Unconventional isotope effects in the high-temperature cuprate superconductors

Guo-meng Zhao\(^1\), H. Keller\(^1\) and K. Conder\(^2\)

\(^1\)Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland
\(^2\)Laboratory for Neutron Scattering, ETH Zürich and PSI Villigen, CH-5232 Villigen PSI, Switzerland

We review various isotope effects in the high-\(T_c\) cuprate superconductors to assess the role of the electron-phonon interaction in the basic physics of these materials. Of particular interest are the unconventional isotope effects on the supercarrier mass, on the charge-stripe formation temperature, on the pseudogap formation temperature, on the EPR linewidth, on the spin-glass freezing temperature, and on the antiferromagnetic ordering temperature. The observed unconventional isotope effects strongly suggest that lattice vibrations play an important role in the microscopic pairing mechanism of high-temperature superconductivity.

I. INTRODUCTION

Developing a correct microscopic theory for high-\(T_c\) superconductivity is one of the most challenging problems in condensed matter physics. More than ten years after the discovery of the high-\(T_c\) cuprate superconductors by Bednorz and Müller \(^1\), there have been no microscopic theories that can describe the physics of high-\(T_c\) superconductors completely and unambiguously. Due to the high \(T_c\) values and the earlier observation of a small oxygen-isotope effect in a 90 K cuprate superconductor YBa\(_2\)Cu\(_3\)O\(_{7−\delta}\) \(^2\), many theorists believe that the electron-phonon interaction cannot be the origin of high-\(T_c\) superconductivity. Most physicists have thus turned their minds towards an alternative pairing interaction of purely electronic origin (e.g., see Ref. \(^5\)–\(^7\)). As a matter of fact, the idea that the highest \(T_c\) is only 30 K within the conventional phonon-mediated mechanism is not justified. In principle, \(T_c\) can increase monotonically with both the phonon frequency and the electron-phonon coupling constant within the phonon-mediated Eliashberg theory \(^8\). The limitation of the \(T_c\) within the phonon mechanism is only imposed by a possible structural instability in the case of too strong an electron-phonon interaction. However, there is no universally accepted, simple, and quantitative stability criterion \(^9\).

It is well known that the observation of a gap in the electronic excitation spectrum \(^8\) and the discovery of an isotope effect \(^10\)–\(^11\) in conventional superconductors provided important and crucial clues to the understanding of the microscopic mechanism of superconductivity. In particular, the effect of changing isotope mass on the superconducting transition temperature \(T_c\) implies that superconductivity is not of purely electronic origin, but that lattice vibrations (phonons) play an important role in the microscopic mechanism for this phenomenon.

The first evidence for an isotope effect was reported in 1950 by Maxwell \(^10\) and independently by Reynolds et al. \(^11\). They found that the critical temperature \(T_c\) of mercury is an inverse function of the isotope mass. In the same year Fröhlich \(^12\) pointed out that the same electron-lattice interaction which describes the scattering of conduction electrons by lattice vibrations gives rise to an indirect interaction between electrons. He proposed that this indirect interaction is responsible for superconductivity. Fröhlich’s theory got strong support from the observed isotope effect, and played a decisive role in establishing a correct mechanism. In 1956, Cooper \(^13\) demonstrated that electrons with an attractive interaction form bound pairs (so called Cooper pairs) which lead to superconductivity. However, the existence of electron pairs does not necessarily imply a phonon mediated pairing. Indeed, Bose condensation as considered in 1955 by Schafroth \(^14\), is also a possible mechanism for superconductivity, but the model was not able to explain the isotope effect. Finally, in 1957, Bardeen, Cooper and Schrieffer \(^15\) developed the BCS theory which can explain most physical properties observed in conventional superconductors.

