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Charge ordering in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ studied by resonant soft x-ray diffraction

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Resonant soft x-ray scattering with photon energies near the O *K* and the Cu L_3 edges was used to study the charge ordering in the system $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ as a function of temperature for $x=0.125$ and 0.15. From the superstructure diffraction intensities, a charge ordering with a doping-dependent wave vector is derived which is in this system well below the transition temperature of the low-temperature tetragonal phase but well above the onset of spin ordering. This indicates that structural changes and magnetic interactions are not in general the driving force for the formation of stripelike phases in two-dimensional-doped cuprates. Analysis of the lineshape of the scattered intensity as a function of photon energy yields evidence for a high hole concentration in the stripes.

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In the doped cuprates there exists a complex interplay between lattice, charge, and spin degrees of freedom yielding several phases in a narrow concentration range: the antiferromagnetic insulating phase, the high-T_c superconducting phase, the pseudogap region, and charge- and spin-ordered phase. The latter is usually divided into checkerboard phases and stripelike phases. The stripelike phase in which antiferromagnetic antiphase magnetic domains are separated by periodically spaced domain walls to which the holes segregate was predicted from Hartree-Fock analysis of the single-band Hubbard model.[1] Fluctuating stripelike order of spins in $La_{2-x}Sr_xCuO_4$ (LSCO) near $x=1/8$ has been inferred from neutron scattering showing incommensurate magnetic correlations.[2,3] In $La_{1.875}Ba_{0.125}CuO_4$ (LBCO), superconductivity is strongly suppressed and a low-temperature tetragonal (LTT) phase appears which stabilizes a static stripelike order due to the corrugated pattern of the in-plane lattice potential.[4] A static stripelike order of the Cu spins has also been detected in $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ (LNSCO) by neutron scattering. In these compounds, the corrugation of the CuO_2 plane is more pronounced due to the smaller ionic radius of Nd compared to La.[5] Replacing Nd by even smaller Eu ions, a phase diagram of the system $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ (LESCO) has been proposed based on muon-spin rotation (μSR) experiments.[6] There the magnetic stripe order almost completely replaces the superconducting range between $x=0.08$ and 0.2. Only above $x\approx 0.2$ superconductivity could be detected in a narrow concentration range.

Using neutron scattering[5] and nonresonant x-ray scattering,[7] the ordering of the charges can be only monitored indirectly by the associated lattice distortion. The reason for this is that neutron and x-ray diffraction are mainly sensitive to the nuclear scattering and the core electron scattering, respectively. More direct information on the charge modulation in cuprates can be obtained by resonant soft x-ray scattering (RSXS) using photon energies at the O *K* and the Cu *L* edge.[8,9] In particular at the threshold of the O *K* level, the form factor for a charge carrier is enhanced by a factor of 82.[9] Near the Cu *L* edge there is a strong enhancement of the form factor as well, but mainly lattice distortions are probed which may be caused by charge modulations.[10] In the high-T_c superconductor LSCO ($x=0.15$), no static stripelike modulation of the charge carriers could be detected by RSXS (Ref. 8); while in the compound LBCO ($x=1/8$) a strong modulation of the charge carriers has been observed in the range below the LTT phase-transition temperature $T_{LTT}=55$ K. We emphasize a striking feature of all investigations of stripelike charge and spin order in these systems: the ordering seems to be of cooperative nature, i.e., charge and spin order show similar temperature dependence and the appearance of a spin-ordered state at T_{SO} is slightly below the charge order temperature T_{CO} and the latter is close to T_{LTT}.[4,9,11] Similar results have been obtained for LNSCO.[12,13] In the compounds LESCO, which is the focus of this study, $T_{LTT}=125$ K (almost independent of the dopant concentration for $0.08<x<0.17$)[6] and $T_{SO}=45$ K (for $x=0.15$)—derived from neutron scattering[14]—are distinctly different. The possible appearance of a separate charge and spin ordering should therefore be readily observable in this system.

