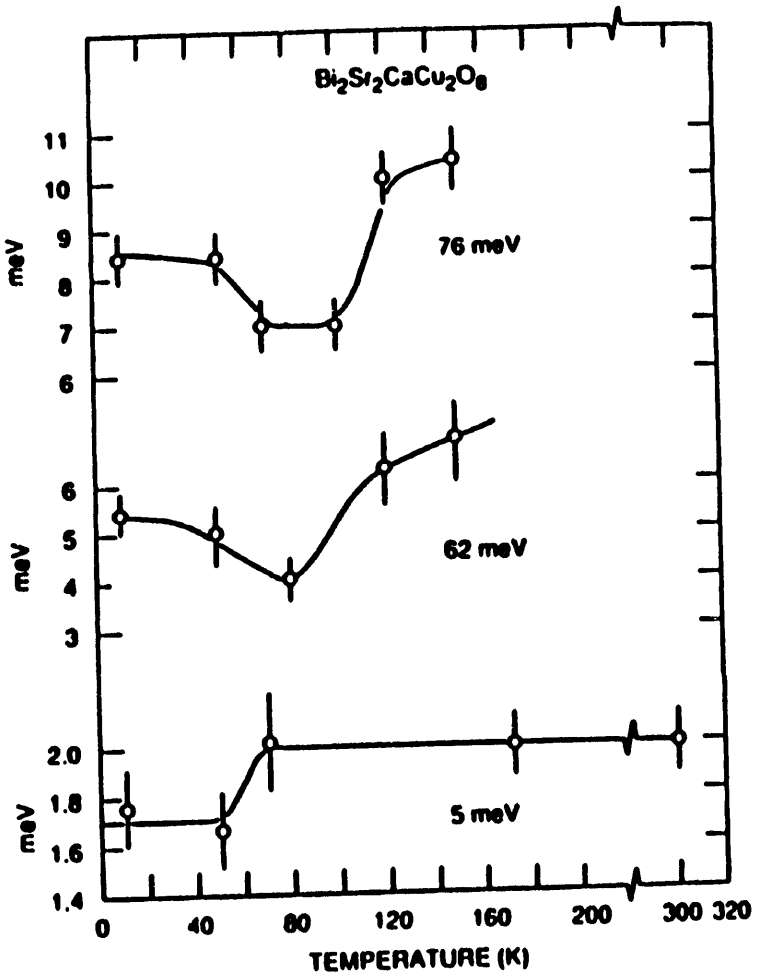
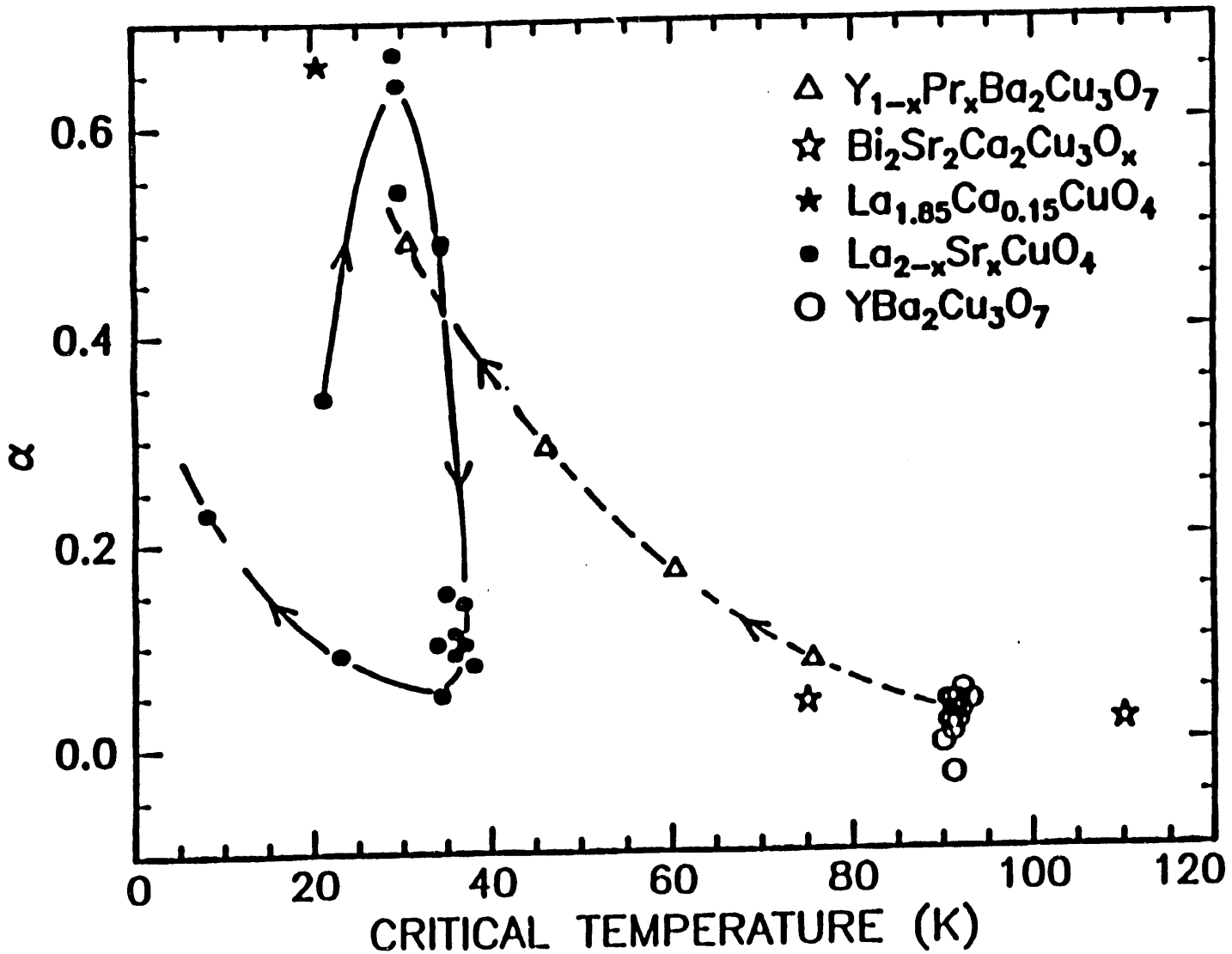

$Bi_2Sr_2CaCu_2O_8$
11
10
9
8
7
6
meV
76 meV
6
5
4
3
meV
62 meV
2.0
1.8
1.6
1.4
meV
5 meV
0
40
80
120
160
200
300 320
TEMPERATURE (K)

Fig 1


Δ $Y_{1-x}Pr_xBa_2Cu_3O_7$
☆ $Bi_2Sr_2Ca_2Cu_3O_x$
★ $La_{1.85}Ca_{0.15}CuO_4$
● $La_{2-x}Sr_xCuO_4$
O $YBa_2Cu_3O_7$
α
0.0
0.2
0.4
0.6
0
20
40
60
80
100
120
CRITICAL TEMPERATURE (K)

