The Local Structure of La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$ determined by $^{63}$Cu NMR Spectroscopy and Van Vleck Paramagnetism of Eu$^{3+}$ Ions

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We investigate the local symmetry of the tilting of the CuO$_6$ octahedra in La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$ by means of $^{63}$Cu NMR spectroscopy and the Van Vleck susceptibility of the Eu$^{3+}$ ions. The Cu NMR central line lineshape is sensitive to local structure through the coupling of the $^{63}$Cu nuclear quadrupole moment to the local electric field gradient. The Eu$^{3+}$ Van Vleck susceptibility, as a single ion effect, locally probes the symmetry of the crystal field at the Eu site. Both techniques independently provide clear evidence for a change of the local tilt symmetry at the first order structural transition from the orthorhombic to the low temperature tetragonal phase, in excellent agreement with the average structure obtained by diffraction techniques. We conclude that the symmetry of the average crystal structure accurately represents the symmetry of the octahedral tilt pattern on a local scale.

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Lanthanum cuprate La$_{2-x}$Sr$_x$CuO$_4$, the single layer high temperature superconductor, has been extensively studied over the past few years to understand the mechanism of superconductivity. Recently, rare earth co-doped lanthanum cuprates La$_{2-x-y}$R$_y$Sr$_x$CuO$_4$ (R = Eu or Nd) have attracted considerable attention because of the subtle interplay between charge stripes and superconductivity. In this family of compounds it is possible to tune the optimally doped La$_{2-x}$Sr$_x$CuO$_4$ from a superconducting to a magnetic phase where charge is spatially modulated by changing the tilt distortion of the CuO$_2$-layers. These modifications of the structure result if La$^{3+}$ is partially substituted by smaller R$^{3+}$ ions. The suppression of superconductivity observed in these doping experiments clearly shows an intimate connection between structure and electronic properties in the high temperature superconductors. Based on the structural data obtained from diffraction experiments it has been argued that both the symmetry and the magnitude of the tilt distortion of the CuO$_2$ layers are key factors determining the electronic properties in La$_{2-x-y}$R$_y$Sr$_x$CuO$_4$. These neutron and x-ray diffraction techniques, sensitive to the average structure, show that rare earth co-doped lanthanum cuprates can exist in three structural phases dependent upon Sr$^{2+}$ and R$^{3+}$ doping and upon temperature: the high temperature tetragonal phase (HTT), the low temperature orthorhombic phase (LTO) and the low temperature tetragonal phase (LTT). All three phases can be described by different patterns of rotated CuO$_6$ octahedra. The CuO$_2$ plane is flat in the HTT phase and the transition to LTO (spacegroup $Abma$) consists of a tilt of the CuO$_6$ octahedra along the [110] direction using the notation for the HTT unit cell ($I4/mmm$); see Fig. 1. The tilt angle increases gradually as the temperature is lowered and the compound undergoes a first order structural transition to the LTT phase ($P4_2/nmc$) via a discontinuous change of the tilt phase, which is then oriented alternately along [100] and [010] in adjacent CuO$_2$ planes.

Over the past few years local structure models which seem to contradict these findings have been published. Based on pair distribution function (PDF) analysis of neutron diffraction and x-ray absorption fine-structure (XAFS) it was concluded that, locally, the octahedra always tilt with the LTT symmetry. The long range LTO tilt pattern was interpreted as the superposition of two out of four equivalent short range LTT patterns with their tilt axes rotated by 90°, and the flat planes in the HTT phase as the result of a superposition of all four LTT variants. Furthermore, the amplitude of the octahedral tilt is thought not to change in this model. This is in sharp contrast to $^{151}$Eu Mössbauer spectroscopy which also probes the local structure and shows a temperature dependence of the local tilt angle in La$_{1.83-x}$Eu$_{0.17}$Sr$_x$CuO$_4$, which corresponds well with average structure results.

