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Evidence of incommensurate structural fluctuations in $\text{Bi}_2\text{Sr}_{1.9}\text{La}_{0.1}\text{CuO}_{6+\delta}$

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Using synchrotron X-rays, we evidenced in single crystals of $\text{Bi}_2\text{Sr}_{1.9}\text{La}_{0.1}\text{CuO}_{6+\delta}$ the existence of diffuse scattering streaks associated with the incommensurate modulation. Detailed structure factor calculations show that the diffuse scattering is due to two-dimensional correlations of phase defects, which we suggest to be related to the extra oxygen atoms.

The Bi-Sr-Ca-Cu-O high-temperature superconductors¹, as well as the closely-related Tl-Ba-Ca-Cu-O ones, can be prepared in a variety of phases, the most interesting ones having a common chemical formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$, where $n=1,2,3$ gives the number of Cu-O layers per unit cell. Their crystal structures consist basically of an alternate stacking along the c-axis of a tetragonal sublattice² of Bi-O double layers and Cu-O polyhedra, which can be either Cu-O octahedra as in the case of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{Sr}, \text{Ba}$), or Cu-O pyramids as in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$. The critical temperature T_c increases with n and is influenced by the possible presence of a doping element. Moreover, it depends, strongly for the 2212-phase³ and to a much lesser extent for the 2223-phase⁴, on the conditions of sample preparation (annealing temperature and time, oxygen pressure, cooling procedure). As it has been for many other high- T_c systems ($\text{La}_{2-x}\text{M}_x\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-\delta}$, etc) this variation is assigned to a change of the oxygen content in the structure^{3,4} and, also, to the oxygen ordering⁵. The location of the excess oxygen in the structure is still debated, but it is almost generally assumed that the oxygen atoms are incorporated as interstitial defects in the BiO double layers. In contrast to the situation that occurs in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ for instance, T_c increases with the reduction of the oxygen content in the 2212- and 2223-phases, leading thus to the natural assumption that these compounds are in the "overdoped" régime. The experimentally observed consequences upon T_c of the cooling procedure seem consistent with this idea and, besides, show that defect ordering can have an important effect on the superconducting properties. Thus, rapid quenching has been reported to raise T_c ^{3,6,7}.

Systematic structural studies were carried out on Bi-2201 single crystals grown in the Laboratoire Léon Brillouin in Saclay. We used undoped samples with chemical compositions described by $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$, with two distinct values of x (it is known that the Bi/Sr ratio varies to form solid solutions) and crystals doped with

Fe, Pb and La. The X-ray diffraction experiments were performed on the D43 beam line at the LURE synchrotron. We used a precession camera equipped with an Imaging plate and a $1.15 \text{ \AA}$ wavelength from a Ge(111) monochromator.

In all the examined samples, at room temperature, X-ray diffraction shows, in addition to Bragg peaks, satellite reflections of first, second and third order, as reported previously⁸ and shown in the next figure for the case of $\text{Bi}_2\text{Sr}_{1.9}\text{La}_{0.1}\text{CuO}_{6+\delta}$.

The positions of the satellite reflections corresponding to the modulation wave-vector are given by $\vec{q} = \beta\vec{b}^* + \gamma\vec{c}^*$, where β and γ depend on the composition. We find that the b^* -component increases slowly when substituting with higher valence cations (like Bi^{3+} on the site of Sr^{2+} in $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$, Fe^{3+} on the site of Cu^{2+} , La^{3+} on the site of Sr^{2+}). Substitution of Pb^{2+} on the site of Bi^{3+} has opposite influence on β . Doping with either Fe, La or Pb has the same drastic effect upon γ , which increases abruptly from the incommensurate value it has in the pure system to $\gamma = 1$, corresponding to an out-of-phase modulation of the Bi-O bi-layer.

The amplitude of the modulation is given by the intensity of the satellite peaks compared to the intensity of the main Bragg peaks. In X-ray studies the main contribution to the intensity comes from the Bi atoms. A rough estimate indicates strong distortion amplitude of the Bi-O layer of about $1 \text{ \AA}$, inducing necessarily a deformation of the Cu-O layer, that we study separately using neutron scattering.