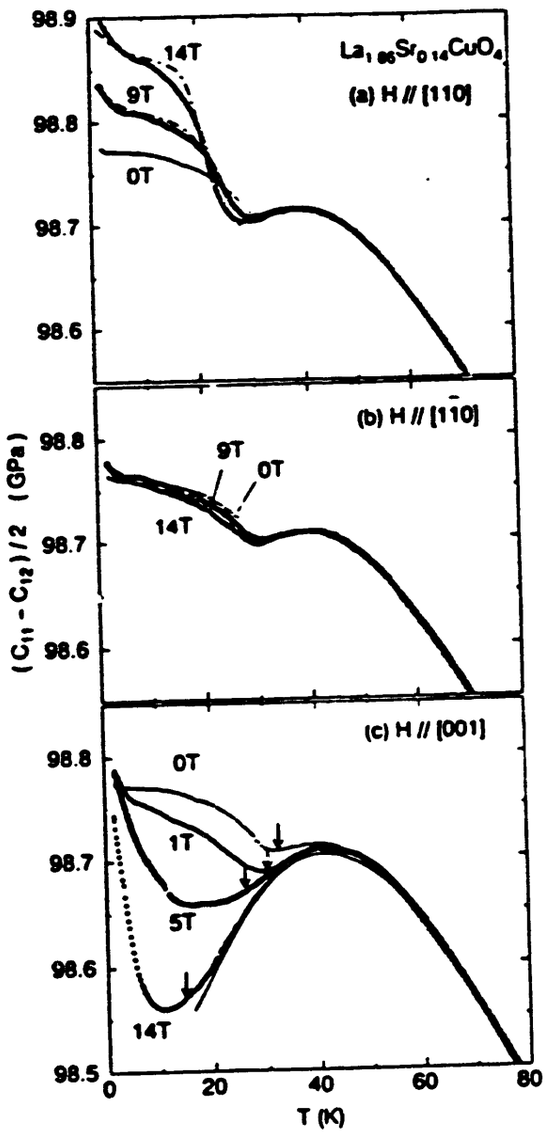
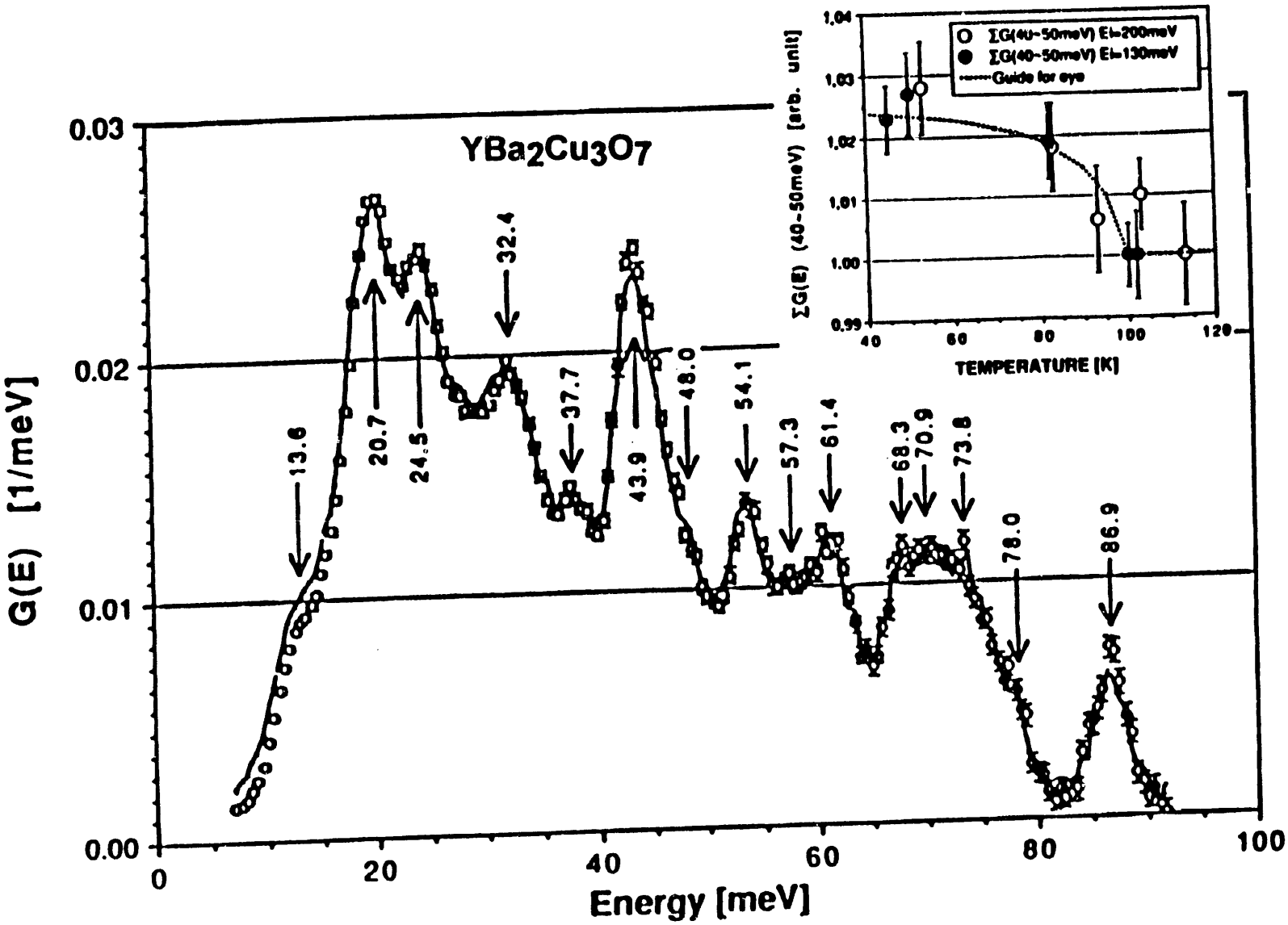

98.9
98.8
98.7
98.6
14T
9T
0T
$La_{1.86}Sr_{0.14}CuO_4$
(a) H // [110]
(b) H // [1$\bar{1}$0]
9T
0T
14T
(c) H // [001]
0T
1T
5T
14T
98.8
98.7
98.6
98.5
0
20
40
60
80
T (K)
$(C_{11}-C_{12})/2$ (GPa)

Fig. 3


YBa2Cu3O7
G(E) [1/meV]
Energy [meV]
0.00
0.01
0.02
0.03
0
20
40
60
80
100
13.6
20.7
24.5
32.4
37.7
43.9
48.0
54.1
57.3
61.4
68.3
70.9
73.8
78.0
86.9
ΣG(E) (40-50meV) [arb. unit]
TEMPERATURE [K]
ΣG(40-50meV) Ei=200meV
ΣG(40-50meV) Ei=130meV
Guide for eye

