Local structural change close to $T_c$ in Nd$_{2-x}$Ce$_x$CuO$_{4-y}$

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A pair distribution function (PDF) analysis of pulsed neutron powder diffraction data has been carried out to investigate the local atomic structure of Nd$_{2-x}$Ce$_x$CuO$_{4-y}$, $x=0.165$, over a range of temperatures close to $T_c$ ($T_c \approx 20$ K). Simulation of the PDFs using structural models indicate that, at all temperatures up to 50 K, the local atomic structure is significantly distorted from the $T'$ structure. Both O(1) (in-plane) and O(2) (out-of-plane) oxygen atoms are displaced from their average sites. Furthermore, stronger evidence of a structural modification occurring between 15 and 40 K. Such a change is not observed in a non-superconducting $x=0.2$ sample down to 10 K, which suggests that this modification may be connected with the superconductivity.

Introduction

A characteristic of all the high-$T_c$ superconducting (HSC) cuprates is the complexity of their crystal structures [1-7]. Large unit cells are required to describe them, and even then crystal structure refinements indicate that significant amounts of disorder are present. Large, temperature-independent B-factor reported in all these materials [8]. To characterize this disorder, techniques sensitive to local structure have been used, including the pair distribution function (PDF) analysis of neutron powder diffraction data. This technique is a very sensitive probe of atomic arrangement on length scales up to 10 Å or more [9].

A study on Tl$_2$Ba$_2$CaCu$_2$O$_{8+}$ (Tl:2212) has determined that thallium and oxygen atoms are displacing from their average positions in the rocksalt intergrowth layer [10]. The displacements form a locally ordered structure. A further study of this material has detected ordered displacements of the copper and oxygen atoms associated with the CuO$_2$ plane [11]. There is evidence that the nature of these displacements changes close to the superconducting transition temperature, $T_c$. These changes were not observed in Rietveld analyses and thus must be short range and nonperiodic in nature. Similarly the structure of the high-temperature tetragonal phase in La$_2$Sr$_{2}$CuO$_4$ (La:214) was found to be locally orthorhombic by the same technique [12]. The long-range tetragonality is due to orientational fluctuations of the local orthorhombic units.

We have studied the local atomic structure of the n-type superconductor Nd$_{2-x}$Ce$_x$CuO$_{4-y}$ [13,14] using the PDF analysis of neutron diffraction data. It exhibits local atomic arrangements that deviate significantly from the $T'$ [15] structure. Furthermore, we have noticed a temperature dependence to this local structure which may be associated with the superconductivity. A change in the PDF is seen to occur at a temperature just above $T_c$ in a superconducting $x=0.165$ sample. The same structural modification was not observed in a very closely related but non-superconducting $x=0.2$ sample. The local structure of the $x=0.2$ sample, at temperatures down to 10 K, agrees well with that of the $x=0.165$ sample above 40 K.
2. Experimental

Nd$_2$Co$_{1-x}$Cu$_{x}$O$_{4+y}$ samples were prepared by solid state reaction from Nd$_2$O$_3$, CoO, and CuO. The powder mixtures were fired in alumina boats at 1800°C for up to 40 h, after thorough mixing and grinding process in a ball mill, then quenched to room temperature on a cold copper plate. Two compositions were prepared with x=0.165 and x=0.2. The x=0.165 composition has close to the maximum $T_c$ for this system and phase diagram studies indicate that it is the only superconducting composition which is not multiphase [16]. x=0.2 was chosen for comparison because it is very close in composition to the x=0.165 sample yet exhibits no superconductivity. It can also be prepared as a single phase [16]. Both of these were quenched by heating for 16 h at 900°C in flowing high-purity argon gas which had passed through a hydroxy purifier, giving an oxygen partial pressure of less than 10$^{-5}$. The samples were characterized by neutron diffraction and seen to be single phase. AC susceptibility measurements indicated that the x=0.165 sample exhibited a superconducting transition at 22 K. $T_c$ was taken as the onset of diamagnetism in a 1 G field. The x=0.2 sample showed no transition down to 4.5 K. Zero-field cooled diamagnetic susceptibility measurements indicated a full superconducting fraction for the x=0.165 sample.

