Oxygen-Ordering Effects in High- T_c Superconductors

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In the superconducting oxides the value of T_c may be a sensitive function of both the concentration and the distribution of oxygen defects, the latter quantity itself being a function of both temperature and pressure. Recent high-pressure experiments on $\text{Th}_2\text{Ba}_2\text{CuO}_{6+\gamma}$ have revealed distinct low- and high-temperature relaxation processes above 15 K, presumably originating in the oxygen sublattice. In $\text{TlSr}_2\text{CaCu}_2\text{O}_{7-\gamma}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ only relaxation above 250 K is observed. The relaxation time τ in $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ is found to increase rapidly with pressure from approximately 10 hours at 1 bar to 550 hours at 2.3 GPa. In systems where such relaxation effects occur, T_c is thus not a unique function of pressure, but rather depends in a complicated way on the pressure-thermal-time prehistory of the sample.

[high- T_c superconductivity, oxygen defects, pressure effects, defect structures, thermal relaxation]

Introduction

To further the understanding of the superconducting state in a given class of materials, it is of obvious importance to determine those quantities whose variation causes sizeable changes in the value of the transition temperature T_c . In the high- T_c oxides two such quantities are the *concentration* and the *arrangement* of oxygen defects in the lattice. A modest increase in the oxygen content ($y = 6.35 \rightarrow 6.95$) raises the T_c -value of $\text{YBa}_2\text{Cu}_3\text{O}_y$ (Y-123) from 0 K to 92 K [1]; the change in T_c is much more rapid in the single-layer compound $\text{Th}_2\text{Ba}_2\text{CuO}_{6+\gamma}$ (Tl-2201) where increasing the interstitial oxygen content from $y = 0$ to 0.15 results in a decrease of T_c from 92 to 0 K [2]. Even at constant oxygen content, annealing an oxygen deficient Y-123 sample at room temperature (RT) following a quench from high temperature leads to a local ordering of oxygen defects and to an increase in T_c from 0 to 20 K [3].

Short-range ordering of oxygen defects is made possible by the relatively high mobility of oxygen in the superconducting oxides, even at RT [4]. The most likely scenario for the sensitive changes in T_c is the following: the ordering of oxygen defects is believed to switch selected ambivalent cations outside the conducting CuO_2 plane(s) to a lower valence state (e.g. $\text{Cu}^{2+} \rightarrow \text{Cu}^{1+}$ in the chain layer of Y-123 or $\text{Tl}^{3+} \rightarrow \text{Tl}^{1+}$ in the Th_2O_2 double-layer in Tl-2201), thus generating an increase in the average concentration of hole carriers in the CuO_2 plane(s) and, in an underdoped system like Y-123, to an increase in T_c [5].

The degree of oxygen ordering is continuously enhanced as the temperature is lowered. This means that the measured temperature dependences of such quantities as the electrical resistivity, Hall effect and spin susceptibility may contain both a normal and an anomalous term, the latter originating from oxygen ordering. Such effects can be quite subtle and easily overlooked. It would be useful to have a method to detect the presence of oxygen ordering effects at a given fixed temperature. The application of hydrosatic pressure to a sample affords just such a technique.

The first evidence that the application of high pressure can enhance the degree of oxygen defect ordering was obtained in an experiment on Tl-2201 by Sieburger and Schilling [6]. The method is well illustrated by the data from Klehe et al. [7] on Tl-2201 in Fig. 1: if 0.8 GPa hydrostatic pressure is applied at RT using a He-gas system, T_c decreases from 40 K to somewhat

below 33 K at the largest rate of decrease (-8.9 K/GPa) ever observed for any high- T_c superconductor. If, however, the pressure is then fully released at 55 K, T_c does not increase back to its initial value of 40 K, but instead *decreases further* by ~ 0.3 K! The pressure derivative dT_c/dP thus changes both its magnitude and sign depending on whether the pressure is changed at low (55 K) or high (300 K) temperatures. This unprecedented behavior has a simple explanation: in response to pressure changes, oxygen defects can readily rearrange at RT, but are frozen in place at 55 K. Subsequent neutron scattering studies [8] on Tl-2201 at high pressure lend support to this picture.

Fig. 1. High pressure data on Tl-2201 single crystal from Ref. 7.