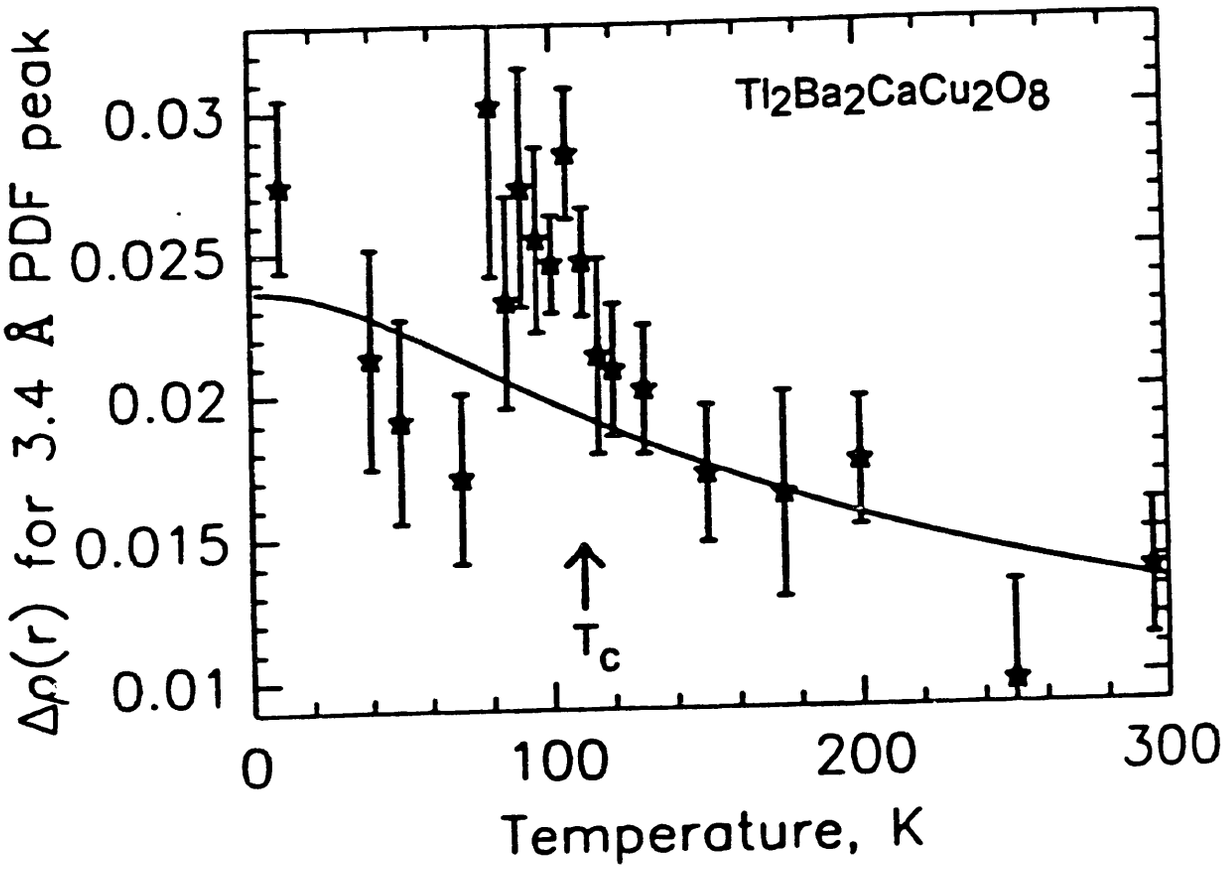

$Tl_2Ba_2CaCu_2O_8$
$\Delta\rho(r)$ for 3.4 Å PDF peak
0.03
0.025
0.02
0.015
0.01
T_c
0
100
200
300
Temperature, K

