Evidence for strong lattice effects as revealed from huge unconventional oxygen isotope effects on the pseudogap temperature in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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The oxygen isotope ($^{16}\text{O}/^{18}\text{O}$) effect (OIE) on the pseudogap (charge-stripe ordering) temperature T^* is investigated for the cuprate superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as a function of doping x by means of x-ray absorption near edge structure studies. A strong x dependent and sign reversed OIE on T^* is observed. The OIE exponent α_{T^*} systematically decreases from $\alpha_{T^*} = -0.6(1.3)$ for $x = 0.15$ to $\alpha_{T^*} = -4.4(1.1)$ for $x = 0.06$, corresponding to increasing T^* and decreasing superconducting transition temperature T_c . Both $T^*(^{16}\text{O})$ and $T^*(^{18}\text{O})$ exhibit a linear doping dependence with different slopes and critical end points [where $T^*(^{16}\text{O})$ and $T^*(^{18}\text{O})$ fall to zero] at $x_c(^{16}\text{O}) = 0.201(4)$ and $x_c(^{18}\text{O}) = 0.182(3)$, indicating a large positive OIE of x_c with an exponent of $\alpha_{x_c} = 0.84(22)$. The remarkably large and strongly doping dependent OIE on T^* signals a substantial involvement of the lattice in the formation of the pseudogap, consistent with a polaronic approach to cuprate superconductivity and the vibronic character of its ground state.

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I. INTRODUCTION

Even 30 years after its discovery, the origin of high-temperature superconductivity in cuprate superconductors (HTSs) is still under debate [1]. A seemingly majority of researchers advocates for a purely electronic mechanism, and consequently ignores the importance of lattice effects [2]. However, in conventional superconductors the role of the lattice as a pairing glue for Cooper pairs has been identified by the observation of an isotope effect on the superconducting transition temperature T_c [3]. Interestingly, in cuprate superconductors, analogous but apparently unconventional and doping dependent isotope effects have been observed on several characteristic quantities, e.g., the superconducting transition temperature T_c , the antiferromagnetic transition temperature T_N , the spin-glass temperature T_g , the spin-stripe ordering temperature T_{so} , and the magnetic penetration depth λ [4–11], which all are in support of the vibronic character of its ground state. So far, only a few studies of the isotope effect on the pseudogap temperature T^* have been reported [12–19].

The pseudogap temperature T^* plays a central role in the phase diagram of HTSs and is considered to be a key ingredient for the understanding of the physics of cuprates [20]. From an experimental point of view, T^* itself is a rather ill-defined temperature scale with varying values depending on the experimental tool and the involved time scale [12–15]. The nature of T^* in cuprates is debated and attributed to controversial origins [21]. These are discussed as precursors to the paired state, spin density formation, charge density

formation, onset of stripe formation, and other exotic scenarios [21]. Here, we define the pseudogap T^* as the temperature where lattice effects are apparent in terms of deviations of the local structure from the average one (this temperature is also denoted as charge-stripe ordering temperature in the literature [14]). The relevance of lattice/polaron effects for the appearance of the pseudogap phase can be tested by oxygen isotope ($^{16}\text{O}/^{18}\text{O}$) effect (OIE) studies. So far, only a limited number of such experiments have been performed [12–19]. First, ^{89}Y nuclear magnetic resonance (NMR) measurements on slightly underdoped $\text{YBa}_2\text{Cu}_3\text{O}_8$ show no appreciable OIE on T^* [12], whereas ^{63}Cu nuclear quadrupole resonance (NQR) spin-lattice relaxation experiments on the same system revealed a small but positive OIE on T^* [13]. However, a large and sign reversed OIE has been reported from Cu K -edge x-ray absorption near edge structure (XANES) studies in underdoped $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$ [14], and from neutron crystal field spectroscopy (NCFS) studies in slightly underdoped $\text{HoBa}_2\text{Cu}_3\text{O}_8$ [15], optimum doped $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{CuO}_4$ [18], and doped $\text{La}_{1.96-x}\text{Ho}_{0.04}\text{Sr}_x\text{CuO}_4$ ($0.11 \leq x \leq 0.25$) [19]. Moreover, NCFS studies of the $^{63}\text{Cu}/^{65}\text{Cu}$ isotope effect evidenced a large negative isotope shift of T^* in $\text{HoBa}_2\text{Cu}_3\text{O}_8$ [17], whereas no copper isotope shift of T^* was observed for optimum doped $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{CuO}_4$ [18].

