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Analysis of the local structure by single-crystal neutron scattering in $La_{1.85}Sr_{0.15}CuO_4$

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We have determined the anisotropic Debye-Waller parameters of $La_{1.85}Sr_{0.15}CuO_4$ with high precision using neutron diffraction on single crystals. The mean-square displacements are explained well by the contribution due to phonons and disorder induced by the mixing of La and Sr ions; the latter was simulated by relaxing the structure locally. Our analysis puts rather low upper boundaries on the amplitude of possible hidden local structural distortions; in particular, there is no evidence for in-plane charge inhomogeneities related to stripe correlations. Further, we conclude that the tilt transition in $La_{1.85}Sr_{0.15}CuO_4$ is essentially displacive and continuous in nature.

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Local structural distortions in $La_{2-x}Sr_xCuO_4$ are of importance for the understanding of high-temperature superconductivity as they may arise from a complex charge-spin-lattice coupling. Such distortions have gained particular interest after the discovery of a static stripe phase in $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$.[1] No such static distortion has been found in $La_{1.85}Sr_{0.15}CuO_4$ by neutron diffraction but a stripe like feature was claimed on the base of Cu extended x-ray-absorption fine structure (EXAFS) experiments.[2] Recently, Bozin *et al.* have reported evidence for charge inhomogeneities in the CuO_2-planes deduced from pair distribution function (PDF) studies.[3] We will comment on both works.

Another type of local structural distortions discussed for $La_{2-x}Sr_xCuO_4$ is associated with the well-known structural phase transformation from a high-temperature tetragonal (HTT) phase to a low-temperature orthorhombic (LTO) phase, characterized by an octahedron rotation around a $[110]_t$ direction of the HTT cell. This transition has been studied extensively and is generally believed to be of displacive character.[4] However, Haskel *et al.*[5] deduce from a La-EXAFS study that the tilt transition is mainly of order-disorder type when regarded as a function of temperature in a Sr-doped sample, and that it has displacive character only as function of the Sr content. According to PDF studies the octahedra remain locally tilted in the HTT phase of $La_{2-x}Ba_xCuO_4$.[6] Surprisingly, these authors find that octahedra are always tilted around a $[100]_t$ direction in contradiction to the EXAFS results[5] and to diffraction studies[7,8] on $La_{2-x}Sr_xCuO_4$. A $[100]_t$ tilt corresponds to the one found in the second low-temperature phase (space group $P4_2/ncm$, LTT) whose most interesting property is that superconductivity is largely suppressed.[9]

To examine the local structure of $La_{1.85}Sr_{0.15}CuO_4$ we have undertaken a detailed neutron-scattering study on high quality single crystals. Firstly, we performed a standard structural analysis on a four circle diffractometer. The crystallographic analysis of Bragg-reflection intensities (for both x-ray and neutron diffraction) measures only the averaged structure and thereby misses local distortions. However, indirect evidence of local distortions may be obtained nevertheless: when the Bragg intensities are analyzed within a nondistorted structural model local structural distortions show up in the form of unusually large Debye-Waller (DW) factors (or mean-square displacements), i.e., DW factors which are larger than expected from the thermal excitation of the phonons. In addition, we have studied the diffuse scattering around the superstructure reflections and thereby obtained detailed information on local deviations of the octahedron tilt.

The two single crystals used in the present experiments of volumes 20 and 500 mm^3 were grown by a floating-zone technique and exhibit sharp superconducting transitions at $T_c = 36$ K. Sets of Bragg-reflection intensities were recorded on the four circle diffractometer D9 at the ILL using a wavelength of 0.54 Å obtained with a Cu-(220) monochromator. The two-dimensional (2D)-position sensitive detector allowed us an effective integration of the intensities even in the case of the 20 K low-temperature structure where the crystal is twinned. At 200 K a set of 1509 reflections was recorded extending to $2\Theta = 100°$, $[\sin(\Theta)/\lambda]_{max} = 1.4$; at 20 K 2439 reflections to $2\Theta = 90°$, $[\sin(\Theta)/\lambda]_{max} = 1.3$. In the distorted phase at 20 K superstructure intensities were recorded only up to $2\Theta = 66°$. The intensities were first averaged according to Laue-groups $4/mmm$ (mmm) yielding an internal R value of 2.7% (2.6%) for the 200 K (20 K) data. However, during the refinements it turned out that extinction effects are better described within an anisotropic model which necessitates the use of a data set averaged according to the space group $P1$. Reflections suffering from extinction corrections stronger than 15% were excluded from the refinements; seven (six) reflections for the data at 200 K (20 K). We applied corrections for thermal diffuse scattering following the formalism in Ref. 10. These corrections, however, are extremely weak; they yield a general enhancement of the mean-square displacements of 2 and 12×10^{-5} Å^2 at