In this Rapid Communication, we have determined directly the charge ordering by means of RSXS in the LESCO system. Contrary to the experiment on LBCO (Ref. 9) in which T_{CO} was found to be very close to T_{LTT} and T_{SO}, we obtain for LESCO completely different results: the charge ordering temperature T_{CO} (directly derived from RSXS) is well below the structural transition temperature T_{LTT} and well above T_{SO}, i.e., there is static charge ordering without static spin ordering over a large temperature range. These findings together with the doping dependence of the wave vector of the charge order support strong-coupling scenarios for the formation of stripes and leave little scope for the weak-coupling nesting scenarios.[15,16] Furthermore, from a lineshape analysis of the superstructure diffraction intensity as a function of photon energy across the O *K* resonance, we

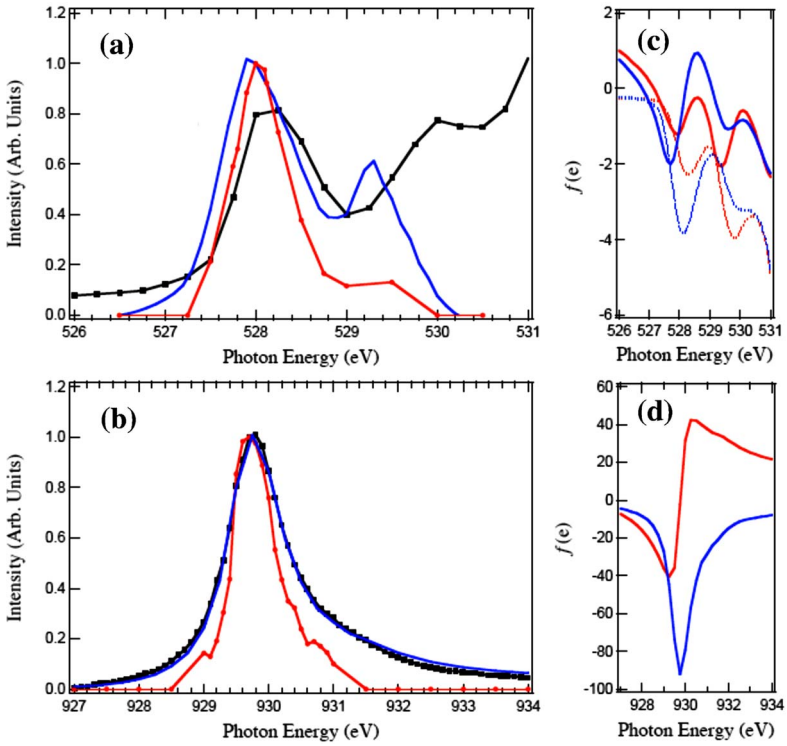

FIG. 1. (Color online) (a) [(b)] The resonant scattering intensity in light gray (red) as a function of photon energy through the O K [Cu L_3] absorption edge for the stripe superstructure peak. Data were taken near the O K [Cu L_3] for $l=0.75$ (1.6). Also shown is the x-ray absorption spectrum in black and the calculated scattering intensity in dark gray (blue). (c) The real (solid line) and the imaginary (dotted line) parts of the atomic form factor f at the O K edge of LSCO for $x=0.07$ depicted in light gray (red) and $x=0.15$ depicted in dark gray (blue). (d). The real part in light gray (red) and the imaginary part in dark gray (blue) of the atomic form factor f at the Cu L_3 edge of LSCO for $x=0.125$.

infer the existence of a high doping concentration per Cu site in the hole stripes.

The RSXS experiments were performed at the BESSY undulator beam line UE 46-PGM working with vertically polarized photons in a horizontal scattering geometry. A two-circle UHV diffractometer was equipped with a continuous flow He cryostat. The detector was a silicon diode which had an angular acceptance of 0.8° in the scattering plane and 4° perpendicular to it. LESCO single crystals were grown using the traveling solvent floating-zone method. X-ray diffraction, ^{63}Cu nuclear magnetic resonance (NMR) spectroscopy, and magnetic-susceptibility measurements yielded for both concentrations a first-order phase transition at $T_{\mathrm{LTT}}=125$ K.[17] The single crystals were cleaved parallel to the (001) surface in air shortly before the transfer to the scattering chamber. At a photon energy of 1100 eV, the (002) peak could be reached which was used together with the superstructure peaks to orient the sample.