Here, we present a systematic study of the OIE on T^* over a broad doping range of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.06 \leq x \leq 0.15$) by means of Cu K -edge XANES studies [22].

II. EXPERIMENTAL DETAILS

Four different $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples with concentrations $x = 0.06, 0.09, 0.12$, and 0.15 were prepared by a conventional

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FIG. 1. Temperature dependence of the zero-field-cooled normalized magnetization $M(T)/M(5\text{ K})$ of the $^{16}\text{O}/^{18}\text{O}$ exchanged samples of $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_4$ in $\mu_0 H = 0.5\text{ mT}$. The superconducting transition temperature was determined by the intersection of the linearly extrapolated magnetic moment and the zero line.

solid state reaction using dried La_2O_3 (99.99%), SrCO_3 (99.999%), and CuO (99.999%). The powders were mixed, ground thoroughly, pressed into pellets, and fired in air at 1000°C for $\sim 100\text{ h}$ with three intermediate grindings. The phase purity of the samples was checked with a conventional x-ray diffractometer. The final ^{18}O and ^{16}O samples were obtained in parallel via oxygen isotope exchange in closed quartz glass tubes under a controlled gas pressure slightly above 1 bar at 800°C during 72 h with subsequent cooling. The oxygen isotope enrichment was determined from the weight changes and was about 90% of ^{18}O for all samples.

The samples were characterized by measuring their superconducting properties using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL). The temperature dependencies of the zero-field-cooled normalized magnetization $M(T)/M(5\text{ K})$ of the $^{16}\text{O}/^{18}\text{O}$ exchanged samples of $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_4$ for $\mu_0 H = 0.5\text{ mT}$ are shown in Fig. 1, with T_c being identified from the zero of the linearly extrapolated magnetic moment. From the values of $T_c(^{16}\text{O})$ and $T_c(^{18}\text{O})$ the OIE exponent α_{T_c} is derived according to $\alpha_{T_c} = -d \ln T_c / d \ln M_0$, where M_0 is the mass of the oxygen isotope. The results of the OIE on T_c for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.06 \leq x \leq 0.15$) will be discussed in more detail below, in connection with the OIE on T^* observed in this work.

In order to ascertain T^* , Cu K -edge XANES measurements were performed on powder samples at the Diamond Light Source on the B18 beamline [23]. The storage ring was operating in a 10-min top-up mode for a ring current of 300 mA and an energy of 3 GeV. The radiation was monochromated with a Si (311) double crystal monochromator calibrated using the K edge of a copper foil, taking the first inflection point as 8979.0 eV. Harmonic rejection was achieved through the use of two platinum-coated mirrors operating at an incidence angle of 7.5 mrad . The incident (I_0), the transmitted (I_t), and the reference (I_{ref}) beam intensities were measured using two 30 cm ion chambers and a helium/argon gas mixture (total ion chamber pressure of 1.1 bar) to absorb 12%, 60%, and 60% of the beam in I_0 , I_t and I_{ref} , respectively [23]. The samples

FIG. 2. (a) Normalized Cu K -edge XANES spectra showing the energy evolution of the normalized intensity I for both isotopes ^{16}O and ^{18}O of $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_4$ at $T = 220\text{ K}$. (b) Extended region of the XANES spectrum depicted in (a) showing a slight change in the shape due to oxygen isotope substitution ($^{18}\text{O}/^{16}\text{O}$).

were positioned between I_0 and I_t and the Cu foil reference is between I_t and I_{ref} .