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20 and 200 K, respectively. Details of the experimental and refinement procedure are given in Refs. 8 and 11.

Refinements of a large number of anharmonic thermal parameters to the sixth order revealed no significant improvement neither for the 200 K nor for the 20 K data. At 200 K the $La_{1.85}Sr_{0.15}CuO_4$ single crystal is very close to the structural phase transition into the LTO phase observed at $T_{t-o}=186$ K. The fact that anharmonic contributions to the scattering distribution are negligible in spite of the precision of our experiment clearly contradicts the idea of an order-disorder transition.[5] In particular, there is no indication for any predominance of local tilts. The probability density map for O2 of the complete anharmonic refinement shows almost perfect cylindric symmetry around the *c* axis. Furthermore, there is no evidence at all for a pronounced anharmonic distribution of the O1 site, which should be split along *c* in the case of local tilts. Further, the perfect description of the 20 K probability density map with harmonic terms strongly disagrees with the idea that the local structure in the tilted phase is essentially different from the LTO symmetry, which has been discussed in Ref. 12.

The phonon contribution to the mean-square displacements can be calculated within harmonic lattice dynamics.[8,13] A precondition for this analysis is detailed knowledge about the lattice dynamics of the compound, which in the case of $La_{1.85}Sr_{0.15}CuO_4$ was acquired by extensive neutron-scattering studies.[14] The lattice dynamical models for $La_{1.85}Sr_{0.15}CuO_4$ were based on the one described in Ref. 15. Two slightly different models were used for $T=200$ and 20 K, respectively, in order to account for the structural change from HTT to LTO and the temperature dependence of the frequency of the soft tilt mode.

In Table I we compare the observed displacement parameters to these lattice dynamical calculations. In earlier measurements larger parameters obtained most likely due to sample imperfections.[8] Only a few values in Table I are still considerably larger than expected from harmonic lattice dynamics, in particular O2-U_{11} and O1-U_{33}, i.e., the two parameters associated to the tilt of the octahedra. The enhancements amount to 165(228) and 422(317) 10^{-5} Å^2 for O1 and O2, respectively, at 20(200) K. These values correspond to root-mean-square tilts of 1.3° and 1.6°, respectively, in the assumption that they totally arise from local tilts. This assumption is, however, not justified, see below.

The DW factor describes the diminution of the Bragg-reflection intensities due to the smearing of the scattering density. Thermal excitation of the phonons leads to inelastic scattering. Static disorder, on the contrast, transfers Bragg-scattering into elastic diffuse scattering in-between the sharp Bragg-peaks. In the idea that the enhancement of the oxygen thermal parameters is partially due to local static tilt distortions one expects diffuse scattering near the superstructure reflections in the LTO structure. Close to the structural transition, there is the critical scattering related to the anharmonicity which, however, rapidly disappears for temperatures away from T_{t-o}.[16,17] In contrast the tilt scattering due to La/Sr mixing should be almost temperature independent.

