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# ORDERING IN $Tl_2CaBa_2Cu_2O_8$ AND $Tl_2Ba_2CuO_6$ STUDIED BY PAIR DISTRIBUTION FUNCTION AND RIETVELD ANALYSIS

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Rietveld analysis indicates that the only long-range structural variation in  $Tl_2CaBa_2Cu_2O_8$  with temperature is a shift of O(2) away from Cu and toward Ba with increasing T. Atomic pair distribution function analysis on two samples of  $Tl_2Ba_2CuO_6$ , one superconducting, the other not, shows substantial differences in their short range structure, but similar medium range structures, while Rietveld analysis shows very similar lattice constants and long-range structures.

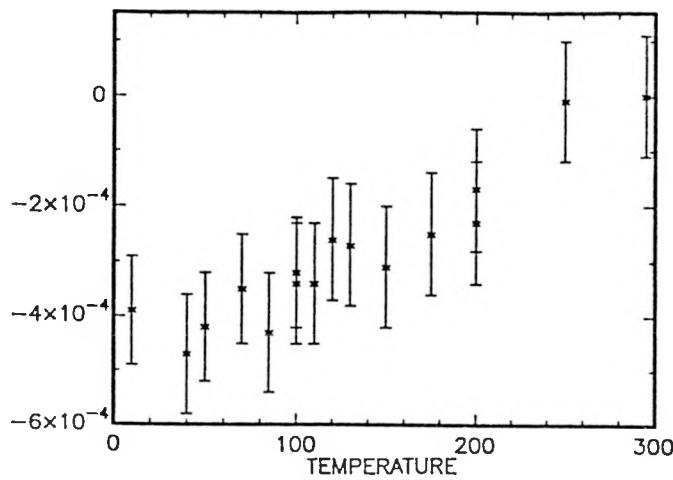
### 1. INTRODUCTION

Atomic pair distribution function (PDF) and Rietveld analysis have been used to examine the structures of  $Tl_2CaBa_2Cu_2O_8$  and  $TlBa_2CuO_6$  using time-of-flight diffraction data from the Argonne National Laboratory Intense Pulsed Neutron Source. Both PDF and Rietveld require measurement of neutron scattering intensities,  $I(Q)$ , as function of the scattering vector,  $Q$ , from which the atom-atom interference function,  $S(Q)$ , can be determined. However, for PDF analysis the pair distribution function,  $\rho(r)$ , is computed by a Fourier transform of  $S(Q)$ . The accuracy of  $\rho(r)$  is limited unless  $S(Q)$  has been measured with high precision up to large values of  $Q$ . This requirement is well met by pulsed-neutron diffraction [1].

The PDF is the atom-atom pair correlation function in *real space*, a 1-D analog to the crystallographic Patterson function. A PDF peak thus represents one or more interatomic distances and the peak area is a function of the scattering cross sections for the contributing atoms and their atomic coordination numbers. The PDF utilizes all diffraction information, including diffuse scattering and thus is a probe of correlations in the local atomic structure even when the structure deviates from perfect periodicity. This is in contrast to Rietveld analysis, which assumes long-range ordering, thus yielding the averaged position for each atom.

### 2. $Tl_2CaBa_2Cu_2O_8$

We measured 17 diffractograms from 10 g of  $Tl_2CaBa_2Cu_2O_8$  at temperatures between 10 and 295 K. Rietveld refinements were performed using a disorder model with both O and Tl displaced in the  $\langle 100 \rangle$  direction. As was previously reported, the lattice constants varied smoothly with temperature [2]. Atomic temperature factors also varied smoothly with temperature and atomic coordinates showed no significant changes in position *with the exception of O(2)*, which is approximately coplanar with Ba, between the Cu-O and Tl-O layers. Atom O(2) shifts toward Cu with decreasing temperature (see Fig. 1). Since the length of the Cu-O(2) apical bond usually reflects the local charge density at Cu, due to the Jahn-Teller distortion, this shift is consistent with a very slight increase in the effective valence of Cu with decreasing temperature. However, contrary to the XANES report on  $YBa_2Cu_3O_7$  [3], there was no significant abrupt change in the O(2) position near  $T_c$ . On the other hand, PDF analysis of the same data did indicate some anomalous structural change in the vicinity of  $T_c$ , likely involving O(1) rather than O(2) [4]. Details of these findings will be reported elsewhere.



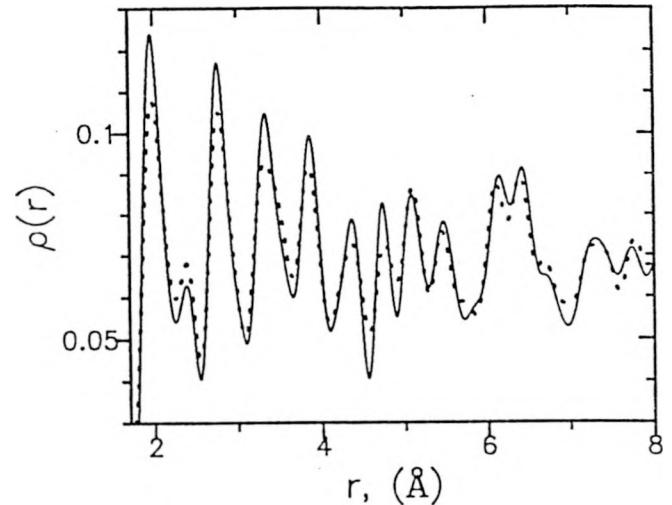
**Figure 1.** Change in fractional  $z$  coordinate for O(2) as a function of temperature. Error bars have length  $2\sigma$ .

### 3. $Tl_2Ba_2CuO_6$

Two samples having nominal composition  $Tl_2Ba_2CuO_6$  were prepared *in sealed gold tubes* using identical synthesis techniques, varying only the reaction temperature: 750° C produced a non-superconducting sample, but 875° C produced a sample with  $T_c$  of 65 K. While both samples show significant amounts of impurity phases (estimated at 20%), the location and integrated intensity of the impurity peaks are very similar between samples. Rietveld refinements yielded no discernable differences between the samples, including identical lattice constants:  $a = 3.8462(1)$  Å and  $c = 23.189(1)$  Å for the superconducting sample;  $a = 3.8462(1)$  Å and  $c = 23.188(1)$  Å for the non-superconducting sample.

In contrast, the PDF measured for each sample are quite different (Fig. 2) in short range ( $< 5$  Å), but are almost identical in medium range ( $> 5$  Å). This suggests that the medium to long range order of each sample is very similar, while there is a significant difference in the *short range order*, specifically the non-superconducting sample has much greater local disorder. It is possible that the increased disorder in the 750° C sample contributes to the destruction of superconductivity. Our result does not support the previous proposal that an increased  $T_c$  for this compound is directly correlated

with an increase in the  $c$  axis length (controlled by oxygen concentration) [5], but instead suggests that both the cell length and degree of short range order play a role in the superconducting state of the sample.



**Figure 2.** Atomic pair distribution function (PDF) experimentally determined by pulsed-neutron diffraction for  $Tl_2CaBa_2CuO_6$  at 100 K: superconducting sample with  $T_c = 65$  K (solid line); non-superconducting sample (dotted line).

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