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Local magnetic and structural properties of the low-temperature orthorhombic to low-temperature tetragonal transition: A ^{139}La NQR study in lightly hole-doped $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$

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^{139}La nuclear quadrupole resistance (NQR) and relaxation measurements in lightly hole-doped $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ have been used to investigate the microscopic properties of the low-temperature orthorhombic to low-temperature tetragonal transition. The transition is characterized by a sharp peak in ^{139}La NQR relaxation rate, indicating phonon softening. We find that the structural phase transition is accompanied by a modification of the spin state. The data for the spin freezing and the recovery of sublattice magnetization at low T are presented and discussed in relation to the studies of $La_{2-x}Sr_xCuO_4$ and $La_2Cu_{1-x}Li_xO_4$.
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The structural phase transition (SPT) from the low-temperature orthorhombic (LTO) to the low-temperature tetragonal (LTT) phase in $La_{2-x}Ba_xCuO_4$ and in rare-earth-doped $La_{2-x-y}M_ySr_xCuO_4$ (M = Nd, Eu) has attracted much attention due to its rich phenomenology: (i) the destruction of superconductivity in a certain range of hole concentration,[1–3] (ii) anomalous changes in magnetic and electronic properties,[3–6] and (iii) the ordering of the charge into stripes.[6,7] Therefore, improved understanding of the LTO→LTT SPT could provide crucial insight into the influence of the lattice on electronic and magnetic properties in high-T_c superconductors.

Better understanding of the character of doped holes and their interaction with the lattice is also needed. Recent ^{139}La nuclear quadrupole resonance (NQR) studies of $La_{2-x}Sr_xCuO_4$ (Refs. 8 and 9) and $La_2Cu_{1-x}Li_xO_4$ (Ref. 10) have revealed a remarkable insensitivity of the magnetic behavior of lightly doped lanthanum cuprate to the detailed nature of dopant. This indicates that the magnetic properties of the antiferromagnetic (AF) CuO_2 planes depend on the collective character rather than depending on the individual character of doped holes.[10,11]

We have performed ^{139}La NQR and relaxation measurements in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ to better understand the local structural and magnetic properties of the LTO→LTT SPT. At the transition, a sharp asymmetric peak in the ^{139}La NQR relaxation rate R_1 is observed, indicating that the transition involves phonon softening. The width of the ^{139}La NQR line, $\Delta\nu$, increases suddenly at the transition, suggesting that the SPT affects the AF spin state resulting in the introduction of faults in the spin-stacking pattern. A strong enhancement of R_1 with a peak at a temperature $T=T_f \cong 6$ K and an increase in the local magnetic field at the La site below ≈ 30 K are observed; all these are reminiscent of very similar features found in $La_{2-x}Sr_xCuO_4$ (Refs. 8 and 9) and $La_2Cu_{1-x}Li_xO_4$.[10] Comparison of these data with that from $La_{2-x}Sr_xCuO_4$ and $La_2Cu_{1-x}Li_xO_4$ provides evidence for a strong interaction between the collective hole structure and the lattice.

Two polycrystalline samples of lightly Sr-doped $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ with $x=0.010$ and 0.015 were prepared by standard solid-state reaction methods described elsewhere.[12] It is well known that in the rare-earth co-doped $La_{2-x-y}M_ySr_xCuO_4$ compounds, a direct LTO→LTT SPT occurs for hole concentration x above a certain value, while at lower hole concentration the transition occurs from LTO to a less orthorhombic phase with $Pccn$ symmetry followed by a continuous change to LTT phase.[2,13] The latter case is complex and is well described in detail elsewhere.[13,14] In this paper, we simply call this transition the ''LT transition'' and use the ''LT phase'' to denote the $Pccn$ and/or LTT phase. It is also known that at very low Sr concentration, $La_{2-x-y}M_ySr_xCuO_4$ compounds, as prepared, contain a considerable amount of excess oxygen which leads to a noticeable reduction of T_N and a significant broadening of the LT transition.[14] Annealing in nitrogen gas removed the excess oxygen producing a very sharp LT transition at $T_{LT}=133 \pm 1$ K for both samples. dc magnetization measurements reveal well-defined AF transitions at $T_N=214\pm 5$ K and 165 ± 5 K for the $x=0.010$ and 0.015 samples, respectively. Lightly hole-doped samples with $T_N > T_{LT}$ were intentionally selected to enable investigation of the effects of the SPT on the AF spin state.