Remarkably, the BCS theory can well explain the isotope effect. The \(T_c\) within the theory is given by

\[
k_B T_c = 1.13 h \omega_D \exp \left( \frac{1}{N(0)V} \right),
\]

where \(\omega_D\) is the Debye frequency, which is proportional to \(M^{-1/2}\). The electron-phonon coupling \(N(0)V\) is the product of an electron-phonon interaction strength \(V\) and the electronic density of states at the Fermi surface \(N(0)\), both of which are independent of the ion mass \(M\) in the harmonic approximation. Eq. 1 implies an isotope-mass dependence of \(T_c\), with an isotope-effect exponent \(\alpha = −d \ln T_c / d \ln M = 1/2\). This is in excellent agreement with the reported isotope effects in the non-transition metal superconductors (e.g., Hg, Sn and Pb). In fact, the isotope effect was the first justification of the proposed electron-phonon coupling mechanism.

The conventional phonon-mediated superconducting theory is based on the Migdal adiabatic approximation in which the phonon-induced electron self-energy is given correctly to the order of \((m_b/M)^{1/2} \sim 10^{-2}\), where \(m_b\) is the bare mass of an electron. Within this approximation, the density of states at the Fermi level \(N(0)\), the
electron-phonon coupling constant $\lambda_{ep}$, and the effective mass of the supercarriers are all independent of the ion mass $M$. However, if the interactions between electrons and nuclear ions are strong enough for electrons to form polarons (quasiparticles dressed by lattice distortions), their effective mass $m^*$ will depend on $M$. This is because the polaron mass $m^* = m_b \exp(A/\omega)$, where $A$ is a constant, and $\omega$ is a characteristic optical phonon frequency which depends on the masses of ions. Hence, there is a large isotope effect on the carrier mass in polaronic metals, in contrast to the zero isotope effect in ordinary metals. The total exponent of the isotope effect on $m^*$ is defined as $\beta = \sum -d \ln m^*/d \ln M_i$ ($M_i$ is the mass of the $i$th atom in a unit cell). From this definition and the expression for the polaron mass $m^*$ mentioned above, one readily finds

$$\beta = -\frac{1}{2} \ln (m^*/m_b).$$

(2)

The above equation implies that there should be a large negative isotope effect on $m^*$ in polaronic metals.

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FIG. 1. Dependencies of $T_c$ and the oxygen-isotope exponent $\alpha O$ on the Sr content for $^{16}O$ and $^{18}O$ samples in La$_{2-x}$Sr$_x$CuO$_4$. After [27].

Therefore, if the electron-phonon interaction is strong enough to form polarons and/or bipolarons, one will expect a substantial isotope effect on the effective mass of carriers. In this article, we will present various isotope effects in cuprates including the unconventional isotope effects on the supercarrier mass, on the charge-stripe formation temperature, on the pseudogap formation temperature, on the EPR linewidth, on the spin-glass freezing temperature, and on the antiferromagnetic ordering temperature. These unconventional isotope effects clearly demonstrate that phonons are relevant to the basic physics of cuprates and may be important for the occurrence of high-temperature superconductivity.

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II. ISOTOPE EFFECT ON THE SUPERCONDUCTING TRANSITION TEMPERATURE

Studies of isotope shifts of $T_c$ have been carried out in almost all known cuprates. A comprehensive review was given by Franck [17]. The role of the anharmonicity of the apical oxygen on the isotope effect was discussed in detail by Müller [13]. Most of the studies reported so far concern the oxygen-isotope shift (OIS) of $T_c$ by replacing $^{16}O$ with $^{18}O$, partly because the experimental procedures are simple and reliable. Now it is generally accepted that optimally-doped cuprates exhibit a small and positive oxygen-isotope exponent $\alpha O$. It was also found that $\alpha O$ for optimally-doped materials decreases with increasing $T_c$ [19]. The small OIS observed in the optimally doped cuprates suggest that phonons might not be important in bringing about high temperature superconductivity.

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FIG. 2. The oxygen and copper isotope exponents as a function of $T_c$ for $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ and $Y_{1-x}Pr_xBa_2Cu_4O_8$. The data were taken from [22, 23].