Following the release of pressure at 55 K, the Tl-2201 sample was annealed for ~ 1 hour at ever higher temperatures and T_c remeasured. As seen in Fig. 1, T_c ultimately increases back to its initial value at the outset of the experiment. Interestingly, this relaxation occurs in a pronounced two-step fashion, in the temperature regions 55 - 100 K and 200 - 300 K. There are thus at least *two distinct* relaxation processes in the oxygen sublattice -- a "fast" low-temperature (LT) process, perhaps involving the motion of interstitial oxygen between equivalent sites in a single unit cell, and a "slow" high-temperature (HT) process which appears to arise from the diffusion of interstitial oxygen between different unit cells (see Fig. 2). From studies of the time-dependence of the LT and HT relaxation, activation energies centered about, respectively, 0.2 and 0.7 eV are estimated [7]. Oxygen tracer diffusion studies [4] on a number of other oxide superconductors are consistent with activation energies near 0.8 eV, in agreement with our identification of the HT process with diffusive modes of relaxation.

Since the initial work on Tl-2201 [6], related pressure-induced relaxation effects have been observed in a number of further high- T_c materials, including Y-123 [9], Nd-123 [10], Gd-123 [11], superoxygenated $\text{La}_2\text{CuO}_{4+y}$ [12], $\text{TlSr}_2\text{CaCu}_2\text{O}_{7-y}$ (Tl-1212) [7], and possibly $\text{Sr}_2\text{CuO}_2\text{F}_{2+y}$ [13].

Three important questions left open by previous studies are: (1) Is there a temperature below which the LT relaxation in Tl-2201 completely freezes out? (2) Do any of the above systems besides Tl-2201 exhibit LT relaxation phenomena? (3) What is the microscopic origin of the relaxation phenomena? If the oxygen sublattice is directly involved, what is the precise nature of the oxygen ordering? The third question is best explored using a local probe such as NMR. Neutron scattering studies give evidence for local oxygen ordering in Y-123 [2]. In Tl-2201 the strongest circumstantial evidence that the interstitial oxygen defects are directly involved in both the HT and LT relaxation

Fig. 2. Crystal structure of Tl-2201 from Ref. 2. Each oxygen O(3) in the Tl_2O_2 double layer has four equivalent positions. Each interstitial oxygen O(4) within the double layer has two equivalent positions.

In the present paper we explore questions (1) and (2) by examining results recently obtained on the systems Tl-2201, Tl-1212 and Y-123. In these experiments both a He-gas pressure system and a diamond-anvil-cell loaded with dense He as pressure medium were used to generate (nearly) hydrostatic pressures. Because of space limitations, we will not discuss the experimental techniques in detail here, but refer the interested reader to the relevant publications [14, 15].

Results on Tl-2201

An important question left open by previous work is whether LT relaxation effects in Tl-2201 occur for temperatures well below 55 K. For such studies it is imperative that T_c be brought to as low a temperature as possible, since the measurement of T_c itself, the quantity which we use to monitor the degree of relaxation, allows the sample to be annealed, and thus possibly to relax, at that temperature. The most satisfactory way to lower T_c appreciably in overdoped Tl-2201 is to apply sufficiently high pressures at RT to drive T_c to 10 K or below.

Fig. 3. Dependence of T_c for Tl-2201 on the temperature at which the sample was annealed for 1 hour following the release of pressure at 6 K. The inset is a blow-up of the LT data and gives evidence for oxygen relaxation at temperatures below 15 K. Figure is taken from Fig. 14.

phenomena is the strong dependence of the magnitude of these phenomena on the concentration of oxygen defects.

To this end we placed a minute ($\sim 1 \mu\text{g}$) portion of the Tl-2201 crystal studied in Ref. 7 (see Fig. 1) into the gasket hole and filled the hole with dense He in our diamond-anvil-cell. An internal ruby manometer monitors the pressure at any temperature in the range 1.6 - 320 K. A pressure of 5.6 GPa was applied at RT which was sufficient to drive T_c from 40 to 10.6 K, as seen in Fig. 3. Following the full release of pressure at 6 K over a 3 hour period, T_c had increased to 11.83 ± 0.08 K. Two subsequent measurements of T_c give evidence for relaxation effects at temperatures as low as 13 K, with further relaxation occurring during the 1 hour anneals at higher temperatures.