Neutron powder diffraction experiments were carried out using the special environment powder diffractometer (SEPDD) [17] of the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. The samples were sealed with He exchange gas in a vanadium can and cooled by a dipole closed loop helium refrigeration. Data were collected from the x=0.165 sample at 10, 20, 25, 30, 40 and 50 K, and from the non-superconducting x=0.2 sample at 10 and 40 K. After each recording the sample was allowed to equilibrate for half an hour before data collection began. In order to achieve the desired statistics on the data, collection times were in excess of 4 h per temperature. The temperature of the dipole cold head was stable to within ±0.5 K. Data were collected out to Q=35 Å$^{-1}$, where $Q=|Q|$ is the scattering vector, ($Q=4\pi \sin \theta / \lambda$). The PDF analysis was carried out was followed. The structure factor, $S(Q)$, is determined from the data by normalizing the intensity with respect to the incident flux. Corrections are then applied for background, detector efficiency, sample absorption and multiple scattering. An inelasticity correction is also applied using the method of Planck [18]. The PDF, $\rho(r)$, is recovered by Fourier transforming the structure factor according to

$$\rho(r) = \frac{1}{2\pi r} \int S(Q) \cos Qr \, dQ,$$

where $\rho$ is the mean number density of the material.

In order to minimize the effect of systematic errors that may be introduced during the processing, care was taken to analyze each data set the same way. This analysis procedure has been tested on data from known structures and the systematic errors were determined to be of the same magnitude or smaller than the random errors [19]. Since we will be comparing PDFs, each analyzed in an identical fashion, the effect of systematic errors can be ignored. An estimate of random errors on the PDF is made by propagating the errors due to random counting statistics in the PDF errors. All of the values of $\sigma$ quoted are the estimated standard deviations (ESD) determined in this way. They describe the uncertainty in $\rho(r)$ due to random counting fluctuations. The points in the PDF are not independent variables and errors are correlated from point to point. However, the error calculated on each point is an accurate estimate for that point, coming as it does from the direct error propagation procedure.

3. Results

Initially the PDFs from the data were compared to the simulated PDF of the T' structure and a number of significant differences were observed. The PDF of the T' structure is shown superimposed on x=0.165, T=40 K data in fig. 1(a) over a range of r. Results of the preliminary model indicate that oxygen is displacing from both Fe-O site in the CuO$_2$ plane and its out-of-plane O(1). There is little evidence of significant displacement of copper from its average site in the CuO$_2$ plane and displacements of the rare-earth ions introduce a worse fit of simulated PDF to data. Differences of O(1) and O(2) along the z-direction ≤0.1 Å improved the fit of the simulated PDF.
applied for background, detec-
tion, and multiple wave-
correction and multiple wave-
correction is also applied us-
est [18]. The PDF, \( p(r) \), is
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terature of the material, the effect of systematic er-
er during the processing
log error in the data. Furthermore, in-plane displace-
ents of O(1) of up to 0.1 Å, both parallel and perpen-
dicular to the Cu-O-Cu bond, also gave an improved fit. The data indicate that displacements of O(2) parallel to the Cu-O(1) plane may also be occurring. For example, fig. (2) shows the same data as fig. (1a) but this time the superposed PDF is from a distorted T structure with displacements of O(1) along \( \tau \) of 0.03 Å, O(2) along \( \tau \) by 0.09 Å and O(1) in-plane and per-
dicular to the Cu-O(1)-Cu bond by 0.08 Å. For simplicity, the current modelling assumed that displace-
ments were random from one site to the next.

Actually, atoms are displacing collectively. For in-
stance, the O(1)-O(2) nearest-neighbour correla-
tion in the PDF is very well defined. This indicates that the O(1) and O(2) vertical neighbours are dis-
placing together. The resulting, locally ordered, dis-
placement structure has not been determined in detail. Research on this is in progress.