However, the doping dependence of the OIS has been extensively studied in different cuprate systems [13, 22, 27]. For a particular family of doped cuprates the OIS increases with decreasing $T_c$, and can be even larger than the BCS value. In Fig. 2a, we plot the doping dependence of $T_c$ for the $^{16}O$ and $^{18}O$ samples of the single-layer cuprate La$_{2-x}$Sr$_x$CuO$_4$. It is clear that the $T_c$'s of $^{18}O$ samples are always lower than those of the $^{16}O$ samples. The doping dependence of the isotope exponent $\alpha O$ is
shown in Fig. 1b. The magnitude of \( \alpha_O \) increases with a decrease of doping and becomes very large (> 0.5) in the deeply underdoped regime. The large \( \alpha_O \) value observed near \( x = 0.125 \) might be related to the structural instability \[28\]. The results suggest that the phonon modes related to the oxygen vibrations are strongly coupled to conduction electrons.

In addition to the large oxygen-isotope shifts observed in underdoped compounds, there are also large copper isotope shifts observed in underdoped \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) \[22\], oxygen-depleted \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) \[22\], Pr-substituted \( \text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) \[30\] and \( \text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_4\text{O}_8 \) \[30\], as well as in \( \text{YBa}_2\text{Cu}_4\text{O}_8 \) \[31\]. In Fig. 2, we plot the oxygen and copper isotope exponents as a function of \( T_c \) in \( \text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) and \( \text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_4\text{O}_8 \). As \( T_c \) or doping decreases, both \( \alpha_O \) and \( \alpha_{Cu} \) increase monotonously. Interestingly, \( \alpha_{Cu} \) is about 3/4 of \( \alpha_O \) in the deeply underdoped region, while \( \alpha_{Cu} \) is even larger than \( \alpha_O \) near the optimal doping. This suggests that the Cu-dominated phonon modes (most of them are low-energy modes) are involved in the superconducting pairing.

The large copper-isotope shift also implies that the phonons in the \( \text{CuO}_2 \) planes are relevant to superconductivity. By analogy, one should also expect that the planar oxygen vibrations make more important contributions to the pairing than the apical and/or chain oxygen vibrations. We can distinguish the contributions of the different oxygen sites to the total OIS by site-selective oxygen-isotope experiments. A partially site-selective oxygen-isotope exchange was attempted by Cardona et al. \[22\] and by Ham et al. \[33\]. The experimental difficulty in doing a complete site-selective oxygen-isotope exchange was overcome by Nickel et al. \[34\]. In their experiment the authors replaced the \( ^{16}\text{O} \) by \( ^{18}\text{O} \) in the chain and apical oxygen sites of a fully \( ^{16}\text{O} \) exchanged \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) sample, while keeping the \( ^{18}\text{O} \) unchanged in the plane sites. The site-selectivity was confirmed by Raman spectroscopy \[34\]. A small negative OIS \( [\alpha_O = -0.010(4)] \) associated with the planar oxygen was found. In contrast, Zech et al. \[35\] showed a small positive OIS \( [\alpha_O = 0.018(4)] \) related to the planar oxygen ions. The above discrepancy may be due to a broad superconducting transition in the samples of Nickel et al. \[34\], which makes it difficult to define \( T_c \) reliably.

Although the OIS is small in the optimally-doped samples, the experiment done by Zech et al. \[35\] provided evidence that the planar oxygen ions mainly (80%) contribute to the total OIS (see Fig. 2). Nevertheless it is not obvious that the same conclusion should apply to the underdoped samples where the total OIS is large.
Zhao et al. [30] thus carried out the site-selective oxygen-isotope experiments in the underdoped and optimally doped samples of $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$. In Fig. 4, we show the results of the site-selective oxygen-isotope effect for optimally doped $YBa_2Cu_3O_6.94$. It is striking that the results shown in Fig. 4 are in excellent agreement with those in Fig. 3. This indicates a good reproducibility of these experiments. The results for underdoped $Y_{0.7}Pr_{0.3}Ba_2Cu_3O_{6.97}$ are plotted in Fig. 5. Remarkably, the planar oxygen ions mainly (> 80%) contribute to the total oxygen-isotope shift in this underdoped cuprate. After [30], the planar oxygen ions mainly (>{0.7}) contribute to the total OIS in this underdoped cuprate. After [30],