Five absorption spectra were collected at the same temperature in an Oxford Instruments OptistatPT cryostat and their mean value taken in order to increase the signal-to-noise ratio. Figure 2 shows the normalized Cu K -edge XANES spectra for the ^{16}O and ^{18}O $\text{La}_{1.91}\text{Sr}_{0.09}\text{CuO}_4$ samples at $T = 220\text{ K}$ as a representative for the entire series. The spectra show the typical absorption features of the cuprates with a square planar geometry where the main features are denoted as A_1 , A_2 , B_1 , and B_2 with peak intensities a_1 , a_2 , b_1 , and b_2 . The peak A_1 is essentially caused by the multiple scatterings of the ejected photoelectrons from the La/Sr atoms, while peak A_2 is due to the apical oxygen. The features above the threshold from 8 to 40 eV have been identified as multiple scattering resonances within a 0.5 nm cluster of neighbor atoms surrounding the absorbing atom [22], i.e., B_1 probes the scattering from the oxygen atoms in the square CuO_2 planes. The decrease of the b_1 and b_2 resonance intensities, together with the increase of both A_1 and A_2 multiple scattering photoelectron resonance intensities a_1 and a_2 , indicate deviations from the CuO_2 square plane geometry for anisotropic atomic displacements in the CuO_4 plaquette [22], which has been used to probe the onset of periodic local lattice distortions associated with polaron formation.

The effect of the oxygen isotope substitution on the XANES spectra on the distribution of local Cu-site conformations is hardly seen directly in the raw XANES spectra shown in Fig. 2, but can be extracted from the slightly different

FIG. 3. The temperature dependence of the XANES peak intensity ratio R of oxygen isotope substituted $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. $x = 0.09$: (a) ^{16}O and (b) ^{18}O ; $x = 0.15$: (c) ^{16}O and (d) ^{18}O . The solid straight lines are a guide to the eye. The corresponding charge-stripe ordering temperatures T^* are marked by the vertical dashed lines. The huge OIE on T^* is evident.

XANES peak intensities a_1 and b_1 of the ^{16}O and ^{18}O samples [14]. Deviations from the square plane geometry of the CuO_4 coordination plaquette can be quantified by the XANES peak ratio [14]

$$R = (b_1 - a_1)/(b_1 + a_1). \quad (1)$$

In Fig. 3 the XANES intensity ratio R is plotted for ^{16}O and ^{18}O samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.9$ and $x = 0.15$) as a function of temperature. From the temperature dependence of R , the pseudogap temperature T^* is determined by the interception of the horizontal line above T^* and to the linear slope below T^* as shown in Fig. 3. For all doping levels x , a clear increase in R below T^* is observed, which is typical for a charge density wave and consistent with recent resonant x-ray scattering studies, where charge ordering and the pseudogap formation were intensively studied [24]. Below T_c the quantity R decreases sharply, caused by the decrease of charge carriers due to the formation of the superconducting condensate.

III. RESULTS

The values of the pseudogap temperature T^* as well as the corresponding values of T_c as measured for all ^{16}O and ^{18}O samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.06 \leq x \leq 0.15$) are summarized in Fig. 4(a) and Table I. $T_c(x)$ shows the well-known domelike behavior with a small but clearly visible OIE on T_c . T^* decreases with increasing x as is well known from the literature. The two isotopes show the same trends with x , however, $T^*(^{18}\text{O})$ is pronouncedly raised as compared to $T^*(^{16}\text{O})$ with the largest OIE shift of $\Delta T^* \simeq 61$ K for $x = 0.06$. With increasing x , the OIE on T^* decreases systematically. For comparison, the values for $T^*(^{16}\text{O})$ and $T^*(^{18}\text{O})$ obtained from previous XANES experiments for $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$ [14] and from previous NCFS experiments for $\text{La}_{1.96-x}\text{Ho}_{0.04}\text{Sr}_x\text{CuO}_4$ ($x = 0.15$ [18]; $x = 0.11, 0.15$ [19]) are also displayed in Fig. 4(a). These previous values for $T^*(^{16}\text{O})$ and $T^*(^{18}\text{O})$ are, within experimental error, in good agreement with the present results, demonstrating that the two different experimental

