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## LETTER TO THE EDITOR

**Oxygen-isotope shift of the charge-stripe ordering temperature in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  from x-ray absorption spectroscopy**

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**Abstract.** A very large oxygen-isotope shift of the charge-stripe ordering temperature in the high-temperature superconductors  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  has been observed using x-ray absorption spectroscopy, a fast ( $\sim 10^{-15}$  seconds) and local probe ( $\sim 5$  Å). Upon replacing  $^{16}\text{O}$  with  $^{18}\text{O}$ , the charge-stripe ordering temperature in  $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$  increases from about 110 K to 180 K. The present results provide compelling evidence for a strong electron–phonon interaction in this compound, and thus place important constraints on the microscopic origin of the stripe formation.

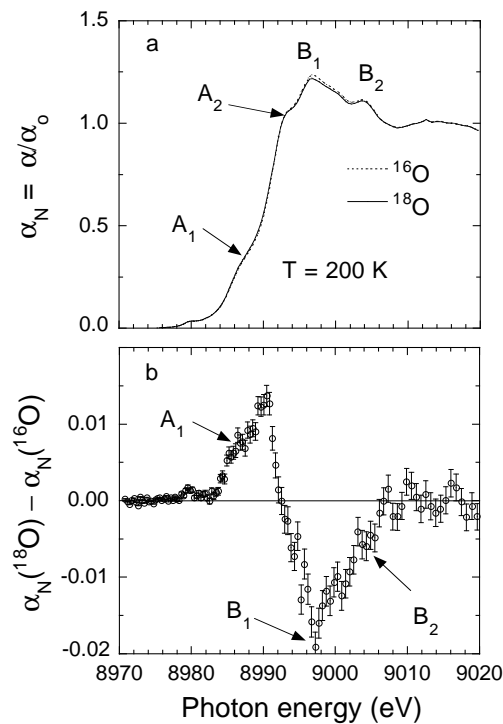
Developing a theory of high-temperature superconductivity is one of the outstanding problems in physics. Despite tremendous experimental and theoretical efforts, the mechanism of high- $T_c$  superconductivity is still not clear. This is primarily due to the complication of the phase diagram for temperature  $T$  and hole concentration  $x$ . The discovery of the stripe phase [1–3] has added a new feature to the already complex phase diagram. Such a stripe phase is believed to be important to the understanding of the pairing mechanism of high-temperature superconductivity [4]. However, the microscopic origin of the stripe phase is still highly debated. It could be caused by purely electronic interactions and/or by a strong electron–phonon interaction.

Although there is increasing experimental evidence for a strong electron–phonon interaction in the cuprate superconductors [3, 5–12], it is not clear whether this interaction is important to the formation of the stripe phase. For the colossal-magnetoresistive manganites, a strong electron–phonon interaction plays an essential role in the formation of the Jahn–Teller paired stripes (or charge-stripe ordering), as implied by a very large oxygen-isotope shift of the charge-stripe ordering temperature observed in both  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  and  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  systems [13]. Therefore it is natural to ask whether the stripe formation temperature in cuprates could also depend on the oxygen-isotope mass if lattice vibrations are strongly coupled to charge carriers. Here we report the oxygen-isotope effect on the charge-stripe ordering temperature in  $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$  using x-ray absorption near-edge spectroscopy (XANES) measurements. We choose this compound where the largest oxygen-isotope effects on both the superconducting transition temperature and the effective supercarrier mass have been observed [7]. The XANES spectroscopy probes a higher order of the atomic pair distribution function and is very sensitive to any small change in the local structure within a cluster of atoms of 5–6 Å around the photoabsorbing atom. Our results show that the oxygen-isotope

substitution strongly modifies the local structure of the  $\text{CuO}_2$  planes, and shifts the charge-stripe ordering temperature  $T^*$  towards a higher temperature by 70(20) K, i.e., 110 K in the  $^{16}\text{O}$  sample and 180 K in the  $^{18}\text{O}$  sample.