^{139}La ($I=\frac{7}{2}$) NQR and relaxation measurements were performed for $4\,K<T<300\,K$ at both the $2\nu_Q$ ($\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$) and $3\nu_Q$ ($\pm\frac{7}{2}\leftrightarrow\pm\frac{5}{2}$) transitions. The NQR spectra were obtained by plotting the integrated intensity of the spin-echo signal as a function of spectrometer frequency. The ^{139}La NQR nuclear spin-lattice relaxation was measured by monitoring the recovery of the magnetization after saturation with a single $\pi/2$ pulse.

The static ^{139}La NQR results are summarized in Fig. 1. The ^{139}La NQR frequency ν_Q increases monotonically with

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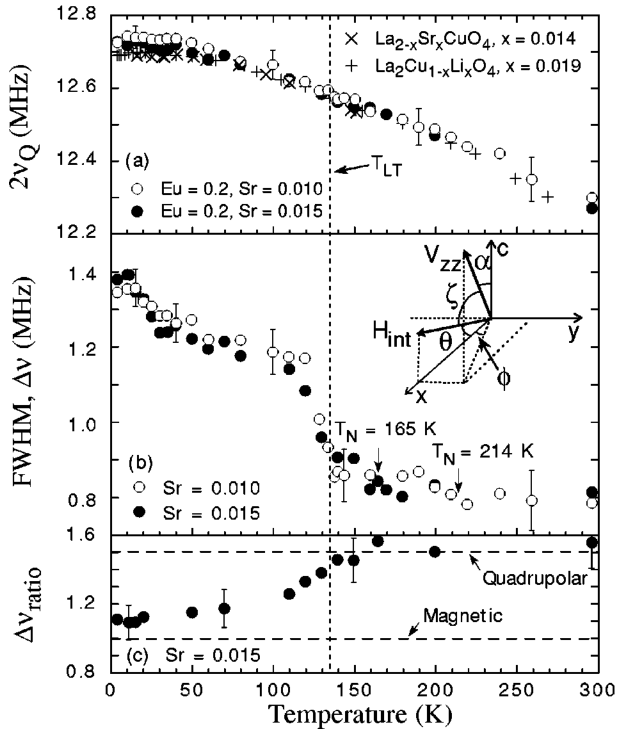

FIG. 1. ^{139}La NQR in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ with $x=0.01$ and 0.015: (a) T dependence of $2\nu_Q$. The T dependence of $2\nu_Q$ in $La_{2-x}Sr_xCuO_4$ from Ref. 8 and of $La_2Cu_{1-x}Li_xO_4$ from Ref. 15 are also plotted for comparison. (b) T dependence of $\Delta\nu$. In the inset we show the geometry of the orientations of the axis of V_{zz} and the internal field $\mathbf{H}_{\rm int}$ with respect to the crystal c axis and ab plane. (c) T dependence of $\Delta\nu_{\rm ratio}\equiv[\Delta\nu(\text{at }3\nu_Q)]/[\Delta\nu(\text{at }2\nu_Q)]$.

decreasing temperature without any noticeable feature at $T_{\rm LT}$ as shown in Fig. 1(a). The ^{139}La NQR line [Fig. 1(b)] is very broad; the linewidth $\Delta\nu$ (the full width at half maximum or FWHM) of the $2\nu_Q$ transition is already about 0.8 MHz at room temperature. With decreasing T, $\Delta\nu$ starts to increase around T_N. The most striking features are the anomalous jumps of $\Delta\nu$ at $T_{\rm LT}$ and around 30 K as shown in Fig. 1(b). The T dependence of the ratio $\Delta\nu_{\rm ratio}\equiv[\Delta\nu(\text{at }3\nu_Q)]/[\Delta\nu(\text{at }2\nu_Q)]$ [Fig. 1(c)] reveals the origin of the line broadening. For pure quadrupolar broadening, $\Delta\nu_{\rm ratio}$ is the same as the ratio of the quadrupole frequencies: $\Delta\nu_{\rm ratio}=3/2$, and for pure magnetic broadening, $\Delta\nu$ is the same for the two transitions: $\Delta\nu_{\rm ratio}=1$.

