Character of Order-Disorder and Displacive Components in Barium Titanate

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Reconciling the apparently contradictory results of NMR and x-ray absorption fine structure measurements on the ferroelectric perovskite $BaTiO_3$ gives insight into the character of the displacive and order-disorder components of the phase transitions of this material. The order-disorder component in the transition consists of local atomic displacements from cubic symmetry of constant magnitude that partially lose long-range order, while the displacive component consists of reorientation of these displacements.

Understanding structural phase transitions in the solid state is one of the central issues of condensed matter physics. The nature of ferroelectric phase transitions in perovskites has been intensely investigated over many decades since they are the simplest structure exhibiting this transition together with the importance of ferroelectricity as an interesting phenomenon with practical applications. This field has recently had a revival due to new experimental evidence that there is a significant order-disorder component present, which was in conflict with the then prevailing displacive theory as introduced by Cochran [1]. The most recent publication of this kind [2] showed evidence by NMR of the coexistence of both order-disorder and displacive components in $BaTiO_3$ in the tetragonal ferroelectric to cubic paraelectric transition. Yet, the details of the character of the two components have not been elucidated. In this Letter we determine the character of the two components for $BaTiO_3$.

Reference [2] is an NMR study of the Ti atom in $BaTiO_3$ indicating that up to 35 °C above T_c, the tetragonal ferroelectric to cubic paraelectric transition temperature, the Ti atoms remain displaced from their cubic sites with a local *tetragonal* type distortion. The cubic structure found by diffraction in the paraelectric phase indicates that the local tetragonal displacements are disordered with no long-range correlation. In addition, a displacive component is found as the electric field gradient (EFG) tensor decreases by a factor of 100 after passing through T_c. These results appear to be in disagreement with a previous publication [3] using the x-ray absorption fine structure (XAFS) technique to investigate $BaTiO_3$. Resolving this apparent disagreement helps elucidate the local structural changes occurring in passing through T_c, and the character of the order-disorder and displacive components.

The local displacements of the Ti atoms from their cubic sites in the tetragonal phase were found by Ti K-edge XAFS on a single crystal to be approximately rhombohedral, deviating from the (111) directions by 12(1)° toward the c axis. This information was obtained

from the x-ray absorption near edge structure (XANES) portion of the XAFS. The XANES has a weaker absorption feature below the main edge due to transitions into unfilled atomic d levels. Since the angular momentum $\ell = 0$ $1s$ state excited at the K edge is electric dipole forbidden for transitions to the $\ell = 2$ d states, this transition is weak when the Ti is not displaced from its cubic symmetry site. However, if the Ti atom is displaced from the cubic site breaking its inversion symmetry, this perturbation mixes $\ell = 1$ p-state symmetry into the unfilled d states, allowing electric dipole transitions. For the relatively small displacements present in $BaTiO_3$ the strength of this dipole allowed transition is proportional to the square of the component of the displacement along the x-ray polarization direction. Aligning the polarization along the a and c axes determines the two displacement components and the displacement angle to the c axis. Note that this local *rhombohedral* distortion measured by XAFS is in apparent disagreement with NMR which finds a local *tetragonal* distortion.

Such precision of the deviation from the (111) directions cannot be obtained by XAFS for the cubic phase because of its higher symmetry which shows no orientation dependence as a function of the angle between the x-ray polarization and the crystal axes. However, XAFS can still determine, in apparent disagreement with the NMR results, that the displacements are most closely directed along the (111) directions than the (001) directions in the cubic phase by the different distribution of the nearest neighbor oxygen distances to the Ti atoms [3]. In fact the XAFS measurements indicate that the displacements remain closely along (111) directions throughout all of the $BaTiO_3$ phases, and their magnitudes decrease monotonically by only 13% from 35 to 590 K, showing no steps at the phase transitions. Such eight equivalent (111) displacements (the eight-site model of Comes [4]) remained for temperatures even 350 °C above T_c, almost twice T_c. The equal population of the eight sites averages to the cubic structure found by diffraction methods. In summary, XAFS found that a local eight-site displacement model is valid for $BaTiO_3$, and there was not a

significant change in the *magnitude* of the displacements across the phase transitions, but there could be some *orientation* change through T_c.

The apparent disagreement between the NMR and XAFS results for the type of local displacement of Ti in $BaTiO_3$ is due to the different averaging times of the measuring techniques [5]. The NMR technique, which measures the nuclear quadruple transitions, motionally averages dynamic displacements that vary in times less than $\sim 10^{-8}$ s; while the XAFS technique is a much faster measurement with an averaging time of less than 10^{-15} s. Since atoms are essentially static in 10^{-15} s, XAFS measures the instantaneous local structure.