In Fig. 1 we present a comparison of x-ray absorption spectroscopy (XAS) measurements using the fluorescence method with the photon-energy dependence of the superstructure intensities near the O K and the Cu L_3 edges for a LESCO ($x=0.125$) single crystal at a temperature $T=6$ K. We denote the wave vector $\mathbf{Q}=(2\pi h/a, 2\pi k/b, 2\pi l/c)$ with Miller indices (h,k,l) where in the LTT phase $a=b=3.79$ Å and $c=13.14$ Å for $x=0.125-0.15$. In accordance with previous electron energy-loss spectroscopy (EELS) and XAS studies,[18,19] we see [Fig. 1(a)] at 528 eV transitions into the O $2p$ doped hole states in the conduction band (CB) and at 530 eV transitions into the Cu $3d$ upper Hubbard band (UHB) hybridized with O $2p$ states. The RSXS intensity of the (0.23, 0, l) superstructure reflection displays a strong resonance at the energy of the doped hole states, indicating a strong density modulation of the charge carriers. There is also a weaker resonance at the UHB of the O K edge which has been related to a modulation of correlation effects.[9] For the Cu L_3 edge, transitions into the Cu $3d$ hole states are observed. The shoulder near 931 eV is usually ascribed to Cu $3d^9\underline{L}$ ligand-hole states which increases with increasing doping concentration. The superstructure peak also shows a strong resonance at the white line of the Cu L_3 edge [see Fig. 1(b)].

In order to glean information about the electronic structure of the stripes, we have modeled the lineshape of the scattered intensity at both the O K and Cu L edges. In Figs. 1(a) and 1(b), we also present the results of these calculations. In general, the scattering intensity I_{sc} will be given by

$$I_{sc}(\mathbf{Q}) \propto \left| \sum_j f_j(E, x+\delta x_j) e^{-i2\pi \mathbf{Q}\cdot(\mathbf{r_j}+\delta \mathbf{r_j})} \right|^2, \qquad (1)$$

where δx_j is the change in the local hole doping away from x arising from an electronic ordering and $\delta\mathbf{r_j}$ is a change in the lattice position due to a lattice distortion. Similar to the treatment of the RSXS data of LBCO at the O K edge,[9] we assume that the predominant contribution to the scattering is

from the electronic ordering and we neglect the lattice distortions ($\delta \mathbf{r_j}=0$). XAS measurements on LSCO at different Sr doping levels[20] allows us to determine $f_j(E,x+\delta x_j)$ by making use of the proportionality between $\Im(f_j)$ and the x-ray absorption followed by a Kramers-Kronig transformation to obtain $\Re(f_j)$.

The precise structure of the stripe order and magnitude of the charge modulation—whether there is a sinusoidal variation in charge modulation or whether we have the extreme case of half-filled charge stripes separated by undoped antiferromagnetic domains—will determine the appropriate expansion of Eq. (1). At the O K edge, the x-ray absorption[19] and subsequently the atomic scattering form factor varies roughly linear with doping for x less than ≈ 0.2 so that $f_j(E,x+\delta x_j)=f(E,x)+(\Delta f(E,x)/\Delta x)\delta x_j$. Assuming that this linear expansion is valid, the lineshape of the superstructure intensity only depends on $\Delta f(E,x)/\Delta x$ and not on other details of the stripe order. As such, we can use XAS measurements[20] at $x=0.07$ and 0.15 to determine $f(E,x=0.07)$ and $f(E,x=0.15)$ [shown in the Fig. 1(c)] and calculate $I_{\mathrm{sc,O}\,K} \propto |\Delta f(E,x)/\Delta x|^2$, as shown in Fig. 1(a). This calculation captures the measured peak positions correctly but produces two unexpected discrepancies. Similar to the case of LBCO (Ref. 9), the measured lineshape is narrower than calculated and, most strikingly, the second peak at 529.3 eV is too large.

At the Cu L edge, the intensity of the superstructure reflection is associated with structural distortions.[10] In the case $\delta x_j=0$, the energy-dependent lineshape is given by $I_{\mathrm{sc,Cu}\,L}=|f_{\mathrm{Cu}}|^2$. The corresponding results of the Kramers-Kronig analysis using Cu L_3 XAS results from the literature[20,21] are shown in Figs. 1(b) and 1(d). The calculated RSXS lineshape is almost identical to the XAS data, but the width is much larger than that of the resonant scattering intensity.