The T dependence of the ^{139}La NQR spin-lattice relaxation rate R_1 [Fig. 2(a)] shows a sharp peak at $T_{\rm LT}$ and a strong enhancement at low T with a peak at $T=T_f\cong6$ K. To determine R_1, the data for the first decade was fit to a single exponential recovery law. Above ≈30 K the recoveries are single exponential, but below this stretched exponential behavior is observed [similarly to the Sr (Ref. 8) and Li-doped cases[10]]. The same fitting procedure was applied for the entire temperature range investigated; while this increases the uncertainty in R_1 at low T, we find that varying the fitting procedure has essentially no effect on the position of the peak at T_f and at $T_{\rm LT}$, and the value of the activation energy E_a discussed later. The T dependence of the ratio $R_{1\rm ratio}\equiv[R_1(\text{at }3\nu_Q)]/[R_1(\text{at }2\nu_Q)]$ [Fig. 2(b)] was also investigated in order to understand the origin of the dynamical fluctuations in this system. Theoretically, it is known that

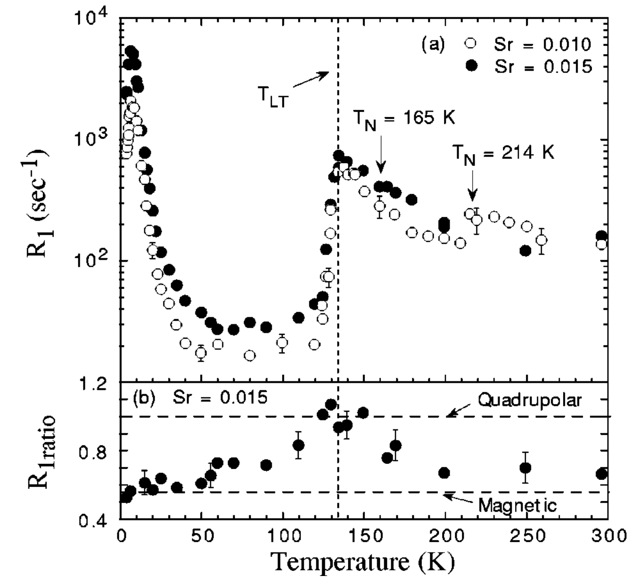

FIG. 2. (a) ^{139}La NQR relaxation rate R_1 vs T in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$. (b) T dependence of $R_{1\rm ratio}\equiv[R_1(\text{at }3\nu_Q)]/[R_1(\text{at }2\nu_Q)]$.

$R_{1\rm ratio}\cong0.56$ and 1 for ^{139}La ($I=\frac{7}{2}$) NQR relaxation for pure magnetic and pure quadrupolar origin, respectively.[8,15] Note that although the separation of the total relaxation into its magnetic and quadrupolar contributions is not straightforward,[16] trends in $R_{1\rm ratio}$ still provide useful insight into the origin of the relaxation.

Our discussion will focus on two aspects: (i) the structural and magnetic properties of the LT transition which generates a sharp asymmetric peak in R_1 and a sudden increase in $\Delta\nu$, and (ii) the anomalous static and dynamic magnetism observed at low T ($\lesssim30$ K); behavior very similar to that observed in $La_{2-x}Sr_xCuO_4$ (Refs. 8 and 9) and $La_2Cu_{1-x}Li_xO_4$.[10]

Near $T_{\rm LT}$, $R_{1\rm ratio}\cong1$ [Fig. 2(b)]; this indicates that R_1 is primarily of quadrupolar origin due to the fluctuations of the electric-field gradient (EFG) associated with the rearrangement of ions surrounding the La site at the SPT. The strong enhancement of R_1 above $T_{\rm LT}$ in Fig. 2(a) is a typical result of phonon softening at a SPT.[17] This reflects the slowing down of the critical-mode fluctuations as the SPT is approached.[17] As mentioned earlier, the LT transition is very abrupt by x-ray diffraction, suggesting the transition is first order.[14] However, the observed strong and gradual increase of R_1 is not expected from a discontinuous change of the order parameter in a pure first-order transition in which there is no well-defined T-dependent critical behavior of the order parameter. Therefore, we characterize the LT transition as an abrupt but continuous (so called, ''weak'' first order or ''quasi'' second order) SPT.[17,18]

In contrast to the strong signature of the SPT in the dynamical parameter, R_1, no noticeable change in ν_Q is observed [Fig. 1(a)]. In addition, the magnitude and T dependence of ν_Q are found to be nearly identical to Sr (Ref. 8) and Li-doped cases[19] with similar hole concentration as shown in Fig. 1(a) even though the more distorted local structure is expected in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ due to the large amount of Eu ($=0.2$). In fact, we find that the particular changes in the local EFG associated with the LT transition have very little effect on the ^{139}La ν_Q. Calculation of the EFG at the La site by summing the contribution from all neighboring ions within a radius of 60 Å reveals only 0.5% change in the principle component of the EFG (V_{zz}) due to the 45° rotation of the tilt axis of the CuO_6 octahedra arising from the SPT.[1,13] We do find, however, that the ^{139}La ν_Q is sensitive to the magnitude of the CuO_6 octahedral tilt. The absence of a change in ν_Q at T_{LT} indicates that there is no abrupt change of the tilt angle of the CuO_6 octahedra at the LT transition, consistent with the results of x-ray, neutron diffraction[2,13] and Mössbauer spectroscopy studies.[20] Our calculations also show that the angle (α) of V_{zz} from the crystal c axis does not change, either. We find that $\alpha \cong 13°$ in both phases with negligible change at T_{LT} ($\Delta\alpha < 1°$), in good agreement with other experimental results.[9,21]