The temperature dependence of the ferroelectric transition in eight-site $BaTiO_3$ starts at low temperatures in the rhombohedral state where only one of the eight sites is occupied. As the temperature is increased the hopping between the sites first starts at the rhombohedral to orthorhombic transition to average out one of the cubic components and produce the [011] orthorhombic average periodic structure. Similarly, additional hopping barriers are overcome at the orthorhombic to tetragonal transition to produce the [001] tetragonal average periodic structure, and, finally, overcoming all hopping barriers to produce the cubic structure where all sites are occupied and the local displacements average to zero.

With temperatures up to 35 °C above T_c the NMR results show that the dynamic hopping time of the local displacements corresponding to the rhombohedral and orthorhombic phases are much less than 10^{-8} s, while that due to the tetragonal phase is more than 10^{-8} s. Presumably, when the temperature is far enough above T_c, the hopping time of the tetragonal phase becomes shorter than 10^{-8} s and NMR will measure no local distortions, as is found for order of magnitude faster Raman measurements [5].

Finally, XAFS gives an explanation of the changes in the electric field gradient (EFG) tensor found by the NMR measurements in passing through T_c. If the Ti ions in the cubic phase are displaced precisely along the (111) direction, the axially symmetric EFG tensors are pointed with their largest principal axes along the same direction, placing them at the magic angle $\theta = 54.7°$ where their perturbation is zero. The large change in the NMR perturbations is caused by the biasing of the displacements toward the c axis by 12° in the tetragonal phase that decreases to about 0.1° near T_c in the cubic phase. The orientation shift toward the c axis being much larger for the tetragonal than cubic phase is expected since the long-range correlated local tetragonal displacements in the ferroelectric phase produce an elongation along the c axis causing the tetragonal diffraction structure, which is not present in the paraelectric cubic phase. The displacive component in $BaTiO_3$ is an orientation shift of the displacements, not a change in their magnitude.

It should be emphasized that though the NMR measurements of Ref. [2] indicate that a decrease of a factor of 100 occurs in the EFG at the Ti site, they do not determine the cause of this decrease. There are two factors involved in producing an EFG change. One is any change in the magnitude of the Ti displacement from a cubic symmetric site and the other is any change in the orientation of the displacement from the magic angle relative to a cubic axis. The NMR measurements alone cannot separate these two contributions. Only in combination with the XAFS is this possible.

Although no XAFS measurements on single crystal $BaTiO_3$ have been made on the rhombohedral and orthorhombic phases we can predict what the results will be based on the 8-site model modified by the XAFS result on the tetragonal phase. The tetragonal phase has its local displacements deviating from the (111) directions by 12° (and 43° from the c axis) because of the tetragonal field. Diffuse scattering measurements on all the phases of $BaTiO_3$ have not been made, just on the cubic phase [6]. However, diffuse scattering measurements have been made [4] on all of the phases of isostructural ferroelectric $KNbO_3$, and one expects similar behavior for $BaTiO_3$. The rhombohedral phase of $KNbO_3$ has no diffuse elastic scattering background of x-rays or neutrons, in contrast to the higher temperature phases, indicating that there is no disorder and both the local and diffraction structures are the same. Thus the XAFS also should find the local displacements exactly along the (111) direction. In the orthorhombic phase one of the components of the displacement becomes disordered averaging to zero and we might expect that the orthorhombic field would cause the local displacement to deviate from the (111) direction by biasing toward the (011) direction. However, the amount of bias might be expected to be less than the 12° of the tetragonal phase since only one component is disordered, instead of two. From this reasoning one could predict, keeping in mind that the displacement in the cubic phase is closely along (111), that the largest displacive effect occurs in the tetragonal to cubic phase transition.

It should be emphasized that the phase transformations are not caused by the instability of a transverse optical mode because the local displacements do not disappear well above T_c and the soft mode frequency does not go to zero at T_c [7](it becomes overdamped there causing the zero peak). A theory [8] incorporating the interaction of the local displacements with the soft mode gives good agreement with the properties of perovskite ferroelectrics, including explaining the over damping of the soft mode near T_c, and the large Curie-Weiss constant. It was the inability to explain the large Curie-Weiss constant by the pure order-disorder theory without interactions with the soft mode that led to the acceptance of the pure displacive theory, even by Comes who retracted his 8-site model.

In conclusion, the order-disorder component of phase transitions in $BaTiO_3$ consists of local displacements from cubic symmetry partially losing long-range correlations but remaining constant in magnitude across phase transitions, while the displacive component is reorientation of the local displacements relative to the (111) directions as the disorder increases. It is predicted that the largest displacive effect occurs in the tetragonal to cubic transition.

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