However, in the calculations presented above, several assumptions have been made which could influence the calculated linewidths. For instance, it could be insufficient to consider only a purely structural modulation for the RSXS at the Cu L_3 edge. Regarding the O K edge, it may be that the essentially ionic (local) description above is not a good approximation for the bandlike states probed at the O K edge. It is also not obvious whether or not the form factors deduced from XAS measurements outside the stripe phase provide a good description for the scattering centers in the stripe-ordered phase.

Another assumption made for the O K edge is the strict linearity of the form factor with respect to x. The small scattering intensity for the UHB relative to the CB may be explained by a deviation from the linear concentration dependence of the absorption coefficient for the two bands. For $x<0.2$, EELS and XAS experiments[18–21] as well as theoretical calculations for strongly covalent charge-transfer insulators[22] indicate that the x-ray absorption and hence in a first approximation also the form factor for the CB and the UHB is proportional to $2x$ and $1-x$, respectively. Based on this, the intensity ratio $I_{\mathrm{CB}}/I_{\mathrm{UHB}}=|[\Delta f(E,x)/\Delta x]_{\mathrm{CB}}/[\Delta f(E,x)/\Delta x]_{\mathrm{UHB}}|^2=4$ in fair agreement with the calculated curve in Fig. 1(a). On the other hand, the cited experiments indicate at higher x values a strong reduction in the linear decrease in the UHB absorption. Thus the strong reduction in the measured scattering intensity for the UHB can be readily explained by a deviation from the linear model used in the calculations together with a high doping concentration per Cu site ($x \gg 0.2$) within the hole stripes in agreement with a previous analysis for LBCO.[9]

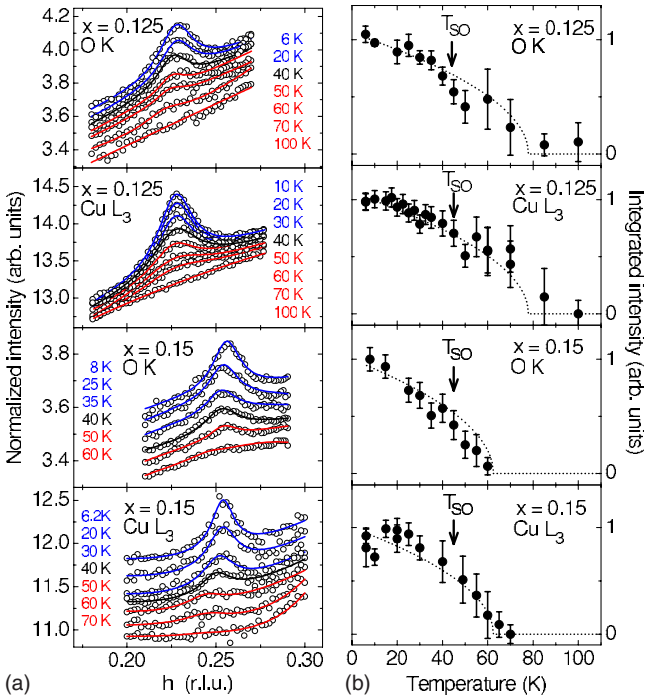

FIG. 2. (Color online) (a) Temperature dependence of h scans along $(h,0,l)$ showing superstructure reflections of LESCO ($x=0.125$ and 0.15) using O K ($l=0.75$) and Cu L_3 ($l=1.6$) photon energies. Points depict RSXD data; the solid lines represent fits to the data. (b) Temperature dependence of the intensities of the superstructure reflections shown in (a) normalized to the intensity at $T=6$ K. The dotted line is guide for the eyes $[\propto(T_c-T)^{1/2}]$. To highlight the existence of charge ordering above T_{SO}, the fit of data near T_{SO} is marked by a black line in (a) and by arrows at T_{SO} in (b). For $x=0.15T_{\mathrm{SO}}$ was taken from neutron-scattering data (Ref. 14) and for $x=0.125T_{\mathrm{SO}}$ was extrapolated from data in the literature (Refs. 6 and 14).