Fig. 5

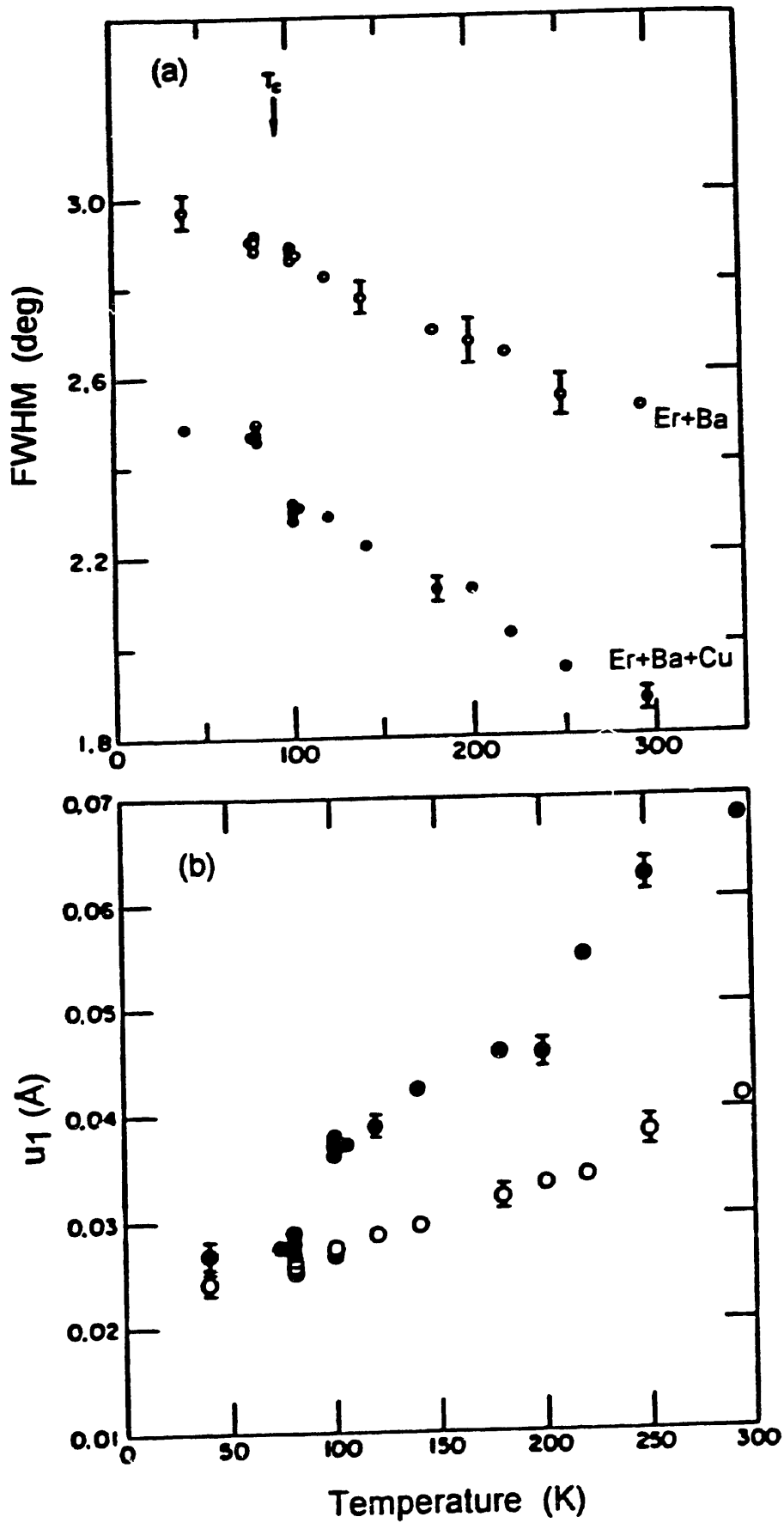
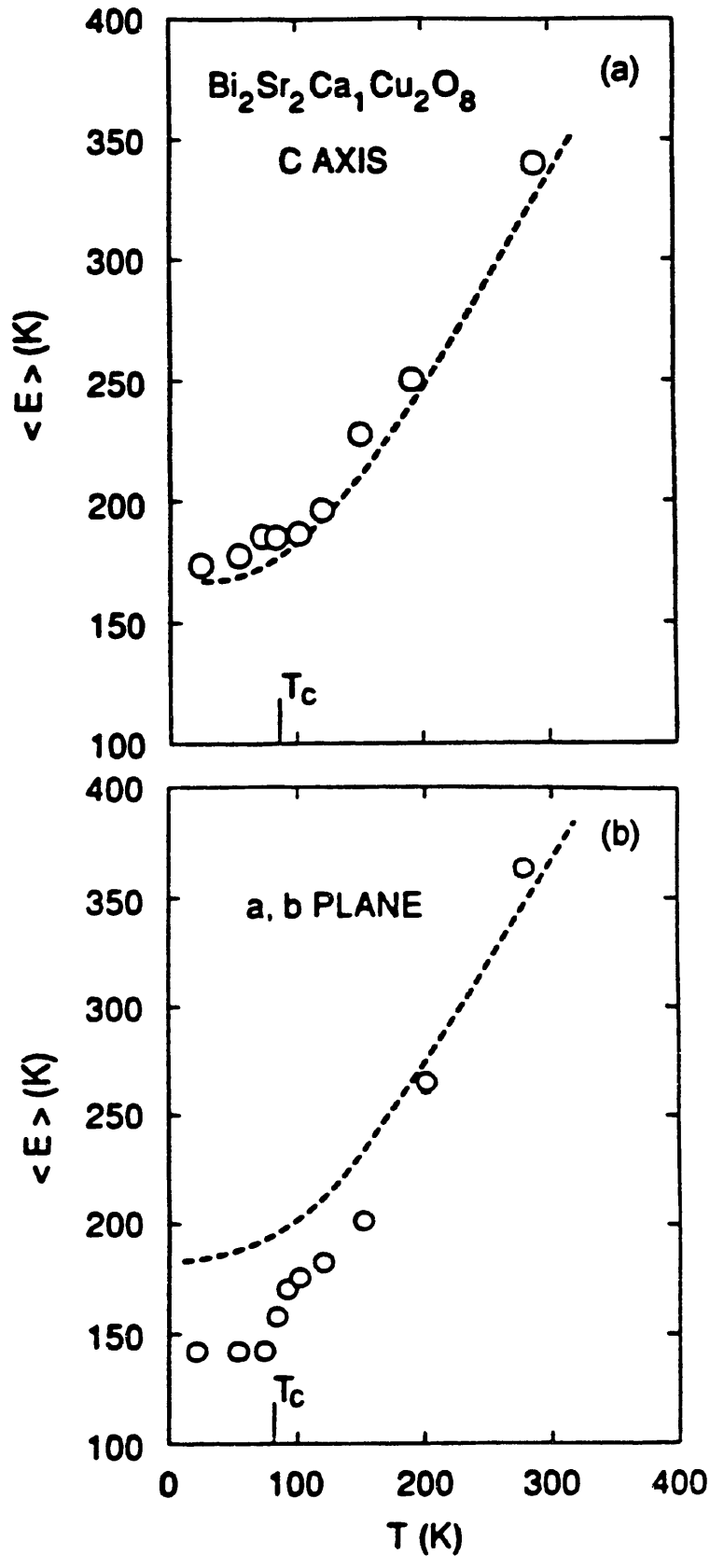