It is crucial to clarify this issue in order to gain better insight into the relation between charge stripes and structural ordering in lanthanum cuprates. In particular, evidence from XAFS for locally different Cu-O(1) and Cu-O(2) bond lengths in the LTO phase of La$_{2-x}$Sr$_x$CuO$_4$ have been interpreted as indicating the coexistence of LTO and LTT like domains. Note however that similar XAFS experiments performed on La$_{2-x-y}$R$_y$Sr$_x$CuO$_4$ do not yield evidence for spatially varying bond lengths. Also, no anomalies related to the LTO→LTT transition or the presence of static stripe order could be detected with this technique. Recently,
PDF results on La$_{2-x}$Sr$_x$CuO$_4$ were discussed in terms of spatially modulated combinations of HTT, LTT, and LTO tilt patterns which are locally induced by dynamic charge stripes. But a detailed analysis of Debye-Waller factors and diffuse scattering in a neutron diffraction experiment performed on a La$_{1.85}$Sr$_{0.15}$CuO$_4$ single crystal agrees with the average structure, and places low upper limits on the amplitude of any hidden local structural distortion, including those induced by stripe correlations.

In this manuscript, we report $^{63}$Cu NMR and DC magnetic susceptibility measurements performed on a La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$ single crystal. According to diffraction data La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$ undergoes a second order transition from HTT to LTO at $\sim 350$ K and a first order transition from LTO to LTT at $T_{LTT} = 135$ K. It is known from $\mu$SR studies that its ground state is magnetic and a detailed investigation of the low frequency spin dynamics by NMR supports the existence of a glass forming stripe liquid below 30 K.

We will show that the combination of $^{63}$Cu NMR and DC magnetic susceptibility enables us to probe the local structure around Cu$^{2+}$ and Eu$^{3+}$ ions as a function of temperature. The $^{63}$Cu central line NMR spectrum reflects interaction of the $^{63}$Cu nuclear quadrupole moment with the surrounding EFG, and is sensitive to the angle between the dominant component of the EFG tensor and the applied magnetic field $\mathbf{H}_0$. The magnetic susceptibility is dominated by the Van-Vleck paramagnetism $\chi$(Eu) of the Eu$^{3+}$ ions. Because $\chi$(Eu) is a single ion effect, its anisotropy reflects the local symmetry of the crystal field at the Eu site. These two techniques, $^{63}$Cu NMR and DC magnetic susceptibility, can discriminate between LTT and LTO and provide clear evidence that the tilt pattern displays, on a local scale, the symmetry of the macroscopic structure as determined by diffraction techniques. This leads us to the conclusion that there is no need to distinguish between the symmetry of the local and average structure in this compound.

The La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$ single crystal was grown by the traveling solvent floating zone (TSFZ) method. Two pieces of $2 \times 2 \times 1 \text{ mm}^3$ and $5 \times 5 \times 4 \text{ mm}^3$ were cut from a centimeter size single crystal and oriented by Laue x-ray back reflection. The $^{63}$Cu ($I = 3/2$) NMR measurements were made on the central $(m_I = \pm \frac{1}{2} \leftrightarrow -\frac{1}{2})$ transition of the smaller crystal which is the same used in the x-ray diffraction study. The spectra were obtained by sweeping the static magnetic field $\mathbf{H}_0$ with $[100]$ at a fixed resonance frequency of 80 MHz. The DC magnetic susceptibility $\chi = M/H$ with $H = 1$ T was measured for all three crystallographic directions of the LTO unit cell of the larger crystal using a Faraday balance. The susceptibility data for a La$_{1.75}$Eu$_{0.05}$Sr$_{0.15}$CuO$_4$ crystal are shown for comparison.

In Fig. 1 we schematically show the unit cell in the HTT phase. The local charge surrounding both Cu$^{2+}$ and Eu$^{3+}$ ions will be affected by the tilt of the CuO$_6$ octahedra. Cu NMR is an excellent tool for investigating the local structure because atomic displacements locally alter the charge distribution and hence the EFG. The EFG tensor is described by its three components; by convention we take $V_{xx} \geq V_{yy} \geq V_{zz}$ where $V_{xx}$ is the second derivative of the local electrostatic potential. The quadrupole frequency $\omega_Q$ is proportional to $|V_{zz}|$ and the asymmetry parameter is defined as: $\eta = |V_{xx} - V_{yy}| / |V_{zz}|$ which is zero for a tetragonal symmetry. In the HTT phase, the average tilt angle is 0° and as a result the main component $V_{xx}$ is parallel to the c-axis. We determine from nuclear quadrupole resonance (NQR) that $\omega_Q = 36.4$MHz for $^{63}$Cu and point charge calculations show that in the LTO phase $\eta$ remains close to zero.

