Short-Range Ordering Due to Displacements of Thallium and Oxygen Atoms in Superconducting $Tl_2Ba_2CaCu_2O_8$ Observed by Pulsed-Neutron Scattering

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The atomic positional correlations in superconducting $Tl_2Ba_2CaCu_2O_8$ were studied by pair-distribution-function analysis of the pulsed-neutron scattering data. The results show for the first time strongly correlated local displacements of both thallium and oxygen atoms in the Tl-O plane from the high-symmetry crystallographic sites. As a consequence of the displacements Tl atoms form chains or pairs accompanied by displacement of nearby oxygen atoms, resulting in locally orthorhombic order. The ordering, however, remains very much short range and does not alter the average symmetry. The implications of these results with regard to the superconductivity of these oxides are discussed.

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The crystal structures of superconducting $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n=1$, 2, and 3), which show a critical temperature up to 125 K,[1-4] have been studied by x-ray and neutron diffraction measurements, and the crystal symmetry, lattice constants, and average atomic positions are well known.[4-8] However, the temperature factors in these compounds as determined by single-crystal studies or by the Rietveld powder-diffraction analysis were found to be anomalously large, particularly for Tl and O atoms in the Tl plane.[5-8] Such large thermal factors are usually the consequence of random or incommensurate static atomic displacements, which cannot be readily treated by conventional crystallographic approaches which presume lattice periodicity. These local structural variations are best studied by local probes such as the extended x-ray-absorption fine structure or the atomic-pair-distribution analysis of the diffraction data.

The method of atomic-pair-distribution analysis has so far been almost exclusively used for the structural studies of amorphous materials, but it has recently been shown that this method is useful in studying more ordered solids such as quasicrystals[9-11] or disordered crystals.[12] In this method the atom-atom interference function, $S(Q)$, where Q is the scattering vector, is determined from the total scattered intensities from the sample including the diffuse scattering, and is then Fourier transformed to obtain the atomic pair distribution function (PDF), $\rho(r)$.[13,14] Because of experimental limitations $S(Q)$ can often be measured only up to a limiting value of Q. The requirement of termination at $Q_{\max}$ brought some notoriety to the method because it produces spurious oscillations generally known as termination errors. However, the pulsed-neutron spallation source allows $S(Q)$ to be determined up to large values of Q, as a result of the high intensities of epithermal neutrons,[14,15] thus minimizing termination errors. Our tests on powdered crystalline Al and Si showed that the PDF's thus determined are quite accurate over wide ranges of r.[10,16] Using this method we have previously examined the structure of $La_{2-x}(Sr,Ba)_xCuO_4$, and found that some oxygen atoms are locally displaced in a symmetry-breaking manner even in the tetragonal phase.[17] In this article we report the first observation of the displacive atomic short-range ordering in superconducting $Tl_2Ba_2CaCu_2O_8$.

The pulsed-neutron scattering experiments were carried out at the general-purpose powder-diffraction station of the Intense Pulsed Neutron Source of Argonne National Laboratory, with use of the time-of-flight mode. About 5 g of powdered $Tl_2Ba_2CaCu_2O_8$ was sealed in a thin-wall vanadium sample container with He gas, and cooled by a Displex closed-cycle refrigerator. The scattering data were corrected for the source spectrum, background scattering, sample absorption, multiple scattering, inelastic scattering (Placzek correction[18]), and incoherent scattering to obtain the total structure factor, $S(Q)$, up to $Q_{\max}=30$ Å^{-1}. A weak damping in the form of $(\sin x)/x$, where $x=\pi(Q-Q_{\max})/(Q_d-Q_{\max})$, was applied beyond $Q_d=20$ Å^{-1} to $S(Q)$ in order to reduce the effects of noise and termination at 30 Å^{-1}. We have tested various values of $Q_{\max}$ and damping functions to assess the reliability of the Fourier-transformation process, and found that the results are only very weakly dependent on the termination schemes. In the time-of-flight method $S(Q)$ is the integral of the energy-dependent structure factor $S(Q,\omega)$ over ω, up to the energies of the incident neutrons which are up to about 0.5 eV at high values of Q, within the accuracy of the Placzek correction. Thus our PDF describes a nearly instantaneous atomic correlation. The sample contained a small amount (few %) of impurity phases identified by extra peaks as described in Ref. 8; however, their effect is believed to be negligible.

