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Development of Pair Distribution Function Analysis

Robert Vondreele*, Simon Billinge, George Kwei, and Andrew Lawson

Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). It has become increasingly evident that structural coherence in the CuO_2 planes of high- T_c superconducting (HTSC) materials over some intermediate length scale (in the nanometer range) is important to superconductivity. In recent years, the pair distribution function (PDF) analysis of powder diffraction data has been developed for extracting structural information on these length scales. This project sought to expand and develop this technique, use it to analyze neutron powder diffraction data collected at the Manuel Lujan Jr. Neutron Scattering Center (LANSCE) and elsewhere, and apply it to problems of current scientific interest. In particular our interest is in the area of high- T_c superconductors, although we planned to extend the study to the closely related perovskite ferroelectric materials and other materials where the local structure affects the properties where a detailed knowledge of the local and intermediate range structure is important. In addition we planned to carry out single crystal experiments to look for diffuse scattering. This information augments the information from the PDF.

1. Background and Research Objectives

It has become increasingly evident that structural coherence in the CuO_2 planes over some intermediate length scale (in the nanometer range) is important to superconductivity [1]. A number of recent studies [2, 3] have indicated that small displacements of oxygen may accompany the appearance of superconductivity in the high- T_c superconducting (HTSC) materials. The pair-distribution-function (PDF) analysis of powder diffraction data pioneered by Egami and coworkers indicate that these displacements of oxygen persist at all temperatures [3]. However, close to T_c the local correlations between the displacements change, indicating that the detailed ordering of the displacements is important for the appearance of

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superconductivity. In general the order does not extend over long range and thus does not give rise to an easily detectable superlattice in a powder diffraction pattern, thus crystallographic analyses of such data are unable to characterize these important locally-ordered structures. Displacements of atoms from their crystallographic sites lead to a reduction of intensity of the Bragg peaks and to an increase in the diffuse scattering signal. If these displacements are locally ordered, the diffuse scattering will have a structure and the local structure can be extracted with PDF analyses. Similar behavior has also been observed in a wide variety of displacively transforming materials, including metals, perovskites and ferroelectrics [4] and are thought to play an important part in the unique physical properties they display. The analysis of diffraction data from nanocrystalline materials has traditionally only focused on the Bragg scattering. Since much of the scattering from these materials is expected to be diffuse, PDF analysis of both Bragg and diffuse scattering should reveal much more about the structural organization of these increasingly important materials. In this project, we planned to use PDF analysis to study the mesoscale structure of nanocrystalline materials.

However, the PDF analysis of powder diffraction data still has limitations in that it leaves a fair amount of leeway in modeling the structural distortions. Analysis of single crystal data is essential to a more complete understanding of the short range structural behavior in the 124 cuprate superconductors and in ferroelectric materials such as BaTiO₃. In this project, we sought to develop analysis techniques for single crystal diffraction data to study these structural instabilities.

We sought to develop techniques of pair distribution function analysis of single crystal diffraction data to better understand mesoscale structural instabilities and coherence in heavy fermion systems and perovskites, including ferroelectrics and high temperature superconducting materials. These materials have been the focal center for a great deal of experimental and theoretical work in solid state physics and materials science in the past decades but the structural instability and coherence inherent in these materials have not been easily accessible through other techniques [4]. The emergence of PDF analysis and its success in elucidating local structural changes in HTSC materials now provides the opportunity to address these problems [5]. Our goal was to understand the relationship between local structure and the properties of these important classes of materials. We also sought to apply PDF techniques to the study of the structure of nanocrystalline materials.

2. Importance to LANL's Science and Technology Base and National R&D Needs

In addition to the above work, we have done a great deal of work on the cation ordering and oxygen stoichiometry in the high temperature superconductors that has led to a much better understanding of the role of hole doping by cation substitution and by superoxygenation. In pursuing this work, we have begun strong collaborations with scientists at Dupont, the International Superconductivity Technology Center (Japan), and Sandia National Laboratories. These collaborations, pursued independently of later agreements, strengthen the efforts to establish formal collaborative ties in an area that is important to the Laboratory mission. This project supports a Los Alamos core competency in nuclear and advanced materials. Finally, our research takes advantage of the two types of user facilities, neutron and synchrotron sources, strongly supported by DOE, and establishes a new area of research that has made strong contributions to science and to the credibility of these facilities.