![Graph showing susceptibility vs. temperature](image)

**FIG. 5.** The site-selective oxygen-isotope effect in an underdoped $Y_{0.7}Pr_{0.3}Ba_2Cu_3O_{6.97}$. The results show that the planar oxygen ions mainly (> 80%) contribute to the total oxygen-isotope shift in this underdoped cuprate. After [30].

show the results of the site-selective oxygen-isotope effect for optimally doped $YBa_2Cu_3O_6.94$. It is striking that the results shown in Fig. 4 are in excellent agreement with those in Fig. 3. This indicates a good reproducibility of these experiments. The results for underdoped $Y_{0.7}Pr_{0.3}Ba_2Cu_3O_{6.97}$ are plotted in Fig. 5. Remarkably, the planar oxygen ions mainly (> 80%) contribute to the total OIS in the underdoped samples as well. In Fig. 6, we show the total isotope shifts as a function of $T_c$ for $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ together with the isotope shifts from the planar (P) oxygen ions as well as from the apical and chain (AC) oxygen ions. The partial data of the total oxygen-isotope shifts are taken from Ref. [17] and have been corrected for 100% oxygen-isotope exchange. The other data are from Refs. [35,36].

![Graph showing total isotope shifts](image)

**FIG. 6.** The total (T) isotope shifts as a function of $T_c$ for $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ together with the isotope shifts from the planar (P) oxygen ions as well as from the apical and chain (AC) oxygen ions. The partial data of the total oxygen-isotope shifts are taken from Ref. [17] and have been corrected for 100% oxygen-isotope exchange. The other data are from Refs. [35,36].

There are three indirect experiments which have demonstrated that the difference in the hole densities of the $^{16}O$ and $^{18}O$ samples is smaller than 0.0002 per Cu site [25,26]. Now we are able to determine the oxygen content very accurately using a very precise volumetric analysis [37]. Fig. 7 shows the oxygen contents of the $^{16}O$ and $^{18}O$ samples of $La_{2-x}Sr_xCuO_4$ with different doping $x$ (unpublished data). The oxygen content was determined from a very precise volumetric analysis [37]. The weight of each sample used for the analysis is about 500 mg. The oxygen content can be determined more precisely for a higher $x$ and a heavier sample. The oxygen contents of two isotope samples are the same within ±0.0002 per Cu site.

![Graph showing oxygen content vs. Sr content](image)

**FIG. 7.** The oxygen contents of the $^{16}O$ and $^{18}O$ samples of $La_{2-x}Sr_xCuO_4$ with different doping $x$ (unpublished data). The oxygen content was determined from a very precise volumetric analysis [37]. The weight of each sample used for the analysis is about 500 mg. The oxygen content can be determined more precisely for a higher $x$ and a heavier sample. The oxygen contents of two isotope samples are the same within ±0.0002 per Cu site.

III. NEGLIGIBLE OXYGEN-ISOTOPE EFFECT ON THE CARRIER DENSITY

From the above results, an important question arises: Are the observed large isotope shifts in underdoped cuprates caused by a possible difference in the carrier densities of two isotope samples or by a strong electron-phonon coupling? It is very unlikely that the isotope effect is due to a difference in the carrier densities of two samples. This is because the $T_c$’s of the $^{18}O$ samples are always lower than the $^{16}O$ samples by more than 1 K in the underdoped region, independent of whether $dT_c/dx$ is positive, negative, or zero (see Fig. 5).