FIG. 4. (a) The superconducting transition temperature T_c and the pseudogap temperature T^* of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as a function of doping x for ^{16}O (red symbols) and ^{18}O (blue symbols). With increasing doping x , a continuous decrease of T^* is observed for both isotopes. The solid lines are obtained from Eq. (2). The dashed line is a guide to the eye. For comparison, the values for $T^*(^{16}\text{O})$ and $T^*(^{18}\text{O})$ obtained from previous XANES experiments for $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$ (open circles) [14] and from previous NCFS experiments for $\text{La}_{1.96-x}\text{Ho}_{0.04}\text{Sr}_x\text{CuO}_4$ [$x = 0.15$ (open triangles) [18]; $x = 0.11, 0.15$ (open squares) [19]] are also displayed. (b) Doping dependence of the isotope effect exponent α_{T_c} (solid diamonds) and α_{T^*} (solid circles) for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as determined in this work, together with published values for α_{T_c} (open symbols) [25] and values for α_{T^*} extracted from the previous XANES and NCFS results shown in (a): XANES (open circle) [14], NCFS (open triangle) [18], and NCFS (open squares) [19]. The dashed lines are a guide to the eye.

techniques XANES and NCFS yield consistent values for T^* . Note that for overdoped $\text{La}_{1.96-x}\text{Ho}_{0.04}\text{Sr}_x\text{CuO}_4$ ($x = 0.20$ and $x = 0.25$), NCFS experiments [19] revealed in contrast to other experiments an unexpected upward shift of T^* with an appreciably negative OIE on T^* which, however, is not discussed here.

TABLE I. Summary of the values of the pseudogap temperatures $T^*(^{16}\text{O})$, $T^*(^{18}\text{O})$, and the OIE exponent α_{T^*} for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.06 \leq x \leq 0.15$).

Doping x	$T^*(^{16}\text{O})$ (K)	$T^*(^{18}\text{O})$ (K)	α_{T^*}
0.06	126(10)	187(18)	-4.3(1.1)
0.09	102(12)	135(12)	-2.9(9)
0.12	64(9)	80(10)	-2.2(1.3)
0.15	49(8)	52(8)	-0.6(1.3)

The corresponding OIE exponent α_{T^*} is evaluated analogously to the one on T_c . It is negative and unusually large with $\alpha_{T^*} = -4.4(1.1)$ for the lowest doping $x = 0.06$. The magnitude of α_{T^*} is decreasing with increasing x , reaching a still substantial value of $\alpha_{T^*} = -0.6(1.3)$ at optimal doping $x = 0.15$ (see Table I). The doping dependencies of the OIE exponents α_{T^*} and α_{T_c} of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.06 \leq x \leq 0.15$) are displayed in Fig. 4(b) (solid symbols), together with previous results (open symbols: α_{T^*} [14,18,19], α_{T_c} [25]), which are confirmed here.

IV. DISCUSSION

It is evident from Fig. 4(a) that in the underdoped regime ($0.5 \leq x \leq 0.15$) the pseudogap temperatures $T^*(^{16}\text{O})$ and $T^*(^{18}\text{O})$ exhibit almost linear doping dependencies which can be described by the expression

$$T^*(^{17}\text{O}) = \sigma(^{17}\text{O})[x - x_c(^{17}\text{O})], \quad \gamma = 16, 18. \quad (2)$$