The PDFs of the superconducting \( x = 0.165 \) sample were then compared as a function of temperature
ness, if any modification in structure is evident. Ex-
amples of the PDFs for data taken at 30, 30 and 10 K are shown in fig. 2. The overall correspondence is good. However, significant changes \( > 2\sigma \) are evi-
dent at a number of peaks in various regions of \( r \). This suggests that some structural modification is

\[
(2) - 11 \cos Qr dQ
\]

occurring. Any small change in structure will affect
the PDF in a complicated way. For instance, a shift
in the PDF, say O(2), will change each Cu-O(2),
(Nd,Co)-O(2), O(1)-O(2) and O(2)-O(2) corre-
cation throughout the PDF. It is seen that certain sections of the PDF show much clearer changes
than others. This depends on the balance of changing
and unchanging atom-atom pair vectors contributing
to that feature. It is the "susceptible" regions of the PDF
that we will concentrate on.

Figure 3 shows PDFs for the \( x = 0.165 \) sample at temperatures 50, 40, 30 and 20 K over the range
\( r = 3.8-5.0 \) Å. To test the significance of changes in
\( p(r) \) a function \( \Delta p \) has been defined as
\( \Delta p(r) = p(r) - p_{ref}(r) \). When plotted as a function of temperature in the inset, two points are chosen
in \( p(r) \) corresponding nominally to the peak and
the valley of a certain feature in the PDF that is seen
to be changing. The error bars on these points correspond to \( \pm \sigma \) where \( \sigma \) is propagated from
the random error in the data. The values of \( r_{max} \) and \( r_{min} \) are indicated by arrows in the figure. The inset in fig. 3 indicates that a change of greater than 2\( \sigma \) can be seen in \( p(r) \) occurring between 30 and 40 K. Below 30 K
the PDF does not show any further significant
change. This change can be seen by eye in \( p(r) \) itself.
The features between 4.1 and 4.5 Å broaden and
change phase going from 30 to 40 K. Further evi-
Fig. 3. PDFs from the x=0.165 sample for temperatures in the range 10° to 50° K on an expanded r scale. The inset shows Δρ(r), as defined in the text, for r1=4.37 Å, r2=4.25 Å. The arrows in the figure indicate the positions of r1 and r2. Error bars in the Δρ(r) function correspond to 1σ.

Fig. 4. PDFs in the range r=6.8-8.0 Å for the x=0.165 sample at various temperatures as indicated. The inset shows Δρ(r) for r1=7.31 Å, r2=7.47 Å. The arrows in the figure indicate the positions of r1 and r2. Error bars in the Δρ(r) functions correspond to 1σ.

Evidence of change can be seen in the shoulder on the peak around 4.6 Å which gradually becomes more pronounced on cooling from 50° to 30° K at which temperature it stabilises. Similar behaviour can be seen on features throughout the PDF. In fig. 4 the same analysis has been applied to the region 6.8-8.0 Å. Again the Δρ test indicates that the low-temperature and high-temperature structures are different. This time however the discontinuity occurs between 25 and 30° K rather than between 30 and 40° K. Similar behaviour is observed in the region 15.4-16.0 Å as shown in fig. 5. In this case a definite shift in intensity can be seen; the peak centered at 15.80 shifts to the right between 30 and 25° K.

Since the evidence suggests that a structural modification is occurring at temperatures just above 7° K in this material it is of considerable interest to know whether this structural instability is related to the superconductivity. The PDFs of the non-superconducting x=0.2 sample were thus compared at the temperatures 40° and 10° K. The PDF in the range 1.8-6.0 Å is shown in fig. 6. The structures of the x=0.2 and x=0.165 samples are very similar as can be expected. There is a smaller overall variation in PDF as a function of temperature in the x=0.2 sample than the x=0.165 sample. Over the range 3.5-20° K the root-mean-square difference in ρ(r) between the 10° and the 40° K data is 24% higher in the x=0.165 sample than in the x=0.2 sample. The same susceptible regions of the PDF that were considered in the x=0.165 sample were again analysed. The region 3.8-5.0 Å is reproduced in fig. 7. The dotted inset is the 40° K data of the x=0.165 sample which is included for comparison purposes. The Δρ results for the x=0.2 sample are in the inset to fig. 7, with error bars imposed on the results from the x=0.165 sample. They indicate that there is no significant change.
between 30 and 40 K. Similarly, in the region 15.4-16.0 K a definite shift in the centroid of 15.80 shifts 2.2 K.