In Fig. 2(a) we present h scans of the superstructure reflections with photon energies near the O K edge (528.0 eV) and the Cu L_3 edge (929.7 eV) for $x=0.125$ and for $x=0.15$. Typical signal to background ratios were near 0.05. The scans presented in Fig. 2(a) could be readily fitted by a Lorentzian plus a polynomial background. Besides the scans shown in Fig. 2(a), we have also measured various scans for different l values. In agreement with previous studies[9] of LBCO ($x=1/8$), we do not observe a pronounced variation in the diffraction intensities within the small accessible l range at the resonant energies. This indicates rather short coherence lengths along the c axis which are shorter than two times the lattice constant c. The intensities of the superstructure peaks, as derived from the area of the Lorentzians, as a function of temperature are shown in Fig. 2(b). In all cases studied here, there is a monotonic decrease in the intensity with increasing temperature. The transition temperatures T_{CO} are tentatively identified with that temperature where the extrapolated intensity of the superstructure reflec-

tion disappears. In this way, we obtain from both O K and Cu L_3 edge data, for $x=0.125$ and $x=0.15$ $T_{CO}=80\pm10$ K and 65 ± 10 K, respectively. The lower T_{CO} with increasing x can be rationalized by a reduced stripe stability for doping concentrations away from $x=1/8$.

The widths of the superstructure peaks at low temperatures derived from the fits are four to eight times larger than the instrumental widths checked at the (001) Bragg peak. This means that the width is determined by a finite correlation length of the charge order. This correlation length is of the order of 85 and 100 lattice constants a and then decreases by about a factor of 2 before T_{CO} is reached. Increasing x from 0.125 to 0.15 leads to a slight increase in the correlation length. This probably indicates that the disorder is primarily not caused by the impurity potential of the Sr atoms.

More interestingly, the wave vector ϵ for the lattice distortion superstructure reflection increases between the two concentrations from 0.228 to 0.254. These values are perfectly in line with the general incommensurability curve of low-energy spin excitations $\epsilon/2$ versus x, which for smaller x is determined by $\epsilon/2=x$ and saturates above $x=0.125$.[23] From this excellent agreement, we can conclude that the fluctuating magnetic stripes and the charge order directly detected by RSXS correspond to the same phenomenon. Furthermore, in a more conventional model, stripes are often explained by a nesting between segments of the Fermi surface near the antinodal point with a nesting vector parallel to the Cu-O bond and being close to ϵ. However, in this model the nesting vector should decrease with increasing x, while the present data show for the charge ordering an increase of ϵ with increasing x. This clearly excludes this simple weak-coupling nesting scenario for the explanation of stripes.

Comparing LESCO with other cuprates having an LTT phase, one realizes an interesting difference: for the dopant concentration $x=0.125$ (0.15), the three transition temperatures $T_{LTT}=125$ (125) K, $T_{CO}=80$ (65) K and $T_{SO}=45$ (45) K are distinctly different. Most importantly, the present RSXS data at the O K edge prove the appearance of a charge order well below the structural transition and the existence of a large temperature range between 45 and 80 K, where charge order exists without spin order. The latter observation is at variance with the Hartree-Fock calculations,[1] according to which the magnetic order drives the formation of charged stripes by a stabilization due to a magnetic interaction between the antiferromagnetic domains across the antiphase domain walls. Nonetheless, the magnetic and the charge order are expected to be coupled.[15] This view of the coupling between the two order parameters is supported by electron spin resonance (ESR) studies revealing a sudden slowing down of the spin fluctuations which sets in close to T_{CO}.[24] Finally, it should be also noted that the difference in the transition temperatures cannot be explained by a different time resolution between RSXS and neutron scattering, since the same methods applied to LBCO did not yield a difference between T_{CO} and T_{SO}.

The results for LBCO, LNSCO, and in particular LESCO clearly indicate that the charge stripes are stabilized by structural distortions that exist in the LTT phase. The corrugated CuO_2 planes create a pinning potential that favors the formation of stripelike structures. On the other hand, the present study on LESCO also reveals additional information compared to the previous work on systems with static stripes. LESCO is a system in which a clear difference (40 K) between the structural and the charge order transition is observed. In this context, we would like to point out that here T_{CO} is larger than in any other cuprate, although the low-temperature tilt distortion in Nd-doped compounds is of similar size or even larger. This means that in the other systems, T_{CO} is more or less determined by the structural transition and not a real entropy-driven transition. From this we conclude that the charge order transition in LESCO takes place at a constant pinning potential, while in all other systems the smaller T_{CO} is due to a temperature-dependent buckling. Thus in LESCO the charge order transition is electronic in origin and possibly in the current study on LESCO, we observe the "intrinsic" difference between charge and spin orders, while in the other systems this difference is affected by the proximity to the structural transition.

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