The ratio $\Delta\nu_{ratio}$ [Fig. 1(c)] shows that above T_N, the line broadening is of quadrupolar origin arising from local inhomogeneity of the EFG due to the high density of Eu ions. In contrast, the small increase of $\Delta\nu$ below T_N and the substantial jump in $\Delta\nu$ at T_{LT} [Fig. 1(b)] are both consequences of increased magnetic broadening. The magnetic shift of the ^{139}La NQR line is proportional to $H_z = |\mathbf{H}_{int}| \cos\zeta$ [see the inset of Fig. 1(b)], the component of the internal field ($\mathbf{H}_{int}$) at the La site parallel to V_{zz}.[9] In fact, H_z will split sharp $2\nu_Q$ and $3\nu_Q$ NQR lines into doublets as observed in $La_{2-x}Sr_xCuO_4$,[8,9] $La_2Cu_{1-x}Li_xO_4$,[10] and oxygen-doped La214.[22] However, since the NQR line in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ is already very broad above T_N, the splitting of the broad line is visible only as a small additional broadening of the line. Thus, the small increase of $\Delta\nu$ immediately below T_N is then simply due to the appearance of the internal field in the AF state of the LTO phase and does not indicate a distribution of H_z.

In contrast, the dramatic magnetic broadening at T_{LT} is ascribed to an increase in the distribution of H_z in the LT phase. We argue that it arises from the distribution of the in-plane angle ϕ of $\mathbf{H}_{int}$ with respect to the axis of V_{zz} in LT phase. Referring to the illustration in the inset of Fig. 1(b), the angle ζ is determined by

$$\cos\zeta = \sin\alpha \cos\phi \cos\theta + \cos\alpha \sin\theta. \quad (1)$$

Using the known values: $\alpha = 13-15°$ (Refs. 9 and 21) and $\theta < 1°$;[23] we find that reducing the in-plane angle ϕ from 45° (assumed in LTO phase[9]) to 0° increases $\cos\zeta$ by ~ 1.4. Thus, a distribution of the in-plane angle ϕ can give rise to a considerable distribution of H_z and this can explain the additional magnetic broadening we observe. We note that we observe the same magnitude of $\Delta\nu$ at low T in a sample with the same Eu=0.2 but without holes (Sr=0.0); this indicates that the additional magnetic broadening in the LT phase is a purely structural effect, and is little modified by the presence of doped holes.

This distribution of the in-plane angle (ϕ) in the LT phase implies a distribution of ordered moment orientations in ab plane. This can be ascribed to faults in the spin-stacking pattern induced by the reduction of the interlayer coupling in LT phase. From a neutron scattering study in the LT phase of $La_{1.65}Nd_{0.35}CuO_4$, Keimer *et al.* observed the presence of equal fractions of two magnetic structures; these two differ from each other in that the stacking sequence between nearest-neighbor CuO_2 layers is opposite.[24] A similar argument regarding the stacking faults can be found in Ref. 14 although a discrepancy exists in the spin directions in the LT phase between Refs. 24 and 14. The stacking of spins in neighboring CuO_2 layers is determined by the interlayer coupling and is uniquely determined by a net AF interlayer coupling in the LTO phase. Thus, the observation of stacking faults in the LT phase implies that the interlayer coupling is weakened by the structural change to the less orthorhombic LT phase.[24] In fact, in dc magnetization measurements of our samples to be published elsewhere,[5] we observe evidence for the reduction of the AF interlayer coupling in the LT phase which causes a sudden increase in the magnetization at T_{LT}.

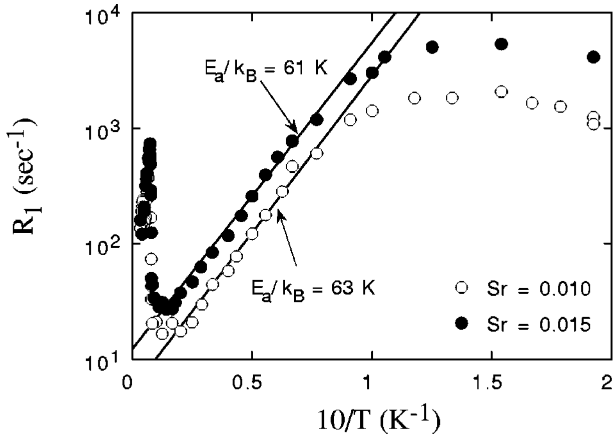

FIG. 3. ^{139}La R_1 vs $10/T$. Lines are fits to the activated behavior; $R_1 \propto \exp(E_a/k_BT)$.