The PDFs of the x=0.2 sample at 80 K and 10 K are shown in fig. 1 and 2, respectively. These compositions show no superconducting transitions. Comparison with fig. 3 shows no structural modification in the x=0.165 sample. The shifted PDFs for the x=0.2 sample show a clear superconducting transition at 15.8 K, with the onset at 16.0 K.

4. Discussion

The structures of Nd_{2-x}Ce_xCuO_4 (x=0.165, 0.2) deviate locally from the T structure. The exact arrangement of atoms is yet to be determined. It is likely that the atom displacements are correlated giving rise to a locally ordered structure which, when periodically averaged, reproduces the T structure. Detailed modelling is currently in progress to find structural models that agree well with the observed PDF. However, we do know the main features of the distortions and their perpendicular and
parallel to the CuO₆ planes. Perpendicular displacements of O(1) have been observed in other cuprates. O(1) and O(4) are seen to displace along the z-direction in Tl₂212 [10]. Perpendicular displacements of O(1) and displacements parallel to the CuO₆ plane of the apical O(2) in La₂14 [4] give rise to a tilting of the CuO₆ octahedra [7, 12]. A joint study, using PDF analysis and lattice energy minimisation calculations of Cu₆O₂Sn₃CuO₆, indicates that even the structure made of infinitely stacked CuO₆ planes with no intergrowth is unstable with respect to such a distortion [20]. Extended X-ray absorption fine structure (EXAFS) studies have also seen a change in the Cu-O(4) bond distance in YBa₂Cu₃O₆₊ₓ, as a function of temperature which could be explained by a motion of the apical oxygen perpendicular to the CuO₆ plane [21, 22]. In the Nd₂₋ₓCeₓCuO₄₋ₓ system, a tight-binding and Mulliken energy calculation [23] predicts a tendency for the copper ion to assume a more tetrahedral coordination with increased doping with electrons. This could come about by collective displacements of O(1) perpendicular to the CuO₆ plane.

The PDF indicates that O(1) and O(2) may also be displaced parallel to the CuO₆ plane. In-plane displacements of O(1) in directions both parallel and perpendicular to the Cu–O–Cu bond yield an improvement in fit to the observed PDF. In-plane displacements of oxygen have not been reported before in the other HTSCs. However, this structure is distinguished from the other HTSCs by the fact that the out-of-plane oxygen resides directly above the in-plane O(1) rather than in the apical position above copper. Thus an in-plane displacement of O(1) may help to accommodate O(2), especially if it is itself displacing along the z-direction. Reichardt [24] has reported a softening of the phonon mode associated with rotation of the CuO₆ squares around the z-axis. Such an instability is consistent with the in-plane displacements observed in our experiments.

The presence on 1-in-3 Nd sites of a small, positively charged cerium ion will also contribute to the disorder of the lattice. However, it is unlikely that this is the only contribution to the observed disorder. It is not clear how the structural change which occurs around 30 K could be explained if the relaxation around the dopant ions is the only driving force for a distortion. The temperature dependent features in the PDF all have large contributions from atom-atom correlations involving O(1) and O(2). Thus, it is likely that the structural modification that occurs around 25–30 K is associated with displacements of these ions. It may simply involve a change in the detailed ordering of the atom displacements, or the nature of the displacements themselves may be modifying.

5. Conclusions

We have produced the PDFs for Nd₀.₇₅Ce₀.₂₅CuO₄₋ₓ (x=0.165, 0.2) from neutron powder diffraction data. Simulation of the PDFs from model structures indicate that the true atomic arrangement differs locally from the average Tc structure in both samples at all temperatures up to 50 K. The distortion involves displacements of O(1) in the plane in conjunction with O(2) and O(1) displacing along the z-direction. The magnitude of the displacements is of the order of 0.05 Å. The real structure is of locally ordered atom displacements with a lower symmetry than the average structure, but the details have not been determined.

We have seen evidence of a modification to the local structure of Nd₀.₇₅Ce₀.₂₅CuO₄₋ₓ (x=0.165) occurring just above Tc. The same change is not evident in a non-superconducting x=0.2 sample down to 10 K which indicates that this structural modification is somehow connected with superconductivity.

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References

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