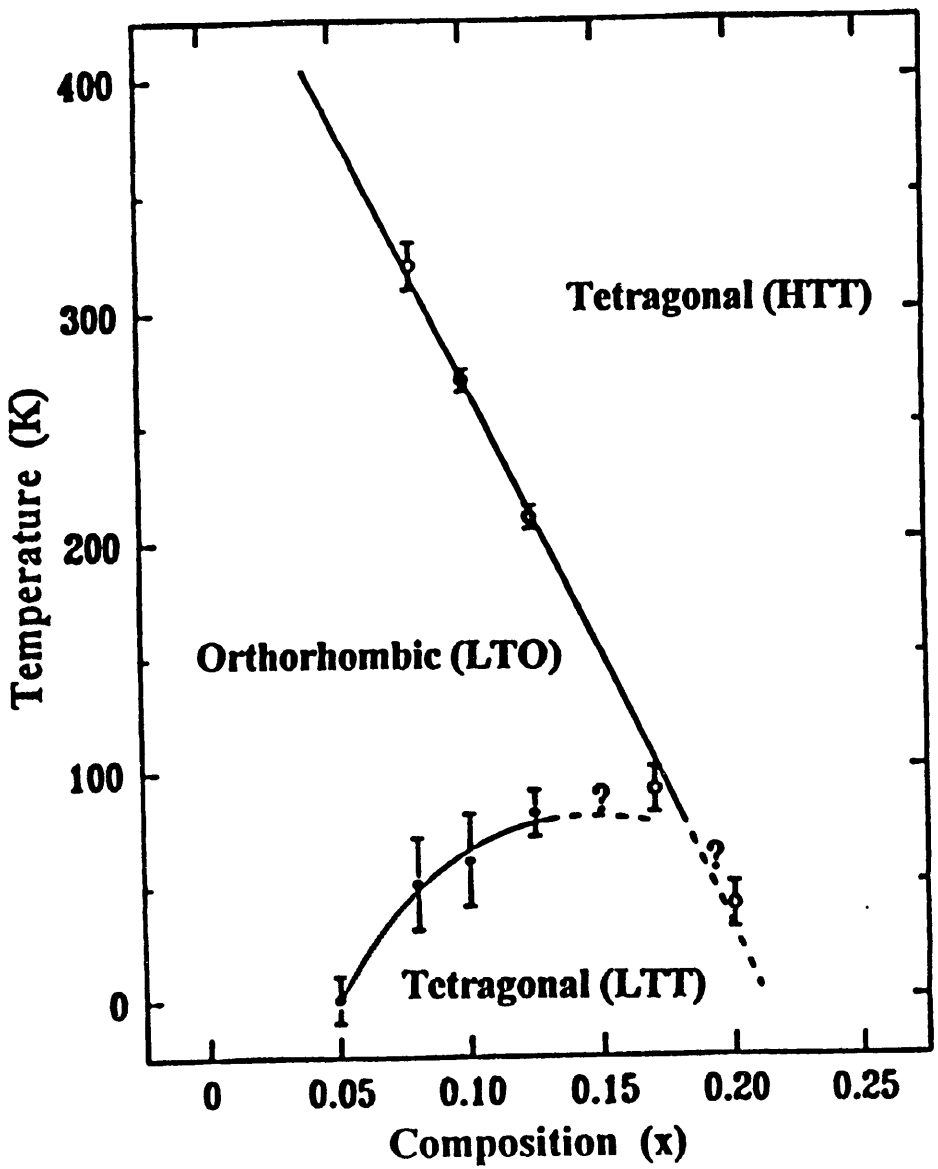
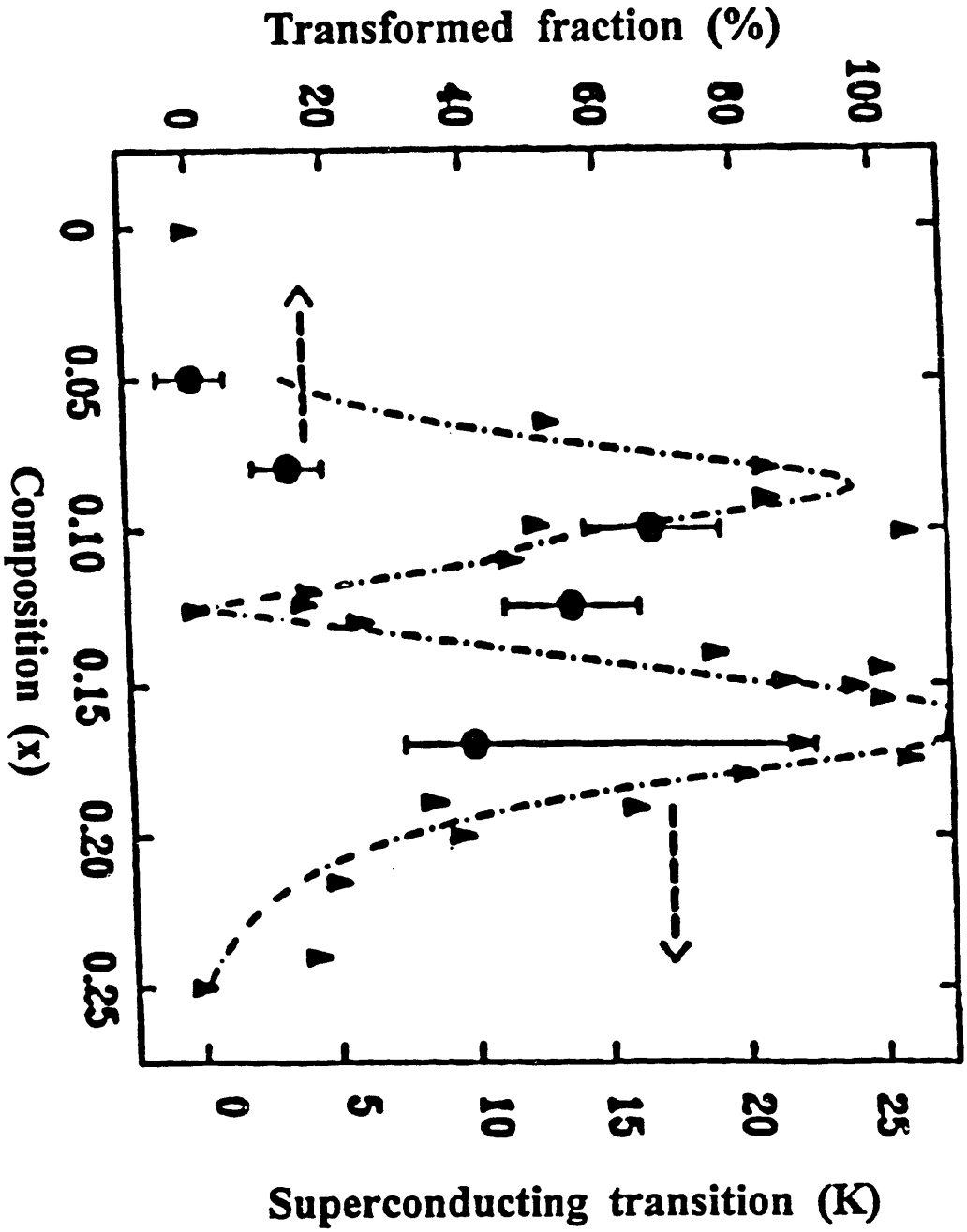
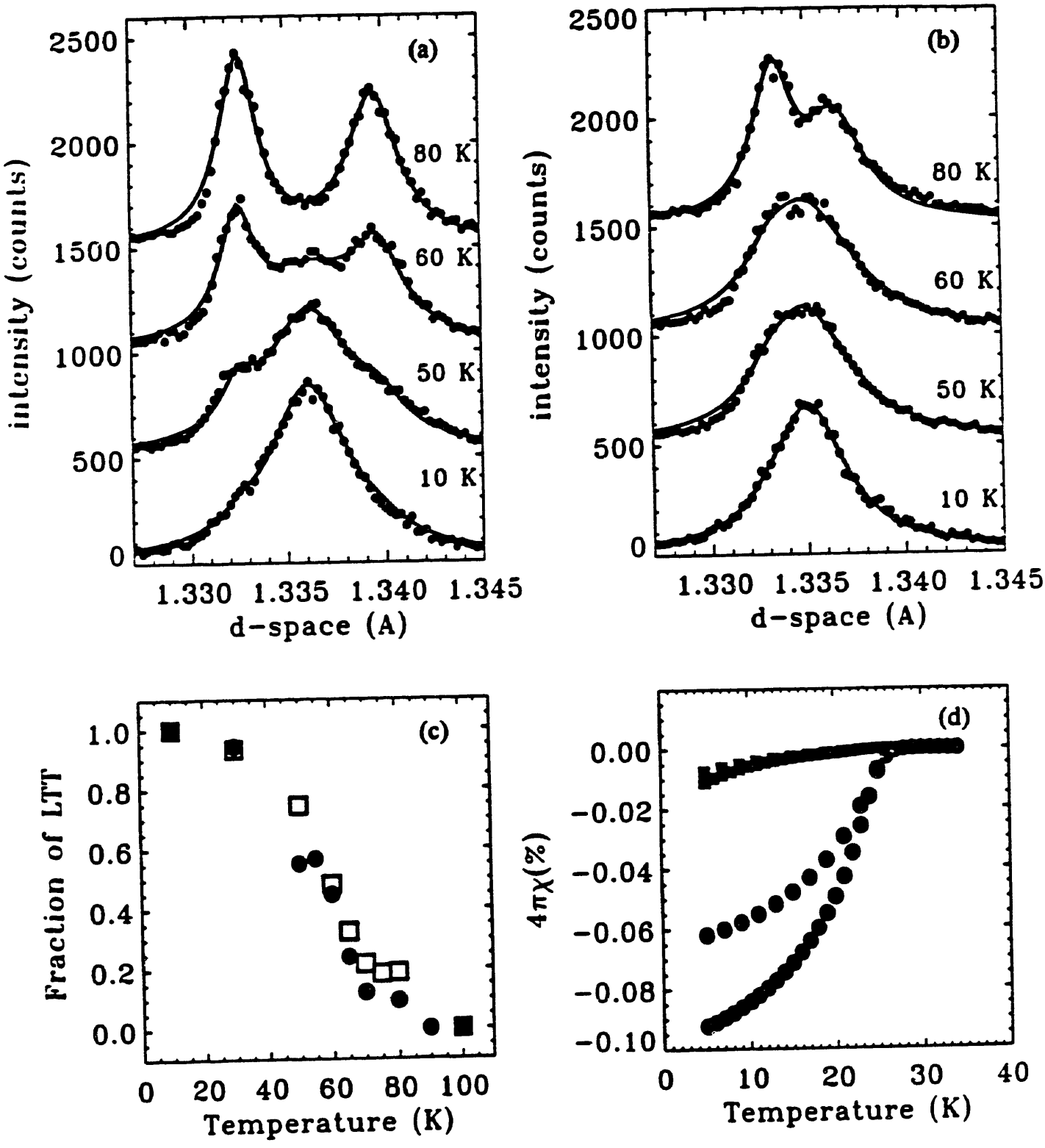