In Fig. 1 we compare scans through a superlattice peak position for temperatures of 10, 190, and 320 K obtained on the triple axis spectrometer 1 Ta with a large crystal previously used for inelastic studies. There is clear evidence for a broad component persisting to high temperatures. At 320 K, the diffuse scattering can be well described by a Lorentzian (in the *a* and *c* directions), $I_L\,\kappa^2/[\kappa^2+(Q-Q_0)^2]$ with κ being 0.18 Å^{-1} and 0.07 Å^{-1} along *a* and *c*, respectively. Compared to the widths typically studied in the context of critical scattering[16,17] these κ values are extremely large. The interpretation in terms of correlation lengths should be considered with caution since the lengths are of the order of the lattice constants, 6 Å in the *ab* plane and 14 Å parallel to *c*. One may compare the total intensity in the diffuse scattering to that of the superstructure peak at 10 K. The peak height amounts to only 0.5% of the low-temperature peak, but when taking the broadening into account one finds a total diffuse intensity of about 5% of that of the superstructure peak. Since the intensity of the sharp superlattice peak is proportional to the square of the tilt, one may roughly estimate that the diffuse scattering corresponds to a local mean square tilt of ~0.4 degrees squared (Ref. 2) or to a ΔU_{11}(O2) of

TABLE I. Results of the structural refinements for $La_{1.85}Sr_{0.15}CuO_4$ for 20 and 200 K: La/Sr at (x,0,z), Cu at (0,0,0), O1 at (0.25,0.25,z), and O2 at (x,0,z). U_{ij} is given in 10^{-5} Å^2, U_{22} was constrained to U_{11} for La, Cu, and O2 at 200 K, in the orthorhombic phase at 20 K, U_{11} and U_{22} for O2 were refined independently to 824(24) and $1146(24)\times10^{-5}$ Å^2, respectively (in the table we give the average in order to compare to the calculations); $U_\parallel$ and $U_\perp$ denote the thermal parameters of O1 in the *ab* plane parallel and perpendicular to the CuO bond. The values in square brackets give the calculated mean-square displacements, first the phonon contribution, second the additional contribution induced by the mixing of La and Sr, and third the sum of these both. Statistical errors are given in parentheses corresponding to the last digits and do not include any systematic contribution.

T (K)	20	200
symmetry	*Abma*	*F*4/*mmm*
Reflections	2384	1459
$R_w(I)/R_u(I)$	5.05%, 3.67%	3.48%, 2.65%
La/Sr−x	0.00450(6)	/
z	0.36073(1)	0.36071(1)
U_{11}	180(4)[138/32/170]	424(3)[421/25/446]
U_{33}	126(5)[108/20/128]	293(4)[288/20/308]
U_{13}	−54(9)[/]	0
Cu−U_{11}	142(5)[114/2/116]	218(4)[204/3/207]
U_{33}	278(8)[231/37/268]	613(7)[548/36/584]
U_{13}	13(14)[/]	0
O1−z	0.00449(3)	0
$U_\parallel$	261(5)[199/19/218]	317(4)[285/18/303]
$U_\perp$	409(5)[358/19/377]	607(5)[541/18/559]
U_{33}	676(9)[519/71/590]	1147(8)[907/51/958]
O2−x	−0.02162(11)	0
z	0.18210(3)	0.18200(2)
U_{11}	985(17)[561/345/906]	1650(8)[1321/300/1621]
U_{33}	367(8)[316/40/356]	523(7)[452/37/489]
U_{13}	−45(12)[/]	0