Samples of  $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$  were prepared by a conventional solid-state reaction using dried  $\text{La}_2\text{O}_3$  (99.99%),  $\text{SrCO}_3$  (99.999%) and  $\text{CuO}$  (99.999%). The powders were mixed, ground thoroughly, pressed into pellets and fired in air at 1000 °C for ~96 h with three intermediate grindings. The diffusion was carried out for 40 h at 900 °C and oxygen pressure of about 1 bar. The cooling time to room temperature was 4 h. The oxygen-isotope enrichment was determined from the weight changes of the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples. The  $^{18}\text{O}$  samples had ~90%  $^{18}\text{O}$  and ~10%  $^{16}\text{O}$ . The  $^{16}\text{O}$  sample has a  $T_c$  of about 8 K, and the  $^{18}\text{O}$  has a  $T_c$  lower by about 1 K than the  $^{16}\text{O}$  sample [7].

The Cu K-edge absorption measurements were performed on powder samples, being more efficient for getting the key information on the high-energy spectral weight transfer from  $E \parallel c$  to  $E \parallel a-b$  plane. The absorption spectra were recorded on the beam-line BM29 at European Synchrotron Radiation Facility (ESRF) at Grenoble. The Cu  $K\alpha$  fluorescence yield (FY) of the samples was measured using a modern multi-element FY detector by summing up to about ten scans to reach up to 2.8 million counts above the threshold (9016 eV). So the relative error of the signal is less than 0.1% above 9016 eV. The samples were mounted in a closed-cycle He refrigerator and the temperature was monitored with an accuracy of  $\pm 1$  K. To measure the spectra with a very high signal-to-noise ratio and with a high resolution at the Cu K edge,

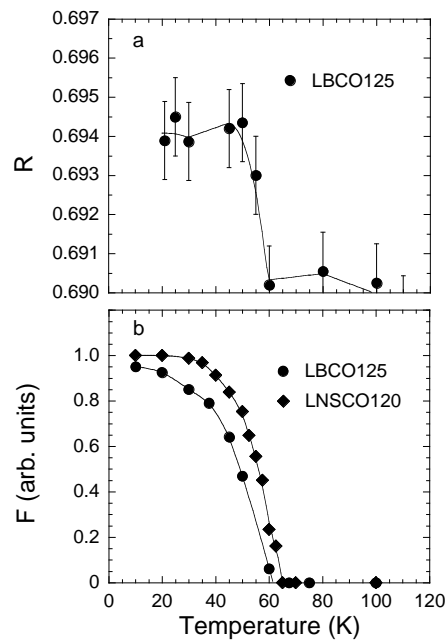


**Figure 1.** The oxygen-isotope effect on local structure distortions in  $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$ . (a) The normalized Cu K-edge x-ray absorption near-edge spectra for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples at 200 K. The spectra were obtained using a standard procedure [14] in which pre-edge constant backgrounds were subtracted. (b) The difference between the spectra of the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples.

we used a Si(311) double-crystal monochromator and collected several absorption scans at the same temperature. The energy drift was well below 0.02 eV, as controlled by a Cu metal reference in the vicinity of the samples. We repeated the measurements on another beam-line (BM32) after several months using a Si(111) double-crystal monochromator with a sagittal focusing on the beam-line BM32. In spite of the different experimental set-ups for the two experimental runs, the spectra showed a very good reproducibility.

Figure 1(a) shows the normalized Cu K-edge x-ray absorption near-edge spectra for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples at 200 K. The spectra show typical features of the cuprates with a square-planar geometry. We denote the well-resolved peak features as  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$ . The peak features which extend from about 8 eV to 40 eV above the threshold have been identified as multiple-scattering resonances of the excited photoelectrons, scattered by neighbour atoms as shown by XANES calculations for  $\text{La}_2\text{CuO}_4$  [15]. The peak  $A_1$  is mainly due to the multiple scatterings of the ejected photoelectrons from the La/Sr atoms, while peak  $A_2$  is due to the multiple scatterings of the photoelectrons from the apical oxygen. The main peak  $B_1$  probes the multiple scatterings from the oxygen atoms in the square  $\text{CuO}_2$  planes. Therefore, a decrease in the intensity of this main peak implies an increase in the deviation of the local structure from the square geometry.