Here, $\sigma(^{17}\text{O})$ and $x_c(^{17}\text{O})$ are constants. The present T^* data [Fig. 4(a) and Table I] follow Eq. (2), yielding $\sigma(^{16}\text{O}) = -880(100)$ K, $x_c(^{16}\text{O}) = 0.201(4)$ and $\sigma(^{18}\text{O}) = -1440(170)$ K, $x_c(^{18}\text{O}) = 0.182(3)$. It is interesting to note that both quantities σ and x_c exhibit a substantial OIE. The physical meaning and the location of the T^* line in the phase diagram (temperature versus hole doping) of cuprates have been extensively discussed in the literature and are still heavily debated (see, e.g., Refs. [26–33]). A linear doping dependence of T^* has been previously reported for various cuprate systems, and the extrapolated generic doping concentration $x_c \simeq 0.19$ – 0.20 has been discussed in terms of a possible quantum critical point underneath the superconducting dome (see, e.g., Refs. [26–28,31,32]). Note that x_c decreases from 0.201(4) to 0.182(3) upon replacing ^{16}O by ^{18}O , implying a large positive OIE of about 10%, corresponding to an OIE exponent of $\alpha_{x_c} = 0.84(22)$ [see Fig. 4(a)]. At present, a theoretical interpretation of this remarkable OIE is not available.

The OIE on T_c has been consistently explained earlier using a polaronic approach [8,10,34–37], and within multigap multicondensate superconductivity at the BEC-BCS crossover near a Lifshitz transition in multicomponent electronic systems [38,39]. It is worth mentioning that in an early work, Kresin and Wolf [40] already proposed to explain the OIE on T_c and on the penetration depth, considering a strong c -axis electron-lattice coupling. More recently, this model was extended by Weyeneth and Müller [10,37] to include a polaronic coupling also to the planes. They succeeded in quantitatively reproducing

the experimental data, thus demonstrating the importance of polaron formation for superconductivity in the cuprates.

The basic ingredients of polaron formation are that strong electron-lattice interactions lead to polaron formation, namely, quasiparticles, which renormalize the electronic as well as the lattice degrees of freedom. The squeezing of the electronic hopping integrals has been identified as the origin of the OIE on T_c [8]. Here, we argue that the OIE on T^* is caused by polaron formation related to an incipient finite momentum lattice instability which manifests itself as a divergence in Cu-O mean-square displacement at T^* as has been observed in Refs. [41,42].

The primary semiclassical response of the lattice to polaron formation is a rigid harmonic oscillator shift, i.e., the phonon creation and annihilation operators b^+ and b transform to

$$\tilde{b}_q = b_q + \sum_i \gamma_i(q) c_i^+ c_i, \quad \tilde{b}_q^+ = b_q^+ + \sum_i \gamma_i(q) c_i^+ c_i, \quad (3)$$

with c_i^+ and c_i being site i dependent electron creation and annihilation operators and $\gamma_i(q)$ the momentum q dependent coupling constants. As a consequence of this coupling, the lattice mode frequencies adopt a temperature dependence [34,35,43],

$$\tilde{\omega}_{q,j}^2 = \tilde{\omega}_{0q,j}^2 - \frac{\gamma_{q,j}^2}{N(E_F)} \sum_k \frac{1}{\varepsilon(k)} \tanh \frac{\varepsilon(k)}{k_B T}, \quad (4)$$

where $N(E_F)$ is the density of states at the Fermi level, $\varepsilon(k)$ the Fourier transform of the site representation of the electronic bands, and $\tilde{\omega}_{0q,j}$ the bare branch j and momentum q dependent lattice mode frequency. The electronic dispersions are explicitly given by a local density approximation (LDA) derived form, namely,

$$\begin{aligned} \varepsilon(k) = & -2t_1[\cos(k_x a) + \cos(k_y b)] + 4t_2 \cos(k_x a) \cos(k_y b) \\ & + 2t_3[\cos(2k_x a) + \cos(2k_y b)] \\ & \mp t_4[\cos(k_x a) - \cos(k_y b)]^2/4 - \mu, \end{aligned} \quad (5)$$

where t_1 , t_2 , t_3 , and t_4 are first, second, third, and interlayer hopping integrals, respectively, and μ is the chemical potential which controls the band filling and is set equal to zero. Here, a and b are the lattice constants in the CuO_2 planes. It is important to note that also the electronic degrees of freedom are renormalized, which leads to an exponential band narrowing for all hopping elements according to the replacement $t \rightarrow t \exp[-\gamma^2 \coth(\hbar\omega/2k_B T)]$ and a rigid level shift.