The two-step shape of the T_c versus T_{anneal} relaxation curve in Fig. 3 above 55 K resembles closely that observed in the lower pressure experiment [7] in the He-gas system. The present work

leaves open the possibility that very fast relaxation processes may be present which saturate at temperatures well below 13 K, and thus cannot be determined in the present experiment. Glass-like relaxation behavior at very low temperatures is well known in amorphous solids and in orientationally or compositionally disordered dielectric crystals and alloys [16]. Esquinazi et al. [17] have even reported relaxation phenomena in polycrystalline samples of the pure elements Ag, Al, Cu, and Nb in the extremely low temperature range 40 μ K to 1 K!

Results on Tl-1212

Two different scenarios have been proposed for the origin of the "fast" LT relaxation modes observed in Tl-2201 (see Fig. 3): (1) motion of the interstitial oxygen between two equivalent sites within the Tl_2O_2 double layer [6], and (2) motion of planar oxygen in the Tl_2O_2 double layer between four equivalent sites [18]. One way to test these scenarios is to remove all interstitial oxygen and see whether the LT relaxation remains or disappears. Unfortunately, such a Tl-2201 sample has its maximum (extremum) T_c -value of ~ 92 K, so that, to first order, the enhanced charge transfer from oxygen ordering causes no change in T_c . Indeed, we find neither LT nor HT relaxation modes in such an optimally doped Tl-2201 sample [6].

Another possibility would be to study a related system which lacks the equivalent interstitial sites within the Tl_2O_2 double layer, i.e. a system, like Tl-1212, with a single TlO layer containing oxygen vacancies. We have recently studied several overdoped Tl-1212 samples with different oxygen concentrations to 0.7 GPa in our He-gas pressure system [19]. Typical results are shown in Fig. 4 where it is seen that T_c drops rapidly after the

Fig. 4. T_c versus pressure for Tl-1212 from Ref. 19. Pressure is applied at RT and released at 60 K, followed by an anneal at increasingly higher temperatures.

application of 0.8 GPa pressure at RT. Holding the sample at this pressure for 0.5, 5 and 31 hours results in further decreases in T_c , signaling relaxation behavior. The decrease in T_c upon full release of pressure at 60 K is quite large. The sample was then annealed for 1 hour at seven consecutively higher temperatures between 60 and 210 K, with no sign of any LT relaxation effects. As seen in Fig. 4, only at 236 K and higher temperatures does the HT relaxation set in which presumably arises from the diffusive motion of oxygen vacancies in the TlO layer. These results thus support the scenario that the LT relaxation processes in Tl-2201 indeed originate from the interstitial oxygen defects and not from the planar oxygen anions in the Tl_2O_2 double layer.

For Tl-1212 samples with higher oxygen content (lower vacancy content), where $T_c(0) = 69$ K, 60 K, and 32 K, the size of the HT relaxation effects is sharply reduced [19], disappearing entirely for the 32K-sample. This is likely the result of the lower oxygen vacancy concentration for samples with decreasing $T_c(0)$. The indicated oxygen vacancy content for the 32K-sample has evidently dropped to zero; this has yet to be confirmed by neutron diffraction studies.

The presence of large relaxation effects seen in Fig. 4 for the 79K-sample give strong evidence that the optimal value of T_c for Tl-1212 lies at an appreciably higher temperature than 79 K. Indeed, Liu et al. [20] obtained the value $T_c(0) = 110$ K for Tl-1212 by optimizing the oxygen content and partially substituting Pb for Tl and Y for Ca. From the time dependence of the relaxation in Tl-1212 we estimate an activation energy near 0.84 eV which lies somewhat higher than that (0.7 eV) for the HT process in Tl-2201.

Results on Y-123

The Y-123 compound is the most thoroughly studied of all high- T_c superconductors, even though, because of its chain structure, it is one of the most difficult to understand. Oxygen ordering effects in high- T_c oxides were first observed by exposing this compound to a thermal quench from high temperatures [21]. One of the more interesting phenomena observed for this system is persistent and transient photoinduced superconductivity [22]. Recent studies by Guimpel et al. [23] show that thermally induced oxygen ordering and persistent photoconductivity have a common physical origin in the rearrangement of oxygen defects. Internal friction studies [24] on Y-123 reveal relaxation peaks in the range 0.08 to 0.2 eV which would yield very short relaxation times, even at low temperatures (10^{-6} sec at 60 K). This has prompted us to suggest [7] that transient photoinduced superconductivity in this compound might originate from fast LT oxygen relaxation processes.