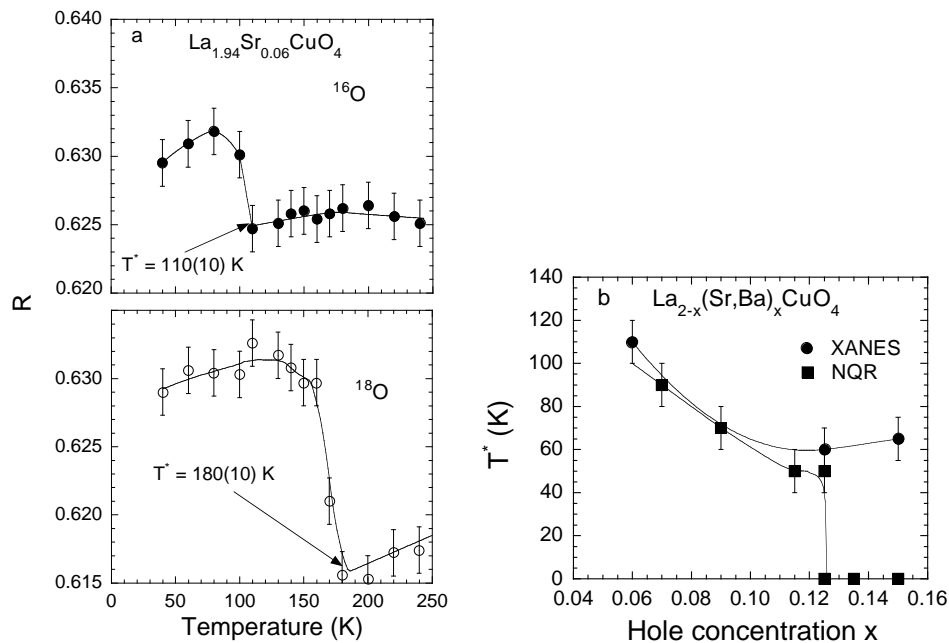
The effect of the oxygen-isotope substitution on the distribution of local Cu-site conformations can be seen directly from figure 1(b) where the difference between the spectra of the two isotope samples are plotted. It is evident that, upon replacing  $^{16}\text{O}$  with  $^{18}\text{O}$ , the intensities



**Figure 2.** The charge-stripe ordering in  $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$  and  $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$ . (a) The XANES peak intensity ratio  $R = (\beta_1 - \alpha_1)/(\beta_1 + \alpha_1)$  for  $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$  (LBCO125), where  $\beta_1$  and  $\alpha_1$  are the intensities of peak  $B_1$  and peak  $A_1$ , respectively. (b) The wipeout fraction  $F$  of  $^{63}\text{Cu}$  NQR for LBCO125 and  $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$  (LNSCO120). The data were taken from [16]. Both  $R$  and  $F$  exhibit a sudden increase below about 60 K, which just corresponds to the charge-stripe ordering temperature ( $\sim 65$  K) observed by means of neutron scattering [1]. This clearly shows that the temperature below which the parameter  $R$  exhibits a sudden increase is the charge-stripe ordering temperature.

of both peak  $B_1$  and  $B_2$  decrease, while the intensities of both peak  $A_1$  and  $A_2$  increase. This implies that the local in-plane structure for the  $^{18}\text{O}$  sample deviates more from the square geometry than for the  $^{16}\text{O}$  sample at 200 K.