3. Scientific Approach and Results to Date

We proposed to study the local structure of the prototypical ferroelectric material BaTiO_3 and the important HTSC materials $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ and $\text{La}_2\text{CuO}_{4+\delta}$ in order to better understand the role that structural instabilities and structural coherence play in determining the properties of these materials. We also planned to adapt PDF techniques to the study of the mesoscale structure of nanocrystalline materials.

The structural instabilities in these systems make them ideal systems for the application of PDF analysis of powder diffraction data to study the local structure [5]. This technique, involving the Fourier transformation of single crystal diffraction data, is unique in its ability to yield direct information about mesoscale structure. Using this technique with powder diffraction data, Egami and coworkers [5] have been able to learn about the detailed arrangement of atoms on length scales from nearest neighbor up to around 40 Å. In the HTSCs the local and intermediate range structure is markedly different from the average long range structure and this type of study is an important complement to conventional crystallographic structure studies.

A. BaTiO_3 . We proposed to study the local structure of BaTiO_3 using pair-distribution-function analysis of neutron single crystal diffraction data. BaTiO_3 is the first perovskite ferroelectric discovered and perhaps displays the most dramatic assortment of structural instabilities of this family of materials [6]. Above 400 K, the structure is cubic. When cooled below 400 K, BaTiO_3 undergoes a series of phase transformations, to tetragonal, then to orthorhombic, and finally to rhombohedral. Comes, et al.[7], based on the analysis of diffuse x-ray scattering, have suggested that the Ti ion sits off-center along equivalent $\langle 111 \rangle$ directions in all phases: at rest in the low-temperature rhombohedral phase, and motionally

averaged between two equivalent $\langle 111 \rangle$ directions in the orthorhombic phase, four in the tetragonal phase, and all eight $\langle 111 \rangle$ directions in the high temperature cubic phase.

We proposed to study the short range structure of BaTiO_3 for the three low temperature phases using PDF analysis of neutron powder diffraction data. The high temperature cubic phase would require the added complication of a furnace and would be saved for a future experiment. Since the oxygen atoms were nearly invisible in the earlier x-ray studies [7] and since they participate strongly in the local structural changes, we expected results from these studies to provide a much more detailed picture of the structural instabilities in BaTiO_3 . At the same time, there is now a wealth of information about the structural instabilities in BaTiO_3 from other techniques, and the information we obtained should help provide a much clearer picture of what is going on.

B. $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$. Recent experiments [3] using the pair-distribution-function analysis of neutron powder diffraction data from $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ indicate that the local atomic structure changes with the appearance of superconductivity. A sample with cerium content $x = 0.165$, which exhibited bulk superconductivity with an onset temperature of $T_c = 22$ K, exhibited significant changes to the local structure at a temperature of 30 K. In an isostructural but nonsuperconducting sample with $x = 0.2$, there was no evidence of any structural change at all down to 10 K. Thus, there is a very close relationship between the appearance of superconductivity and the observation of the structural change. Egami and coworkers [5] have seen similar modifications to the local structure, at temperatures close to T_c , in superconducting samples of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. This leads us to believe that the local atomic structure is important to the superconductivity of these materials.

Billinge, et al. [3] carried out careful structural modeling from the $\text{Nd}_{1.835}\text{Ce}_{0.165}\text{CuO}_{4-y}$ data. This work indicated that, both above and below T_c , the local atomic structure is considerably different from the tetragonal crystal structure. Oxygen ions are displaced significantly from their ideal crystallographic positions. These displacements give rise to a buckling of the CuO_2 plane. As the temperature is lowered through T_c , the nature of this buckling changes. At low temperature, the CuO_2 plane appears to form into microscopic domains with two distinct local environments. Some regions of the plane are flat, while other regions are heavily buckled with oxygen displacements of approximately $\pm 0.12 \text{ \AA}$. The fact that this structural change is so closely associated with the appearance of superconductivity hints that it may be the result of a strong electron-lattice coupling.