For the La-doped system $\text{Bi}_2\text{Sr}_{1.9}\text{La}_{0.1}\text{CuO}_{6+\delta}$, which is the only superconducting 2201-phase among those we investigated, $\gamma = 1$ and $\beta = 0.23$. The value of β is only slightly shifted with respect to the undoped case ($\beta = 0.21$).

The variation of the b^* -component of the modulation wave-vector with doping can be understood in terms of the charge transfer, as discussed earlier⁹. Substitution with higher valence cations increases the number of oxygen atoms in the structure to preserve electrical neutrality. These extra oxygen atoms locate most probably in the Bi-O double layers, between two adjacent Bi atoms, determining a fluctuating Bi-Bi

distance in each layer and creating, thus, Bi-concentrated and Bi-deficient bands along the b-direction with a periodicity which will depend on the number of extra oxygen atoms. Consistently, substitution with lower valence cations, as Pb onto the site of Bi, will deplete the structure of oxygen and will diminish the modulation periodicity. Thus, we could say that the modulation has a direct role in accomodating within the structure the excess oxygen which might be essential in the stabilizing mechanism of the charge transfer.

The [0kl] X-ray patterns of all the examined systems present more or less pronounced streaks, differently oriented for different compositions but with the common feature that they do not pass through the main Bragg peaks (see the left scan in the figure below), but only through the satellite reflections (see the right scan in the figure below; the dots represent experimental points, the continuous line draws the result of the fit of the satellite peaks with gaussian functions).

The observed diffuse scattering is the sign of structural fluctuations existing in the lattice, which we interpret to be mainly fluctuations of the modulation phase, given the fact that the streaks concern only the satellite reflections.

Generally, the streaks make an angle with the c^* -axis, as well as with the modulation wave-vector and their orientation makes them difficult to interpret in terms of simple correlations of phase defects. The most simple situation occurs in $Bi_2Sr_{1.9}La_{0.1}CuO_{6+\delta}$, which we choose to discuss in more detail. Neat streaking is visible along the c^* -axis of the reciprocal space. Its intensity is not uniform, but depends on the scattering vector. We suggest that the corresponding diffuse scattering is due to phase defects subjected to anisotropic correlations, in particular to strong two-dimensional correlations within the atomic (a,b) planes. Had it not been for the interruptions in the streaks, we could have considered that the atomic planes are completely decoupled from each other. Consequently, we interpret these interruptions to be caused by the existence within each unit cell of a correlated bi-layer, but with no correlations from one unit cell to another. The periodicity of the interruptions led us to the assumption that the bi-layers in question correspond to the two Bi-O layers.

variation of the diffuse intensity I_D according to

$$I_D(\vec{Q}) \sim \sum_{\vec{G}} f_{Bi}(\vec{Q})^2 J_1(\vec{Q} \cdot \vec{u}_{Bi})^2 (1 - \cos(2Q_z z_{Bi} + \phi)) g(\vec{Q} - \vec{q} - \vec{G})$$

where J_1 is the Bessel function, ϕ is a phase shift adjusted with the modulation amplitude u_{Bi} of the Bi atoms and with the scale factor. Here the obtained value of u_{Bi} is almost the double of the estimated value from the analysis of the satellite reflections, we believe that this discrepancy can be reduced if we correctly take into account the fluctuation effect which renormalizes the value of u_{Bi} . Note that the periodicity of I_D has nothing to do with the lattice periodicity, but it is given by the thickness of the Bi bi-layer. The result of the computation is presented on the same figure (continuous line) and the comparison with the experimental points supports the proposed picture. Remembering the hypothesis that the extra oxygen atoms locate in the Bi-O double layer, it would be consistent to describe the phase defects as being caused by the insertion of the excess oxygen atoms within the Bi-O planes. *We are pleased to acknowledge interesting discussions with J. Rossat-Mignod*

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