(a)
T_c
FWHM (deg)
3.0
2.6
2.2
1.8
0
100
200
300
Er+Ba
Er+Ba+Cu
(b)
u_1 (A)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
50
100
150
200
250
300
Temperature (K)

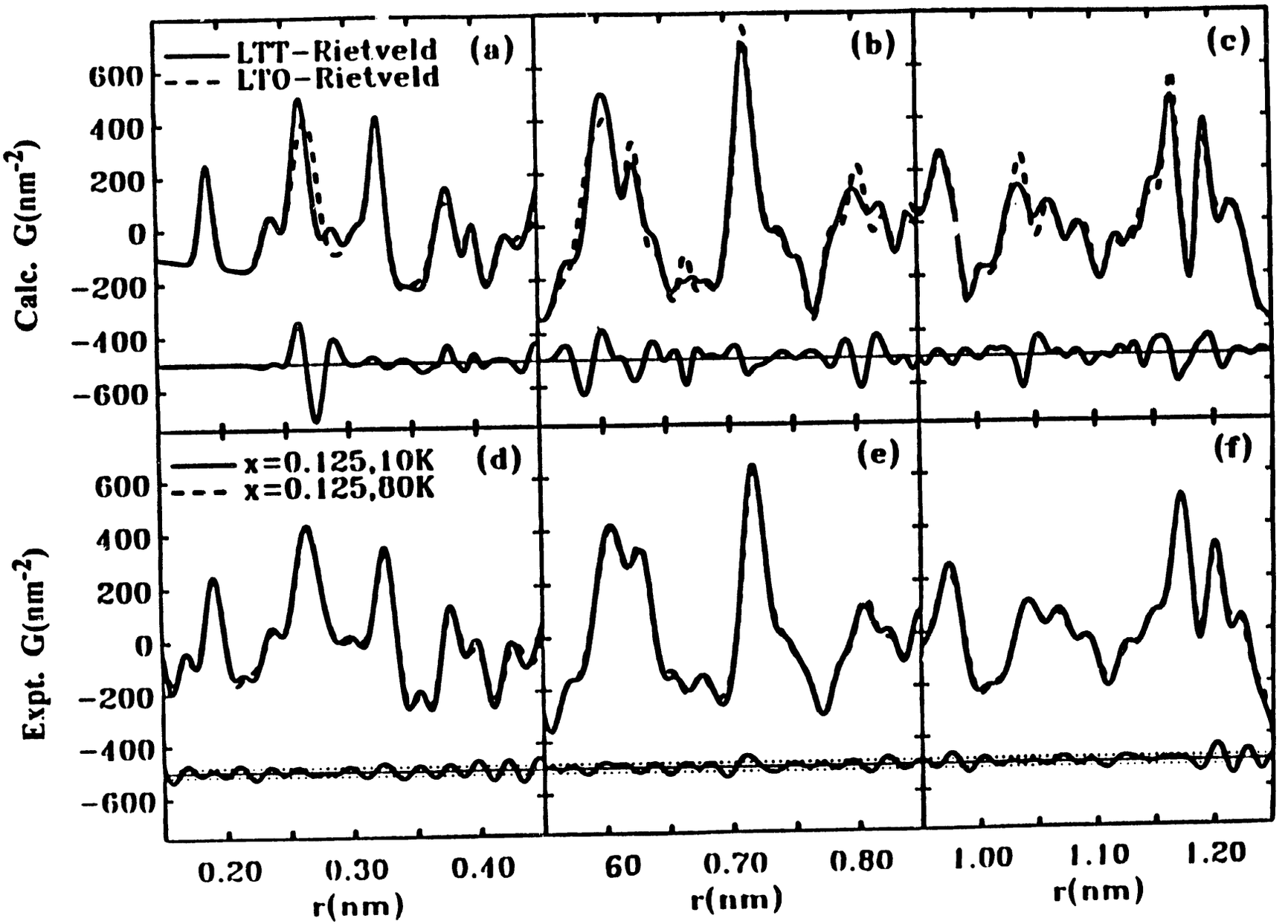
Fig. 6

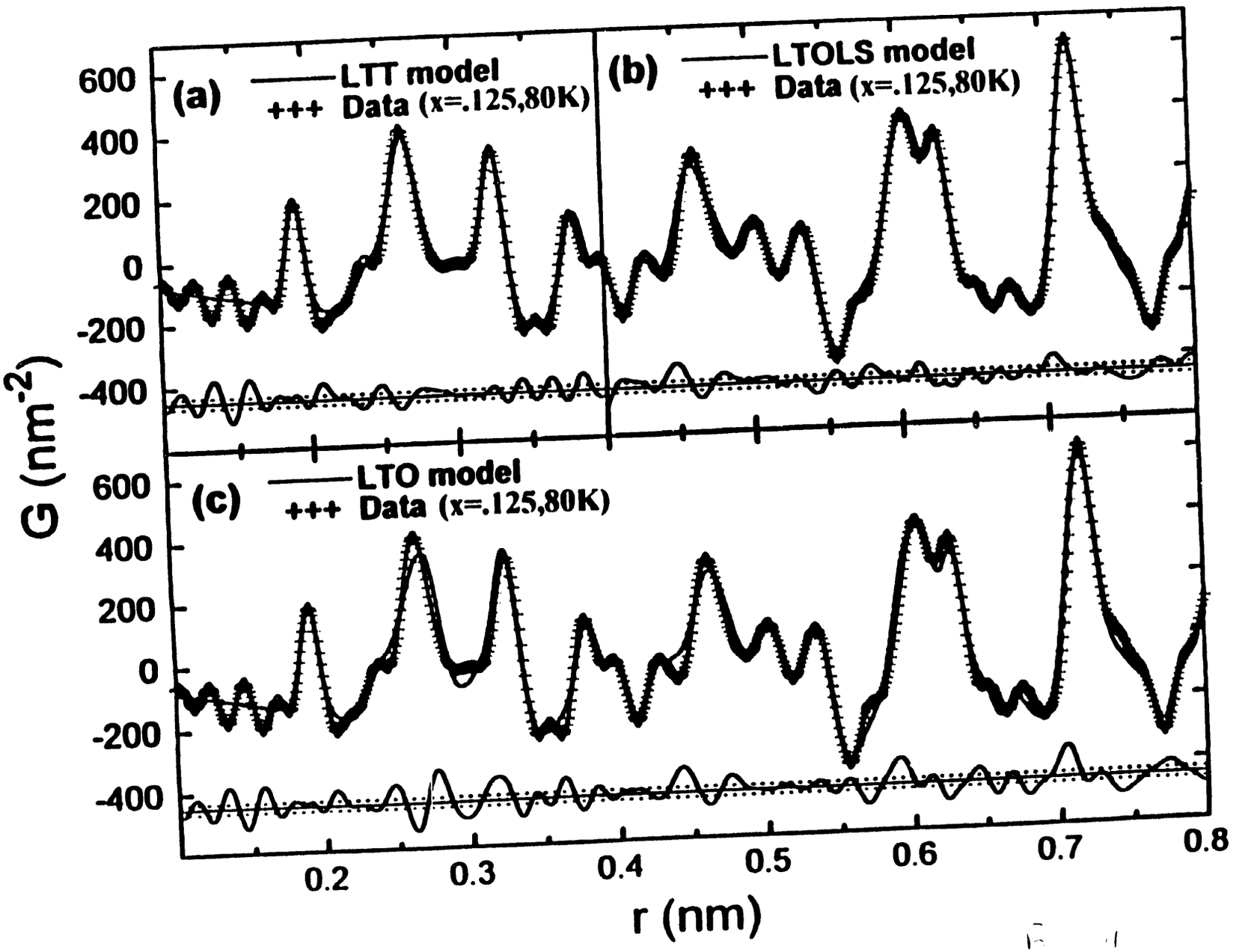

400
350
300
250
200
150
100