It was thus of great interest to look at samples as a function of dopant levels, to see if the observed structural distortions can be correlated with the density of carriers present. The level of carrier doping can be varied by changing the concentration of cerium. It can also be

varied by changing the sample processing history as we will discuss. The PDF technique is a powerful tool to study this problem. The changes to the local structure outlined above are not visible in conventional crystallographic analyses because the atom displacements that cause them are not ordered over a long range. However, the PDF has proved a very sensitive probe of these locally ordered displacements. The PDF technique requires the collection of diffraction data, with good statistics, over a large range of Q , where Q is the diffraction vector, $Q = 4\pi\sin\theta/\lambda$. The PDF is obtained by a Fourier transformation of the sample structure function, $S(Q)$, which is deduced directly from the scattering intensity. The use of a pulsed source for our experiments is essential because it is the only source that provides a large flux of epithermal neutrons. These short wavelength neutrons provide the important information in the diffraction pattern at large values of Q .

We proposed the following experiments. The data already described was from identically processed powder samples with cerium content $x = 0.165$ and $x = 0.2$, taken at temperatures in the range 10 - 50 K. We proposed to collect single crystal diffraction data from similarly prepared samples of undoped Nd_2CuO_4 , and from samples with intermediate cerium contents of $x = 0.05$ and $x = 0.1$. Data were collected at 10 K and 40 K. The PDF's were then be compared as a function of cerium doping at these two temperatures. In this way we hoped to see in detail the way that the carriers affect the local structure.

$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ requires an anneal in a reducing atmosphere to exhibit superconductivity. However, careful analysis of sample oxygen contents indicate that the number of oxygen ions per unit cell is reduced by only approximately 0.02 as a result of the anneal [8]. This would change the average carrier concentration by no more than 0.04 per unit cell. Increasing the number of cerium ions per cell in an unannealed sample by 0.04 raises the nominal carrier concentration the same amount but does not produce superconductivity. The anneal must modify the sample in some important way that is not clear. Earlier Rietveld studies [8] showed no evidence of any structural change accompanying the anneal. However, we proposed to study the local atomic structure, using PDF, since the structure on a local level appears to be very important for superconductivity. Thus, we proposed to collect data from an "as prepared" and an annealed sample of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ with $x = 0.165$, at temperatures of 40 K and 10 K. This information helped us to understand which aspect of the local structure is necessary for the sample to sustain superconductivity. Furthermore, a comparison with the data from the undoped samples helped establish if this structure change was due to an increase in the carrier concentration.

C. $\text{La}_2\text{CuO}_{4+\delta}$. Recent studies by us [3] and other groups [2] indicate that the local atomic structure of HTSC materials may be important in the mechanism for superconductivity. In particular, earlier studies by us have seen changes to the local

arrangement of atoms in these materials. These changes can be closely associated with the appearance of superconductivity. For instance, the local structure of the n-type superconductor $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, $x = 0.165$, changed at around 30 K. Bulk superconductivity appeared in this sample at 22 K. A closely related but nonsuperconducting sample with a cerium content $x = 0.2$ had the same structure but it did not change at any temperature down to 10 K. We believe that these changes in the local structure are intimately involved in the superconductivity and that a detailed understanding of them will shed light on the mechanism of high temperature superconductivity.

When insulating, stoichiometric $\text{La}_2\text{CuO}_{4+\delta}$ ($\delta = 0.0$) is superoxygenated by annealing under high oxygen partial pressure, it becomes superconducting with $T_c = 40$ K. The nominal increase in oxygen content is found by weight-gain measurements to be no more than approximately 1% ($\delta = 0.04$). Careful diffraction studies indicate that the sample phase separates into a stoichiometric, insulating phase and an oxygen rich superconducting phase. However, even this latter phase can have no more than 4% excess oxygen in the structure. The disruption to the local structure of the insulating parent due to the presence of the charge doping species must be small, yet the sample changes from an insulator to a superconductor. This material provides a very stringent test of the condition necessary to support superconductivity in the HTSCs. It is thus of great interest to discover whether similar local structural changes, as were observed in the other HTSC materials, are observed in this material. Furthermore, understanding differences in the local structure between the superconducting and the insulating phase would give information about the role of atomic structure in the superconducting mechanism.

D. Nanocrystalline Materials. Nanocrystalline materials have recently become the focus of a lot of interest because of their possible technological applications. All structural characterization to date has involved the analysis of the Bragg scattering. Since most of the scattering intensity of these materials is in diffuse scattering, we planned to analyze both Bragg and diffuse scattering from nanocrystalline powders by applying PDF techniques to better understand the mesoscale structure of these materials.

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