Since the intensities of both peak  $A_1$  and  $B_1$  are sensitive to the local structure fluctuations involving the tilting of the apical oxygen and the rhombic distortion of the  $\text{CuO}_2$  planes, and their intensity changes are in opposite directions, the XANES peak intensity ratio  $R = (\beta_1 - \alpha_1)/(\beta_1 + \alpha_1)$  should be a good parameter that quantifies such local structure distortions. Here  $\beta_1$  and  $\alpha_1$  are the intensities of peak  $B_1$  and peak  $A_1$ , respectively. If the charge-stripe ordering in high-temperature superconductors induces a sudden change in such local structure distortions, there should correspondingly be a sudden change in the parameter  $R$  at the charge-stripe ordering temperature. This is indeed the case as seen from figure 2(a) where the temperature dependence of the parameter  $R$  for  $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$  (LBCO125) is shown. It is clear that  $R$  is nearly temperature independent above 60 K, and exhibits a sharp increase below 60 K and then saturates at low temperatures. Such a temperature dependence of  $R$  is very similar to the temperature dependence of the so-called wipeout fraction  $F$  of  $^{63}\text{Cu}$  NQR for  $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$  and  $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$  (LNSCO120), as reproduced in figure 2(b) (reference [16]). The parameter  $F$  for both compounds shows a sudden increase below about 60 K, which exactly corresponds to the charge-stripe ordering temperature ( $\sim 60$  K) observed by means of neutron scattering [1]. Thus the temperature below which the parameter  $R$  exhibits a sudden increase is the charge-stripe ordering temperature. Since the charge-stripe ordering in  $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$  is nearly static, it is natural that the  $T^*$  observed by three different



**Figure 3.** The oxygen-isotope effect on the charge-stripe ordering temperature  $T^*$  in  $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$  and the doping dependence of  $T^*$ . (a) The temperature dependence of the XANES peak intensity ratio  $R$  for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$ . (b) The doping dependence of the charge-stripe ordering temperature in the  $\text{La}_{2-x}(\text{Sr},\text{Ba})_x\text{CuO}_4$  systems from NQR [16] and XANES. The  $T^*$  of  $x = 0.15$  is from unpublished XANES data (also see reference [17]).

experimental techniques (with the timescale ranging from  $10^{-6}$  s to  $10^{-15}$  s) are the same.

Having demonstrated that the  $R$  is a good measure of the charge-stripe order parameter, we can determine the charge-stripe ordering temperatures of the two isotope samples from their temperature dependences of  $R$ , as plotted in figure 3(a). From the figure, we obtain  $T^* = 110(10)$  K for the  $^{16}\text{O}$  sample and  $T^* = 180(10)$  K for the  $^{18}\text{O}$  sample. The oxygen-isotope shift of  $T^*$  is about  $70(20)$  K, which is the largest isotope shift ever observed.

Such a large isotope shift cannot be caused by a carrier-concentration difference which has been found to be negligible [6, 7]. Furthermore,  $T^*$  does not strongly depend on the carrier concentration as seen clearly from figure 3(b). One can also see from figure 3(b) that, at low doping, the magnitudes of  $T^*$  observed from NQR and XANES are nearly the same. On the other hand, we also suspect that the NQR data [16] might overestimate  $T^*$  at low doping due to a broad transition in the NQR wipeout order parameter, so the  $T^*$  observed from XANES should be higher due to the dynamic nature of the charge stripe. This can be seen more clearly in the vicinity of the optimally doped range where the NQR is not fast enough to see the dynamic stripe formation. However, XANES is a very fast probe and can see the charge-stripe ordering even for the  $x = 0.15$  sample.

The large oxygen-isotope shift of the charge-stripe ordering temperature suggests that the stripe formation in high-temperature superconductors is not caused by purely electronic interactions. It appears that a strong electron–phonon interaction really plays an important role in this phenomenon. Therefore, the Holstein–Hubbard Hamiltonian should be relevant, as proposed by Castellani, Di Castro and Grilli [4]. This is also supported by the large oxygen-isotope effects on both  $T_c$  and the effective supercarrier mass observed in this material [7]. The large oxygen-isotope effect on the supercarrier mass implies that the nature of charge carriers in this material is of polaron and/or bipolaron type, in agreement with a theoretical model [18] and other independent experiments on the bipolaron formation energy ( $\Delta \gg T^*$ ) [10, 12]. Our present experimental results will place important constraints on the microscopic origin of the stripe phase and indirectly on the microscopic mechanism of high-temperature superconductivity.

After submission of the present letter we learned about the paper of Bussmann-Holder *et al* [19], where the observed oxygen-isotope effect on  $T^*$  reported here was qualitatively explained by a theory of phonon-induced stripe formation and charge ordering in HTSC.

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