Figure 1 shows the PDF of $Tl_2Ba_2CaCu_2O_8$ obtained at $T=17$ K (curve 1). The peak positions and the apparent coordination numbers are listed in Table I. We first compared this PDF with the PDF calculated from the structure determined by the Rietveld method, assuming that all oxygen atoms are at high-symmetry (4*mm*) points (curve 2). The intensities of the calculated PDF were weighted by atomic neutron-scattering lengths, and were broadened by a Gaussian function to account for the effects of zero-point atomic vibration and termination at $Q_{\max}$. The standard deviation of the Gaussian peak width, σ, was chosen to fit to the first peak (Cu-O distances) reasonably well (0.082 Å), corresponding to a Debye temperature of about 500 K. It is quite clear that the agreement is rather poor, and small changes in the Gaussian peak width could not reconcile the differences. In particular the peak at 2.75 Å which represents the Tl-O3 correlation is unreasonably high. Here the notation for the atomic positions follows Refs. 5–8.

In order to improve the agreement the authors of Refs. 5–8 shifted the O3 position by about 0.4 Å randomly along the four ⟨100⟩ directions. The PDF calculated for such a structure (curve 3) shows much better agreement, and the height of the peak at 2.75 Å has been significantly reduced. On the other hand, other peaks, for instance the group of peaks at 3–3.7 Å, show serious disagreement. One also notices that the peak at 3.85 Å, which represents the translation along the cyrstallographic *a* axis, is much higher for the curves 2 and 3 than for the curve 1. This observation suggests that not only O3 atoms but others, most probably Tl atoms which also show large temperature factors, must be displaced from the 4*mm* symmetry points. Indeed when Tl atoms as well as O3 atoms are displaced the PDF peak at 3.85 Å shows much better agreement with the curve 1. This conjecture is reasonable in view of the attraction between Tl and O3 atoms and the very short Tl-O2 distance present in Refs. 4–8. As pointed out in the earlier works the most likely origin of the large shift of O3 atoms is the mismatch between the atomic distance imposed by the lattice structure (2.73 Å) and the ideal atomic distance given as the sum of the ionic radii (2.28 Å).[4–8,19] This situation is very similar to the one we encountered earlier in $La_{2-x}(Sr,Ba)_xCuO_4$.[17] Therefore as O3 atoms are shifted from the high-symmetry positions as a result of attraction by Tl atoms, it is most reasonable to assume that Tl atoms also become displaced from the high-symmetry positions.

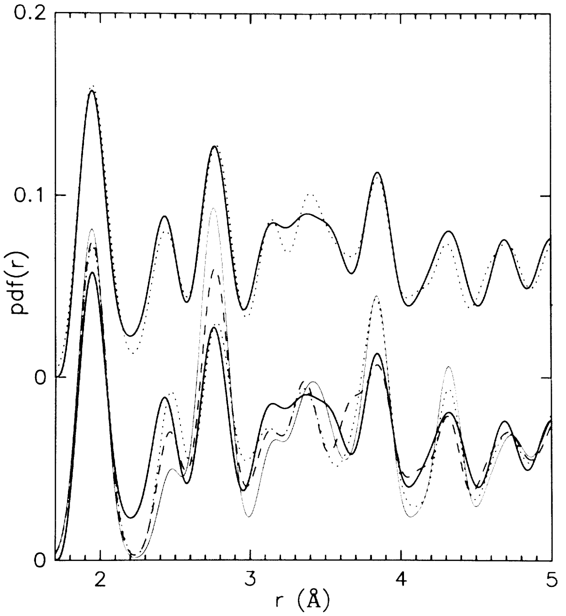

FIG. 1. Atomic pair distribution function of $Tl_2Ba_2CaCu_2O_8$: (Curve 1) experimentally determined by pulsed-neutron scattering (thick solid line, lower and upper plots), (2) PDF calculated for a structure with Tl and O atoms at high-symmetry (4*mm*) positions (thin solid line, lower plot), (3) PDF calculated with O3 atoms displaced randomly by 0.4 Å in ⟨100⟩ directions (dashed line, lower plot), (4) PDF with Tl and O3 atoms randomly displaced by 0.2 Å along ⟨100⟩ directions (dotted line, lower plot), and (5) PDF calculated from the model with local ordering of O3 and Tl atoms as shown in Fig. 2(a) (dotted line, upper plot). The PDF computed from the model in Fig. 2(b) is almost identical to this last curve.