From Eq. (4) *finite momentum mode softening* can occur if the normal mode unrenormalized frequency $\tilde{\omega}_{0q,j}$ is reduced by the electronic energy, corresponding to $\tilde{\omega}_{q,j}^2 \rightarrow 0$. Obviously, this situation is controlled by the dependence of the coupling strength which we use as a variable to calculate the mode freezing temperature where $\tilde{\omega}_{q,j}^2 = 0$. Since the electronic energies due to their coupling to the lattice degrees of freedom and the unrenormalized mode energies are both isotope dependent, the freezing temperature is isotope dependent as well. This dependence is huge and sign reversed [43] as compared to the isotope effect on the harmonic lattice mode frequencies and mirrors the isotope effect on the pseudogap onset temperature T^* , which is identified as the freezing temperature. T^* signals the onset of a dynamically

modulated, patterned structure (composed of local coherent polarons), where the superstructure modulation is defined by the q value, where $\tilde{\omega}_{q,j}^2 = 0$ and T^* is defined through the implicit relation

$$\tilde{\omega}_{0q,j}^2 = \frac{\gamma_{q,j}^2}{N(E_F)} \sum_k \frac{1}{\varepsilon(k)} \tanh \frac{\varepsilon(k)}{k_B T^*}. \quad (6)$$

The Cu-O mean-square displacement, which is momentum q and branch j dependent, can be expressed as

$$\sigma^2(T) = \hbar / (M \tilde{\omega}_{q,j}) \coth(\hbar \tilde{\omega}_{q,j} / 2k_B T), \quad (7)$$

where M is the oxygen ion mass [43]. As has been shown in Ref. [43], the OIE on T_c is caused by the renormalization of the band energies where specifically the second-nearest-neighbor hopping integral yields the correct OIE. This suggests a substantial involvement of a Q_2 -type Jahn-Teller mode in the formation of the pseudogap phase which has already been deduced from the early data for the OIE on T^* [15,17,18]. This is further supported by the observation of a $^{63}\text{Cu}/^{65}\text{Cu}$ isotope effect which is present only in $\text{HoBa}_2\text{Cu}_4\text{O}_8$ [17], but absent in $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{CuO}_4$ [18], since in the former an umbrella type mode including Cu ion displacement is active, which is absent in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Alternatively, the OIE on T^* (but not on T_c) has been explained within a purely electronic model, where lattice effects were built in at specific momentum values [44].

In the above we have not addressed the question why the ^{63}Cu NQR relaxation study [13], opposite to XANES [14] and NCFS [15–19], detects only a small OIE on T^* with reversed sign as compared to the present results. First, the T_1 spin-lattice relaxation measurements performed by NQR probe both magnetic and charge fluctuations. However, magnetic fluctuations dominate in the temperature region investigated. Second, the probing time scales of both techniques are quite

different, namely, NQR is slow and works in the kHz to MHz range, whereas XANES is fast (10^{-15} s) and insensitive to magnetism. This means that NQR and XANES do not probe the same physical quantities, and thus the results obtained for the pseudogap are not directly comparable to each other.

V. CONCLUSION

In conclusion, we have performed a systematic investigation of the oxygen isotope effect on the pseudogap temperature T^* by using XANES and thereby demonstrated its doping dependent evolution. The isotope effect is always sign reversed and large and increases with decreasing doping. The correct trends of the isotope effect are obtained within a polaronic model, where the renormalization of lattice and electronic degrees of freedom are taken into account to calculate the isotope effect on T^* . The present results support the original concept, leading to the discovery of high-temperature superconductivity in the cuprates [1] that a Q_2 -type Jahn-Teller mode is at work in the formation of the pseudogap phase, as has been concluded previously in explaining the OIE on T_c [36,37]. In addition, the data substantiate the notion of the vibronic character of the ground state.

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