$Bi_2Sr_2Ca_1Cu_2O_8$
(a)
C AXIS
<E> (K)
T_c
400
350
300
250
200
150
100
(b)
a, b PLANE
<E> (K)
T_c
0
100
200
300
400
T (K)

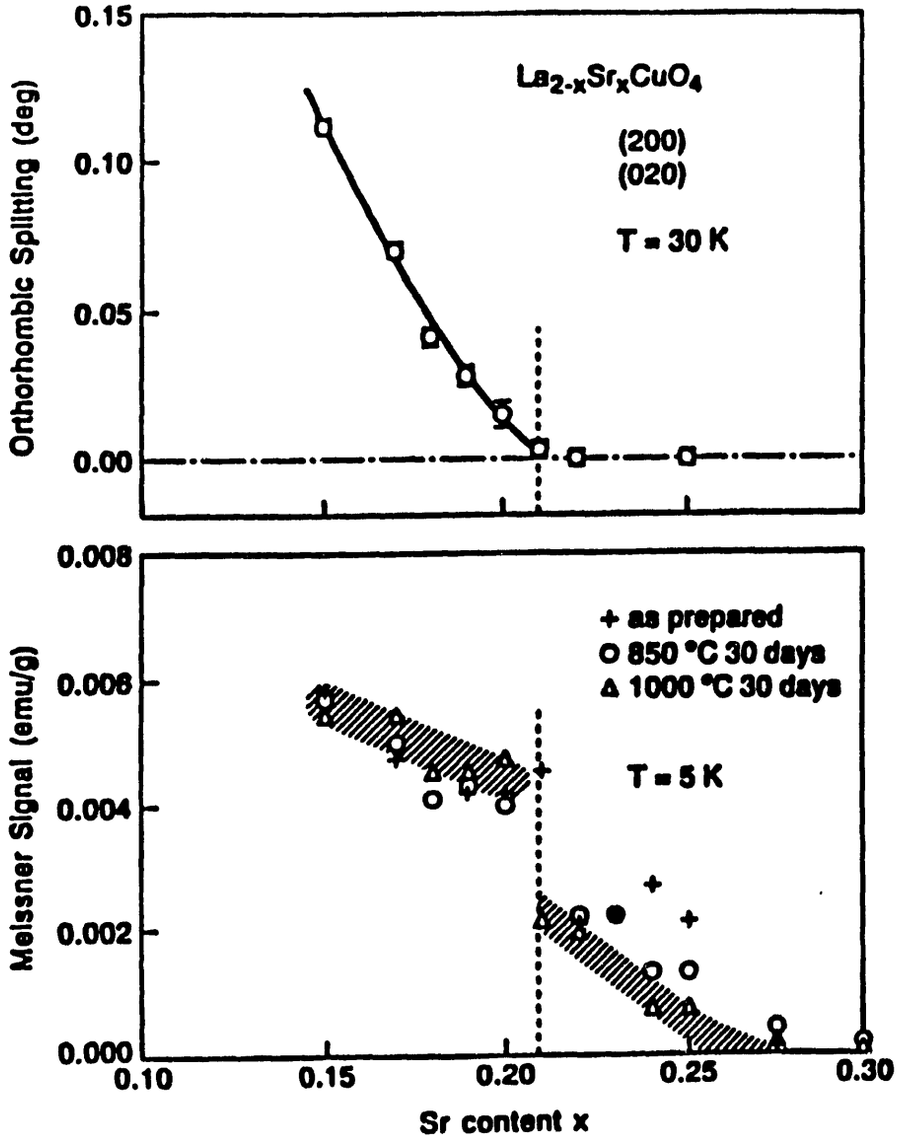

400
300
200
100
0
Temperature (K)
Tetragonal (HTT)
Orthorhombic (LTO)
Tetragonal (LTT)
?
?
0
0.05
0.10
0.15
0.20
0.25
Composition (x)