Pressure-induced oxygen ordering effects have been observed in a series of experiments by Fietz et al. [9] with varying degrees of oxygen deficiency; in these experiments, however, the pressure was changed at temperatures near 90 K, precluding the identification of possible relaxation processes at temperatures below 90 K. To search for possible oxygen ordering effects at low temperatures, a sample should be chosen with a low initial value of T_c ; high pressure cannot be used to drive T_c down to low temperatures, as for Tl-2201, since Y-123 is *underdoped* so that T_c initially increases with pressure.

We have very recently carried out a series of high-pressure

measurements on a strongly oxygen deficient single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ with $T_c(0) = 13.5$ K (pt. 1 in Fig. 5) using our He-gas system [25]. Following the two-month storage of the sample at 295 K, a pressure of 0.10 GPa was applied at 298 K and the sample retained at this temperature for 17 hours to allow the oxygen ordering to reach equilibrium before cooling down rapidly to measure $T_c = 15.3$ K. The very large value of the pressure derivative obtained, $dT_c/dP = +20$ K/GPa, is in reasonable agreement with earlier studies by Fietz et al. [9]. After releasing the pressure fully at 16.5 K, T_c was immediately remeasured and found to have decreased to 15.0 K (pt. 3 in Fig. 5). The sample was then warmed up rapidly to consecutively higher annealing temperatures T_{anneal} , annealed there for 1 hour, and then cooled down to remeasure T_c . Within experimental error, no further change in T_c is observed for annealing temperatures as high as 264 K, as seen in Fig. 5. In this experiment, therefore, we find no evidence whatsoever for relaxation phenomena at low temperatures in Y-123. Experiments to higher pressures, 0.57 and 0.79 GPa, also gave no evidence for relaxation phenomena at low temperatures [25]. Our studies, of course, do not exclude the possibility of relaxation at temperatures below 15 K or on samples with oxygen stoichiometry other than $\text{O}_{6.41}$.

Following the one hour anneal at 280 K (pt. 18 in Fig. 5), the relaxation in T_c at the fixed temperature of 298 K was determined for various annealing times (pts. 19 to 23 in Fig. 5). For pts. 22 and 23, T_c is seen to relax back *past* its initial value for pt. 1. The reason for this behavior is that, prior to measuring pt. 1, the sample had been stored for 2 months at 295 K. Prior to measuring pt. 23, however, the sample had been annealed at the higher temperature of 298 K for 44 hours. The equilibrium state in the oxygen sublattice at 298 K contains a higher degree of disorder than at 295 K, leading to a slightly lower value of T_c . This effect was studied in detail by Veal et al. [21].

Fig. 5. Dependence of T_c for $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ on the annealing temperature following the application of 0.1 GPa pressure at 298 K and its full release at 16.5 K, from Ref. 25. Numbers give order of measurement. Inset shows time dependence of T_c for annealing at 298 K following full release of pressure at 16.5 K.

Fig. 6. Relaxation data at 298 K for $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ at 0.57 GPa and 0 GPa. Lines are best fits to relaxation equation using different values of α . Numbers give order of measurement. Fig. from Ref. 25

The relaxation time τ at a given temperature and pressure can be evaluated by measuring the relaxation in T_c upon annealing at this temperature for various times after the pressure has been applied. In Fig. 6 the dependence of T_c on annealing time at 298 K is given for $\text{YBa}_2\text{Cu}_3\text{O}_{6.41}$ following the application of 0.57 GPa pressure at RT. The initial relaxation data point for $t = 0$ is marked by an asterisk *. After over 200 hours annealing time, the pressure was fully released at 60 K and the relaxation in T_c for annealing at 298 K determined. Evidently the relaxation at ambient pressure proceeds more rapidly than at high pressure.