From a general point of view, the quadrupole coupling is a function of $\cos^2 \xi$ where $\xi$ defines the angle between $V_{zz}$ and $\mathbf{H}_0$. In a 2nd order perturbation expansion the quadrupole shift of the central line of a $^{63}$Cu (spin 3/2) nucleus is given by:

$$\delta \omega = \frac{3\omega_0^2}{16\omega_0}(1 - \cos^2 \xi)(1 - 9 \cos^2 \xi)$$

with $\omega_0$ the Larmor frequency of the nuclear spin in a field $\mathbf{H}_0$. As the CuO$_6$ octahedra start tilting in the LTO phase, the main axis of the EFG rotates through an angle $\phi$ with respect to the c-axis. The connection between the two angles $\phi$ and $\xi$ is shown in Fig. 2; the value of $\xi$ depends on both $\phi$ and the relative orientation of the applied field $\mathbf{H}_0$ and the tilt direction of the octahedra. According to the average structure, the CuO$_6$ octahedra tilt along the diagonal in the LTO phase and alternately...
along the [100] and [010] directions in adjacent CuO₂ planes in the LTT phase. For this reason, if we apply $H_0$ along the [100] or [010] directions, we expect to see a single central line in the Cu-NMR spectra of the LTO phase and a symmetric splitting of this line in the LTT phase, reflecting the two different values of $\xi$ in adjacent CuO₂ planes: $\pi/2$ and $\pi/2 - \phi$ (cf., Fig. 2).

Fig. 3 shows $^{63}$Cu NMR central transition swept field spectra as a function of temperature for $H_0||[100]$. The sharp line at 70.8 kOe is due to the Cu metal of the coil containing the sample. We see at glance that the $^{63}$Cu central line spectra split symmetrically at temperatures below the first order transition from LTO to LTT occurring at 135K. Comparison of swept field spectra obtained at different Larmor frequencies (80 and 94 MHz) shows that the splitting scales as $\omega^{-1}$, thereby confirming its quadrupole origin. From equation (1), we derive the magnitude of the splitting as a function of the tilt angle $\phi$:

$$\Delta \omega = \frac{3\omega_2^2}{16\omega_0}(10\sin^2\phi - 9\sin^4\phi)$$  \hspace{1cm} (2)

We find $\Delta \omega \approx 1.25$ MHz from a fit of the Cu-spectra to two gaussians in the LTT phase (see Fig. 3) and from expression (2) we obtain $\phi \approx 12^\circ$ [9]. In addition, the average of the split lines corresponds to an angle $\xi \approx 82^\circ$. Since $\cos \xi = \cos \pi/4 \sin \phi$ (cf., Fig. 2), we find $\phi \approx 11^\circ$ in the LTO phase. Therefore, the amplitude of the tilt angle does not change significantly at the first order structural transition.

Below 70K, the intensity of the $^{63}$Cu NMR signal drops sharply. In Fig. 4 we show the temperature dependence of the product $I(T) \cdot T$, where $I(T)$ is the integrated intensity of the central $^{63}$Cu NMR line. The spectra were obtained by monitoring the intensity of the spin echo versus the static field oriented along the direction [100] at constant delay $\Delta t = 10\mu s$ between the spin echo excitation pulses.

The Cu signal intensity decreases because, for some Cu nuclei, the transverse magnetization generated by the radio-frequency excitation decays on a timescale shorter than the recovery time of the spectrometer, thereby preventing us from observing the full spin echo signal. This is a manifestation of a dramatic slowing of the fluctuations of the Cu 3d magnetic moments below 70K as charge and magnetic order develop. Since only a fraction of the Cu nuclei contribute to the full spin echo signal, we cannot make any statement about the quadrupole splitting at low temperature.

Further insight into the local structure of La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$ is gained from analysis of its DC magnetic susceptibility $\chi$. The dominant contribution to $\chi$ comes from the Van Vleck paramagnetism $\chi$(Eu) of the Eu$^{3+}$ ions, which is about one order of magnitude larger than the susceptibility of La$_{1.85}$Sr$_{0.15}$CuO$_4$ (cf., Fig. 5). The Van Vleck paramagnetism is a single-ion effect and therefore $\chi$ is a suitable tool to investigate the local symmetry of the O₉ oxygen environment surrounding the Eu$^{3+}$ site highlighted in Fig. 1.

Following Hund’s rules, the free Eu$^{3+}$ ion with its $4f^7$ electronic configuration has a non-magnetic ground state.
the central line of the Cu NMR swept field spectra obtained with $H_0$ along [100] and frequency $\omega_0 = 80$ MHz. The solid line is a guide to the eye.