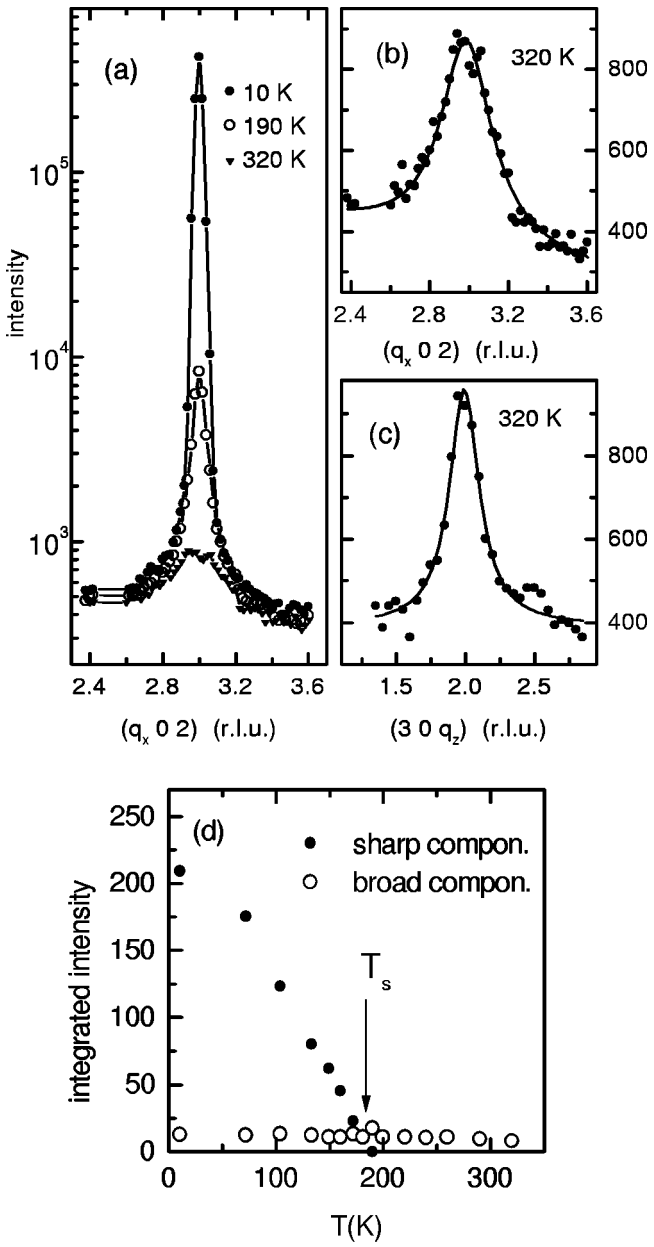

FIG. 1. (a) (logarithmic scale): diffuse and Bragg scattering around the (3 0 2) position. (b) and (c): scans through the diffuse scattering above the structural transition together with their description by Lorentzian profiles; (d): temperature dependence of the integrated intensities of the sharp component reflecting the long-range superstructure and of the broad component.

70×10^{-5} Å^2 which is significantly below the value for the local tilt reported by Bozin *et al.* for slightly higher Sr concentrations in the tetragonal phase.[12] The diffuse scattering directly related to the tilt may explain only one fifth of the thermal parameter enhancement observed for U_{11}(O2). One may not expect that the entire enhancement is due to local tilt distortions, since the larger Sr will, in first approximation, repulse neighboring O2's parallel to the planes. A tilt distortion arises only in second order due to the nearly rigid character of the octahedron and the anharmonicity of the lattice. The entire distribution of the diffuse scattering might, however, be difficult to detect due to its weak Q variation. We conclude that though there is diffuse scattering related to local tilt variation, it can be neglected when compared to the average tilt. *The phase transition in* $La_{1.85}Sr_{0.15}CuO_4$ *can thus be pretty well described by a continuous transition of second order*. The situation may be compared to the transition in K-doped $BaBiO_3$ which is also characterized by an octahedron tilt. There, however, the pronounced disorder completely smears out the transition.[18]

We have used the interaction potential model to simulate the static disorder due to La/Sr mixing using distinct potentials for the La-O and the Sr-O interactions and distinct charges. Large (4*4*4) super cells have been constructed with random occupation of the A site by La and Sr ions corresponding to the Sr content of $x=0.15$. The variation of the interatomic potentials results in nonzero forces on the ions, when these are fixed to values of the average structure. We then allow the ions to relax these forces by positional displacements, whose squares were averaged over the super cell. The results are given in Table I. The sum of the phononic contribution and the La/Sr disorder induced distortions is, in general, in quantitative agreement with the observed mean-square displacements. The only significant discrepancy is found for O1-U_{33}. Our analysis leaves very little space for any further distortions like those proposed by the distinct local probe studies.