Another important source of discrepancy is the assumption that the direction of the displacement of O3 is randomly chosen at each location among the four. This assumption is difficult to accept because the Coulombic interactions among the ions are not likely to be completely screened. Furthermore, when both O3 and Tl atoms are randomly displaced from the high-symmetry positions by 0.2 Å (curve 4 in Fig. 1), the PDF peaks in the range of 2.3 to 3.7 Å show very poor agreement with the experimental PDF. Agreement cannot be improved

TABLE I. Data on peaks of the PDF of $Tl_2Ba_2CaCu_2O_8$ up to 4 Å.

Peak position (Å)	Coordination number[a]	Range of integration (Å)	Composition of the peak
1.93	1.79	1.71–2.22	Cu-O1,Tl-O2, Tl-O3
2.44	1.57	2.22–2.58	Ca-O1,Tl-O3
2.75	2.97	2.58–2.95	Ba-O2,Tl-O3, O1-O1,O3-O3, Cu-O2
3.15 3.38	7.70	2.95–3.67	Cu-Ca,O1-O2, Cu-Ba,Cu-O1 and others
3.85	5.59	3.67–4.05	All-themselves

[a] The coordination number is given by integrating $4\pi r^2 \rho(r)$ over the range of integration indicated, and therefore is weighted by neutron-scattering lengths.

by changing the magnitudes of the displacements. This strongly suggests that the displacements are correlated.

We have examined a number of ordered structures with expanded unit cells, and carried out a Monte Carlo simulation to find structures of whose PDF would replicate the observed PDF. We found that the best agreement was obtained when both Tl and O3 atoms are displaced approximately along the ⟨110⟩ direction ($\Delta x = 0.23$ Å, $\Delta y = 0.22$ Å, $\Delta r = 0.32$ Å for Tl; $\Delta x = 0.29$ Å, $\Delta y = 0.22$ Å, $\Delta r = 0.37$ Å for O3) forming zig-zag chains of Tl atoms, as shown in Fig. 2. To our pleasant surprise, this results in a Tl-O3 distance of 2.39 Å, close to the expected value of 2.28 Å.[19] Two structures which differ in the positions of the O3 atoms [Figs. 2(a) and 2(b)] were found to result in very similar PDF's (curve 5 in Fig. 1), both of which are in excellent agreement with the experimental PDF. These two structures have orthorhombic symmetry with unit cells which are $\sqrt{2} \times \sqrt{2}$ times the original tetragonal cell; therefore they should produce superlattice diffraction peaks. However, we do not see such superlattice diffraction,[20] and hence we have to conclude that this ordering is only short range. Our conclusion is indeed consistent with a recent electron microscopy result which shows short-range structural modulations that are sensitive to heat treatment.[21,22] A related material, the single-layer Cu compound, $Tl_2Ba_2CuO_6$, has recently been reported to exist in both tetragonal and orthorhombic symmetries.[23]

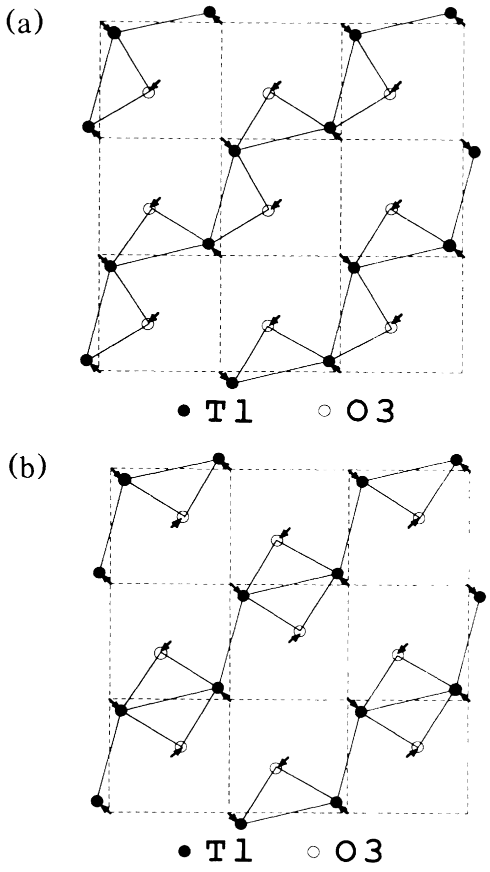

FIG. 2. The displacements of Tl and O3 atoms from the high-symmetry sites in the Tl-O3 plane for two idealized configurations. The ordering, however, is only short range, and the real stucture is most likely the random mixture of these two configurations (see text).