$^7F_0 (2^{8+1}L_3)$. In an external magnetic field however the ground state is mixed with the first excited magnetic state, $^7F_1$, thereby leading to a considerable magnetic contribution: the so called zeroth Van Vleck term. This term is constant at low temperatures but for temperatures $T \gtrsim 50$ K (cf. Fig. 5) the thermal population of the excited states $^7F_{J>0}$ leads to further Van Vleck as well as Curie terms, that cause the susceptibility to be temperature dependent. In a solid, the $(2J+1)$-fold degeneracy of the multiplets is lifted according to the symmetry of the crystal field and as a result, $\chi$(Eu) becomes anisotropic.

A glance at Fig. 5 shows that this is indeed the case in La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$: a large anisotropy is observed for $H \parallel c$ axis vs. $H \parallel ab$ plane. More important is the in-plane anisotropy in the LTO phase, which clearly vanishes in the LTT phase. In order to observe this in-plane anisotropy one must have a partially detwinned La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$ crystal which can be achieved by application of weak uniaxial pressure. The crystal direction predominantly containing the shorter b-axis has the larger susceptibility, i.e., $\chi_b > \chi_a$ in the LTO phase, using the crystallographic a and b axes of the LTO unit cell with $a \parallel [110]$ and $b \parallel [\bar{1}0\bar{1}]$ (cf. Fig. 1).

The increase of the $ab$ anisotropy with decreasing temperature, observed in the LTO phase in Fig. 5, is a consequence of the continuously increasing tilt angle as was also observed by $^{151}$Eu Mössbauer spectroscopy. Close to $T_{LTT}$ the $ab$ anisotropy reaches a value of $1 \times 10^{-4}$ emu/mol. For a sample with $x = 0.08$ (see inset of Fig. 5) the maximum value increases to $3 \times 10^{-4}$ emu/mol, which is approximately three times the total $\chi$ of pure La$_{1.85}$Sr$_{0.15}$CuO$_4$. The larger $ab$ anisotropy for $x = 0.08$ is consistent with the increase of the octahedral tilt angle as the Sr$^{2+}$ content is reduced. The order of magnitude of the $ab$ anisotropy in both crystals shows that it originates primarily from the Eu$^{3+}$ Van-Vleck paramagnetism. The super exchange constant $J$ in the CuO$_2$ planes is very large in these materials ($\sim 100$ meV) hence the susceptibility of the planes is small, so unrealistically large distortions would be required to explain $ab$ anisotropies of the observed magnitude as arising from changes of the Cu spin magnetism.

It is generally assumed that substituting La with smaller rare earth elements such as Nd or Eu induces strain which may possibly cause a local lattice instability of the LTO phase towards the LTT phase. From our susceptibility data we can clearly conclude that in the LTO phase of La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$ the Eu$^{3+}$ site is surrounded by an orthorhombically distorted oxygen environment. A more quantitative analysis of the $ab$ anisotropy requires a more precise knowledge of the degree of twinning that is presently lacking. A quantitative analysis of the crystal field anisotropy between $H \parallel c$ and $H \parallel ab$ will be published elsewhere.

The right side of Fig. 1 shows projections along the unit cell c-axis to demonstrate the distortion of the EuO$_9$ polyhedron for the HTT, LTO and LTT local distortions. The measurements of $\chi$ were performed for $H \parallel a$ and $H \parallel b$. It is obvious from these projections that an $ab$ anisotropy can occur only in the case of LTO-type octahedral tilts and is absent for LTT-type tilts. Furthermore, the $ab$ anisotropy is zero for all of the other LTT variants obtained by $90^\circ$ rotations about the c-axis.
any combination of the short range LTT domains that are required to form the LTO and HTT phases in the local structure model first proposed in Ref 7. The present results, therefore, clearly demonstrate that in the LTO phase the CuO$_6$ octahedra tilt in a LTO-type manner.

To summarize, we have presented investigations of the local structure of a La$_{1.65}$Eu$_{0.2}$Sr$_{0.15}$CuO$_4$ single crystal by means of $^{63}$Cu NMR and Van-Vleck susceptibility of Eu$^{3+}$ ions as a function of temperature. Independently, both techniques provide clear evidence that the symmetry of the local tilt in the LTO and LTT phases is different, in complete agreement with average structure results. We thus conclude that the symmetry of the macroscopic structure accurately represents the tilt pattern of the CuO$_6$ octahedra on a local scale.

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