Haskel *et al.*[5] proposed that the tilt transition in $La_{1.85}Sr_{0.15}CuO_4$ would be of order-disorder character. If one would assume that the static low-temperature tilt of $\sim3°$ would persist in the HTT phase, the O2-U_{11} parameter should be enhanced above T_{t-o} by at least 2000×10^{-5} Å^2. Such a behavior can be clearly excluded. There is only a small and little temperature-dependent local variation of the tilt, whose amplitude even decreases upon heating.

The model proposed on the base of the Cu-EXAFS experiment[2] can be clearly rejected too, since the tilt of 16° in the socalled D stripes which occupy of the order of one third of the volume would result in a contribution to U_{11} of O2 of the order of 0.1 Å^2. This value is, however, almost two orders of magnitude larger than any enhancement compatible with our data. Also the weak diffuse intensity clearly contradicts the stripe model proposed by Bianconi *et al.*:[2] the 7 Å large stripe with a 16° tilt would imply a diffuse scattering even sharper than the one found and about two orders of magnitude stronger in intensity.

Finally, we want to comment on the possibility of local structural distortions related to the type seen by Tranquada *et al.*[1] in the static stripe phase. The superstructure reflections seen by Tranquada *et al.*[1] are about six orders of magnitude smaller than strong fundamental reflections. Tranquada *et al.* estimate the O displacement in the compound presenting static stripe order to 0.004 Å;[19] assuming a dynamic or short-range correlation of the same magnitude one would expect a DW-factor enhancement by 1.6×10^{-5} Å^2, i.e., far below the sensitivity of any DW-factor determination. The minor enhancements still found in our experiment for Cu-U_{11} and O1-$U_{\|}$ should be considered to be within the overall reliabilities of the experiment and the model, though the purely statistical error given in Table I is smaller.

Bozin *et al.* have recently reported evidence for disorder related to stripe order on the base of a PDE analysis. They report a local bond length variation of 0.024 Å, already much higher than what might be expected for stripe correlations similar to those reported by Tranquada *et al.*[19] The PDF analysis further yields a mean-square deviation of the Cu-O(1) distance, σ^2, enhanced by $\sim 200\times10^{-5}$ Å^2 for the Sr concentration of $x=0.15$ when compared to the $x=0.0$ and $x=0.3$ values. One may note that these results are inconsistent with each other, since the proposed bond length variation corresponds to a σ^2 enhancement of only 60×10^{-5} Å^2. Further, the width of the Cu-O1-peak given in Ref. 3 is much larger than we expect from our data. In case of uncorrelated displacements of Cu and O1, σ^2 would correspond to the sum of Cu-U_{11} and O1-$U_{\|}$ which is 403×10^{-5} Å^2. However, we know that at least the thermal vibrations are strongly correlated which leads to a significant reduction of the peak width. Following the lines of Chung *et al.*[20] we calculate from our lattice dynamical model that this reduction amounts to $\Delta\sigma^2=77\times10^{-5}$ Å^2. Therefore, we expect a peak width of not more than $\sigma^2=326\times10^{-5}$ Å^2, i.e., much less than the value of 520×10^{-5} Å^2 reported in Ref. 3. We note that our value is slightly larger than the values given in Ref. 3 for $x=0.0$, 0.25, and 0.3, and it agrees well to the value obtained by single crystal diffraction for $x=0$.[8] *In other words, our results are in clear conflict with the central claim in* Ref. 3, i.e., *the anomalous enhancement of the* Cu-O1-*peak width for optimal doping*.[21,22]

In conclusion, we have used single crystal neutron scattering in order to study the average and the local structure of $La_{1.85}Sr_{0.15}CuO_4$. The comparison of the thermal parameters obtained by crystallographic analysis with lattice dynamical calculations indicates some enhancements which may be quantitatively explained by the local structural relaxation due to the La/Sr mixing. Furthermore, we observe weakly temperature-dependent diffuse scattering indicating static local tilts, which represents, however, only 5% of the total intensity due to the long-range tilt distortion. Our observations indicate that the structure in $La_{1.85}Sr_{0.15}CuO_4$ is pretty well described by a displacive phase transition in a weakly disordered compound; they put low upper limits for the amplitudes of any hidden local structural distortion.

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