It should be noted that the two structures in Fig. 2 are different only with respect to the positions of O3 atoms. The nearest-neighbor environment for these two O3 sites are totally equivalent, as shown in Fig. 3. Therefore it should cost relatively little energy for O3 atoms to move from one site to the other, thus locally switching from the Fig. 2(a) configuration to the 2(b) one, and vice versa. In other words the O3 atoms are nearly frustrated and are likely to occupy these two positions nearly randomly, resulting in a mixture of both structures. The same situation applies to Tl atoms. This explains why the local ordering in Fig. 2 does not develop into long-range order. Further improvement of the model presented here requires direct information regarding the chemical nature of each peak. In our Rietveld refinements, allowing Tl to shift from the high-symmetry position produced a 40% reduction in the Tl thermal factor. However, in contrast to the PDF studies, our Rietveld refinements showed little sensitivity to different disorder models.

The local ordering of Tl and O atoms strongly suggested by the present PDF study has many implications with respect to the origin of superconductivity in these oxides. First, Tl atoms now have four close oxygen neighbors, which is observed[24-26] for Tl^{3+} ions in several compounds. However, the environment is strongly distorted from either square planar as in $Sr_4Tl_2O_7$ (Ref. 25) or tetrahedral as in $Ba_2Tl_2O_5$,[26] suggesting that the holes may be delocalized, resulting in an enhanced metallic nature of the Tl valence electrons. The disorder introduced by the short-range nature of the ordering is also likely to affect the charge fluctuations between the Tl

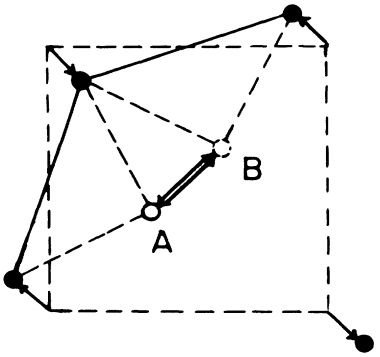

FIG. 3. Local frustration of an O3 atom. At either position the O3 atom is in contact with two Tl atoms. The motion of an O3 atom from A to B results in the local structure of Fig. 2(a) switching to 2(b) or vice versa.

plane and Cu plane.

A second view is that the local ordering of Tl and O3 atoms would produce some pairing potential for electrons at Cu atoms. This may affect the possibility of forming the resonating-valence-bond (RVB) state[27] in the Cu sheet. As a result of local ordering the local symmetry is no longer tetragonal. This breaking of symmetry unbalances the RVB patterns and makes resonance among them more difficult, since it provides a template for forming localized valence bonds, but lowers the classical ground-state energy of the fully localized state. If the off-diagonal coupling among the different patterns is strong enough, the RVB state may still be achievable, which would make the RVB state more preferred over the normal metallic state.

Yet another possibility is that the structural fluctuations among the nearly degenerate states such as the ones shown in Fig. 3 may couple directly to electrons to produce superconducting pairs. Inelastic tunneling of oxygen atoms can provide a coupling mechanism with energies not bound by the Debye frequency as in the case of phonons.[28] Although the probability of O3 atoms tunneling over such a relatively long distance appears rather small, the frequent presence of local structural frustrations in high-T_c oxides suggests a strong possibility that structural frustrations play a direct role.

In conclusion, the PDF study of $Tl_2Ba_2CaCu_2O_8$ using pulsed-neutron scattering strongly suggests short-range ordering due to displacements of Tl and O in the Tl-O plane, which provides interesting insights regarding the mechanisms of superconductivity in this solid. We are currently analyzing the medium range (5–20 Å) correlations and the temperature dependence of these correlations.

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