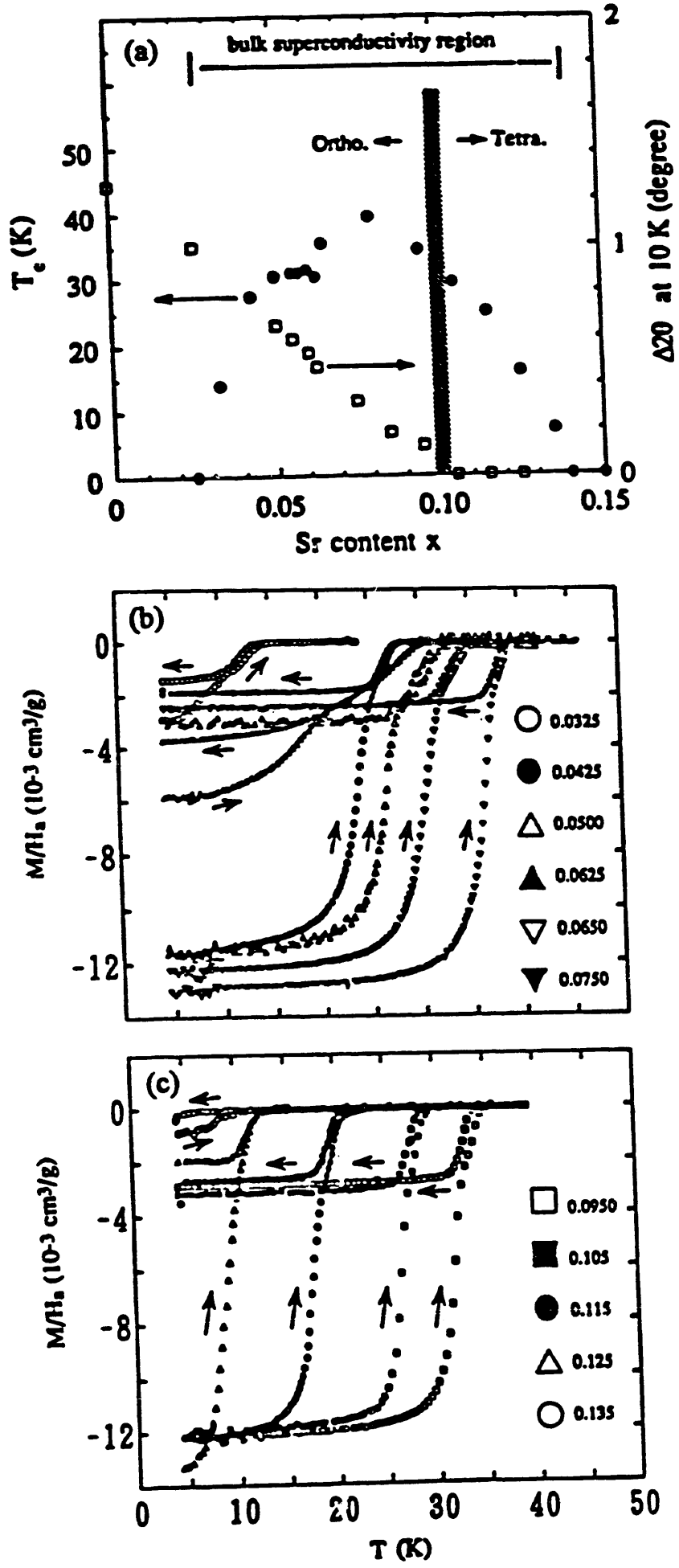

Transformed fraction (%)
0
20
40
60
80
100
Composition (x)
0
0.05
0.10
0.15
0.20
0.25
0
5
10
15
20
25
Superconducting transition (K)

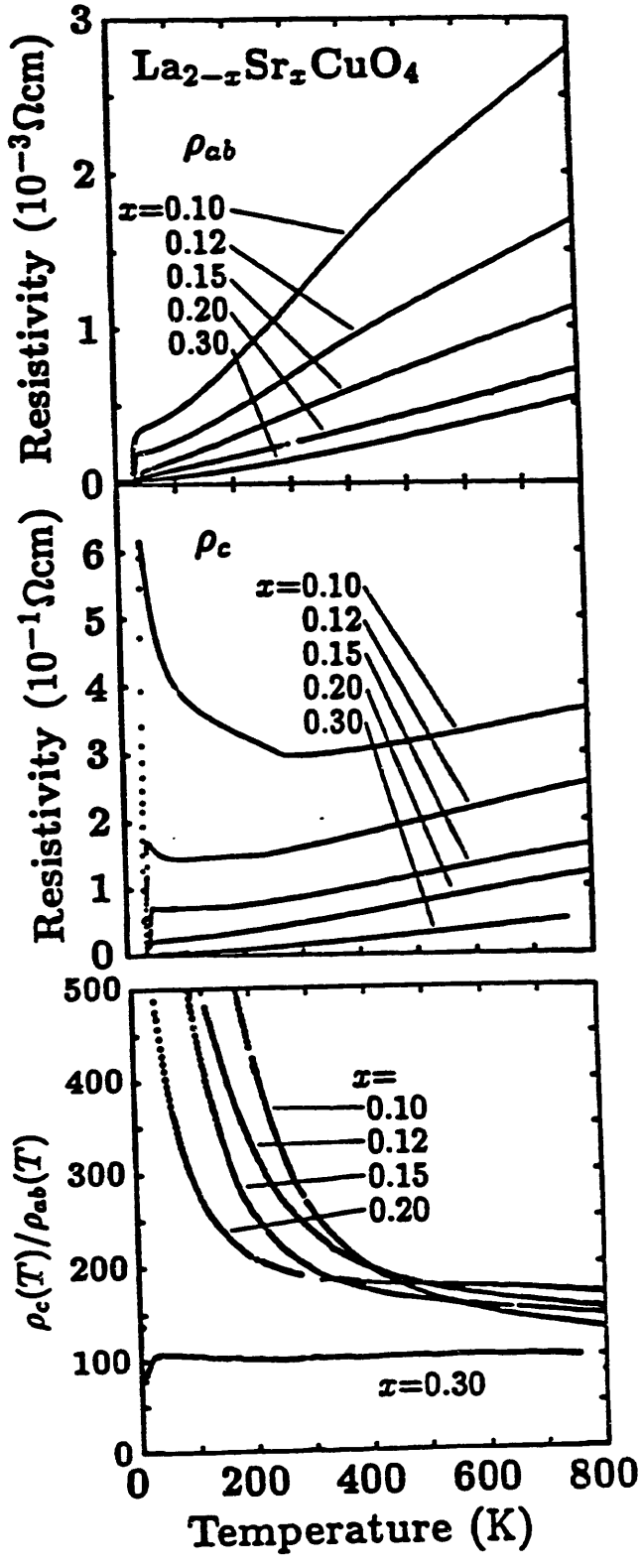

(a)
(b)
(c)
(d)
intensity (counts)
d-space (A)
80 K
60 K
50 K
10 K
Fraction of LTT
Temperature (K)
4πχ(%)


LTT–Rietveld
LTO–Rietveld
(a)
(b)
(c)
(d)
(e)
(f)
x=0.125,10K
x=0.125,80K
Calc. G(nm^{-2})
Expt. G(nm^{-2})
600
400
200
0
-200
-400
-600
0.20
0.30
0.40
60
0.70
0.80
1.00
1.10
1.20
r(nm)
r(nm)
r(nm)


(a)
LTT model
+++ Data (x=.125,80K)
(b)
LTOLS model
+++ Data (x=.125,80K)
(c)
LTO model
+++ Data (x=.125,80K)
G (nm-2)
600
400
200
0
-200
-400
0.2
0.3
0.4
0.5
0.6
0.7
0.8
r (nm)


0.15
0.10
0.05
0.00
Orthorhombic Splitting (deg)
$La_{2-x}Sr_xCuO_4$
(200)
(020)
T = 30 K
0.008
0.006
0.004
0.002
0.000
Meissner Signal (emu/g)
+ as prepared
○ 850 °C 30 days
△ 1000 °C 30 days
T = 5 K
0.10
0.15
0.20
0.25
0.30
Sr content x


(a)
bulk superconductivity region
Ortho.
Tetra.
T_c (K)
Δ20 at 10 K (degree)
Sr content x
(b)
M/H$_a$ (10^{-3} cm^3/g)
0.0325
0.0425
0.0500
0.0625
0.0650
0.0750
(c)
M/H$_a$ (10^{-3} cm^3/g)
0.0950
0.105
0.115
0.125
0.135
T (K)


$La_{2-x}Sr_xCuO_4$
ρ_{ab}
x=0.10
0.12
0.15
0.20
0.30
Resistivity ($10^{-3}\Omega$cm)
ρ_c
Resistivity ($10^{-1}\Omega$cm)
$\rho_c(T)/\rho_{ab}(T)$
x=0.10
0.12
0.15
0.20
x=0.30
Temperature (K)

END

DATE
FILMED
3/15/94