The increase in $\Delta\nu$ cannot be attributed to an increase in either α or θ. First, the absence of a noticeable change in the ^{139}La ν_Q at T_{LT} and our calculation of an EFG tensor shows that the angle α does not change significantly ($\Delta\alpha < 1°$) at the transition. Our recent magnetization study in an oriented polycrystalline $La_{1.8}Eu_{0.2}CuO_4$ powder revealed that the anomalous increase of the magnetization is observed only for $\mathbf{H} \| c$ axis.[5] This result clearly excludes the possibility of an increase in θ (i.e., a rotation of the Cu^{2+} spins up out of the plane); in this case a similar anomaly should be observed in the $\mathbf{H} \perp c$-axis magnetization. We note that neutron scattering did reveal an increase of the out-of-plane component of Cu^{2+} spin at low T in $La_{2-x-y}Nd_ySr_xCuO_4$.[6] However, this is due to the coupling of the Cu moments to the Nd moments[6] and is not intrinsic to the AF CuO_2 plane; hence it is absent in the nonmagnetic Eu-doped La214 and so is not relevant to the increase of the ^{139}La $\Delta\nu$ observed here.

We turn now to the anomalous low T magnetism. The strong enhancement of R_1 at low T with a peak at $T_f \cong 6$ K and the anomalous increase of $\Delta\nu$ below ~ 30 K bear a close resemblance to similar features observed in lightly hole-doped $La_{2-x}Sr_xCuO_4$ (Refs. 8 and 9) and $La_2Cu_{1-x}Li_xO_4$.[10] This behavior now seems to be universal in lightly hole-doped AF La214. Analyzing $R_1(T)$ at low T (above T_f) in terms of activated behavior, $R_1 \propto \exp(E_a/k_BT)$, we find $E_a/k_B \cong 62 \pm 5$ K for both samples as shown in Fig. 3. These values are considerably smaller than those obtained in $La_{2-x}Sr_xCuO_4$: $T_f \cong 15$ K and $E_a/k_B \cong 120$ K at similar hole concentration[8] even though the origin (dopant) of the doped holes is the same. This is in dramatic contrast to the observation that T_f and E_a/k_B found in $La_{2-x}Sr_xCuO_4$ (Ref. 8) and $La_2Cu_{1-x}Li_xO_4$ (Ref. 10) are essentially identical even though they have different dopants (out-of-plane vs in-plane).[10,11] The significant difference between $La_{2-x}Sr_xCuO_4$ and $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ is the local structure. Clearly, the local structure plays a crucial role in determining the low-temperature magnetic properties in lightly hole-doped La214.

Holes added to AF La214 segregate into charged regions (domain walls) surrounding undoped AF domains. The anomalous low-T magnetic behavior indicates a freezing of spin fluctuations accompanied by recovery of the static sublattice magnetization. This has been interpreted as arising from freezing of the domain motion[10,11] and/or disappearance of the domain walls as the constituent holes become pinned to donor impurities.[9] On the other hand, static charge-stripe order has been observed in the LT phase of more heavily doped $La_{2-x-y}Nd_ySr_xCuO_4$,[6,7] indicating that domain walls are more strongly pinned in the LT phase. Thus, the smaller values of T_f and E_a/k_B in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ observed here cannot be simply explained by either the freezing of domain motion[10,11] or the localization of holes at low T (Ref. 9) proposed previously. Re-examination of the domain- or hole-localization picture is desired.

In summary, we have presented ^{139}La NQR results in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ which contribute to a more detailed understanding of the interplay between structural and magnetic properties of the LT (LTO→$Pccn$/LTT) transition. We find that the SPT affects the AF CuO_2 spin structure resulting in faults in the spin-stacking pattern due to the reduction of the interlayer coupling in the LT phase. By comparing the data obtained in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ with the results in $La_{2-x}Sr_xCuO_4$ and $La_2Cu_{1-x}Li_xO_4$, we find that the magnetic properties are very sensitive to the local structure; in fact the local structure plays a more important role for the magnetic properties of lightly hole-doped La214 than the position of the dopant.

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