To determine the relaxation time τ quantitatively, the measured $T_c(t)$ -data was fit using the expression $T_c(t) = T_c(\infty) - [T_c(\infty) - T_c(0)]\exp\{-(t/\tau)^\alpha\}$, where $T_c(\infty)$ is the transition temperature after infinite time, $T_c(0)$ is the initial value of the transition temperature, and α is the stretched exponent. The value $\alpha = 0.6$ gives the best fit to our data [25], indicating that not a single relaxation time, but rather a distribution, is appropriate. A similar analysis was carried out for other applied pressures. An experiment in our diamond-anvil-cell was also included. The dependence of τ (298 K) on pressure is shown in Fig. 7a where τ (298 K) is seen to increase from approximately 10 hours at ambient pressure to 550 hours at 2.3 GPa. The dependence of the activation energy obtained from τ (298 K) using an Arrhenius expression is approximately linear in pressure, as seen in Fig. 7b.

Since only high-temperature relaxation phenomena occur in the present Y-123 sample, holding the sample at temperatures of

Fig. 7. Relaxation data from Ref. 25 for YBa₂Cu₃O_{6.41}. (a) Pressure dependence of relaxation time τ at 298 K obtained from fits to T_c data using both He-gas and diamond-anvil pressure systems. Relaxation processes slow down markedly under pressure. (b) Pressure dependence of the activation energy E_A .

100 K or below during a high pressure experiment will freeze the oxygen defects in place and allow the determination of the "intrinsic" pressure dependence of T_c . The results of such an experiment in our diamond-anvil-cell are shown in Fig. 8 where T_c is seen to increase under pressure before passing through a maximum at 17 K for 3 GPa [26]. Assuming that the hole carrier concentration for this strongly underdoped sample increases with pressure at approximately the same rate as for optimally doped Y-123 (approximately +10%/GPa from Ref. 27), the initial $T_c(P)$ -dependence in Fig. 8 is difficult to understand using a modified charge-transfer model [28]. In contrast to this weak intrinsic dependence of T_c on pressure, if the sample is annealed at RT for over 200 hours after 0.57 GPa pressure is applied (data in Fig. 6), T_c relaxes upward in Fig. 8, yielding the enormous positive dependence $dT_c/dP = +20 \text{ K/GPa}$. The striking difference in the pressure dependence of T_c for pressure changes at RT or LT emphasizes the care that must be taken in interpreting published T_c -data for the superconducting oxides, most of which are obtained following changes of pressure at ambient temperature, and not at low temperatures where oxygen relaxation effects would be less important.

In summary, relaxation effects in T_c are observed in Tl-2201 which extend to temperatures as low as 15 K, and perhaps lower. In this system a distinct HT relaxation process is found above

200 K. In contrast, Tl-1212 and a strongly underdoped Y-123 sample only exhibit HT relaxation phenomena. The relaxation time in the Y-123 sample is found to increase nearly by two orders of magnitude under 2.3 GPa hydrostatic pressure.

The most likely scenario for the HT relaxation is diffusive motion of oxygen defects through the lattice. Many other scenarios for relaxation behavior in the oxide superconductors are conceivable. Cordero and Grandini [29] have measured the dynamic elastic modulus of stoichiometric La₂CuO₄ and found evidence for relaxation dynamics in the lattice on three different time scales corresponding to 450, 150 and 5 K. The slowest relaxation is attributed to the motion of twin boundaries, the intermediate relaxation to thermally activated flipping of unstable CuO₆ octahedra, and the fastest relaxation to quantum tunneling in double-well potentials arising from the tendency of the LT orthorhombic phase to nucleate at low temperatures to LT tetragonal domains. Another potential scenario involves the possible build-up of charge-stripe order, similar to that recently observed by Tranquada et al. [30] in La_{1.6-x}Nd_{0.4}Sr_xCuO₄. Such spatially modulated spin and charge densities might exhibit relaxation behavior with a strong pressure dependence. Experiments on a microscopic scale (NMR) are needed to provide a clear picture of the relaxation processes on a microscopic scale.

Fig. 8. Dependence of T_c for YBaCuO on pressure applied at approximately 100 K, (●) increasing pressure, (▲) decreasing pressure. Point (×) was taken after allowing the sample to fully relax under 0.57 GPa pressure at 298 K. Figure from Ref. 26.

Whether or not oxygen ordering effects occur affects to a greater or lesser degree the dependence of a wide variety of solid state properties on both temperature and pressure. The effects on T_c are particularly dramatic. For Tl-2201, Y-123 and Tl-1212, and perhaps many further systems, the dependence of T_c on pressure is strongly modified when relaxation effects occur. In such systems, T_c is not a unique function of pressure, but rather depends in a complicated way on the pressure-thermal-time prehistory of the sample.

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