![Graph showing susceptibility vs. temperature](image)

**FIG. 4.** The susceptibility of $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ together with the isotope shifts from the planar (P) oxygen ions as well as from the apical and chain (AC) oxygen ions. The partial data of the total oxygen-isotope shifts are taken from Ref. [17] and have been corrected for 100% oxygen-isotope exchange. The other data are from Refs. [35,36].
and $^{18}$O samples of La$_{2-x}$Sr$_x$CuO$_4$ with different doping $x$. It is remarkable that the oxygen contents of two isotope samples are the same within ±0.0002 per Cu site. These experiments consistently show that the difference in the hole densities of the $^{16}$O and $^{18}$O samples is negligible, so that the observed large isotope effects are intrinsic and caused by a strong electron-phonon interaction.

IV. LARGE OXYGEN-ISOTOPE EFFECT ON THE EFFECTIVE SUPERCARRIER MASS

Several groups [21,22] noticed that there is an isotope effect on the diamagnetic Meissner signal in decoupled fine-grained samples. Zhao et al. [25] carefully studied this effect and interpreted it as due to the isotope-mass dependence of the average supercarrier mass $m^{**}$ (≡ $\sqrt{m_{ab}^2 - m_c^2}$). Since the magnetic penetration depth $\lambda(0)$ is proportional to $\sqrt{m^{**}/n_s}$, then

$$\Delta m^{**}/m^{**} = 2\Delta \lambda(0)/\lambda(0) + \Delta n_s/n_s,$$  \hspace{1cm} (3)

where $\Delta$ means any small change of a quantity upon isotope substitution. Thus the isotope dependence of $m^{**}$ can be determined if one can independently measure the isotope dependence of $\lambda(0)$ and of $n_s$. As shown above, there is a negligible oxygen-isotope effect on the normal carrier density $n$, and $n_s = n$ for clean superconductors, so one should expect no significant isotope effect on $n_s$. Indeed, there is a negligible oxygen-isotope effect on the supercarrier density $n_s$ in YBa$_2$Cu$_3$O$_{6.94}$ [28].

The isotope dependence of $\lambda(0)$ can be determined from that of the Meissner fraction $f(0)$ which, for decoupled and fine-grained samples, depends on the penetration depth $\lambda(0)$ and on the average grain radius $R$, as seen from the Shoenberg formula for spherical grains [30]:

$$f(T) = \frac{3}{2}[1 - 3(\frac{\lambda(T)}{R}) \coth(\frac{R}{\lambda(T)}) + 3(\frac{\lambda(T)^2}{R})],$$ \hspace{1cm} (4)

where $\lambda(T) = \sqrt{[(\lambda_{ab}(T))^2\lambda_c(T)]}$ for layered compounds [40]. From equation 4, it is obvious that a change in $\lambda(0)$ will lead to a change in $f(0)$, which implies that the isotope dependence of $\lambda(0)$ can be determined from the isotope dependence of $f(0)$.

In Fig. 8, we show the Meissner effects for the $^{16}$O and $^{18}$O samples of La$_{2-x}$Sr$_x$CuO$_4$ with $x = 0.06$ and 0.105. The samples are loosely packed with rather small grain sizes ($R \approx 2-4 \mu$m). One can clearly see that there are large oxygen isotope effects on both $T_c$ and the Meissner fraction. The most remarkable result is that the Meissner fraction of the $^{18}$O sample is lower than that for the $^{16}$O sample by about 23% in the case of $x = 0.06$. The isotope effects are reversible upon the isotope back-exchange [29,27], and reproducible in several sets of samples. For $x = 0.06$, we evaluate $\Delta m^{**}/m^{**} = 24(2)\%$. This indicates a large negative oxygen-isotope effect on the effective supercarrier mass in the deeply underdoped cuprates.

The above results were obtained from powder samples and correspondingly reflect the average properties of those highly anisotropic superconductors. To gain more insight, it is essential to determine the oxygen-isotope effect on the inplane effective supercarrier mass $m_{ab}^{**}$. Although we have tentatively extracted the isotope dependence of $m_{ab}^{**}$ from experiments on powder samples [20], more reliable results should be obtained from experiments on single crystals.

Unfortunately, a complete oxygen-isotope exchange by gas diffusion is impossible in single crystals with a large volume. In order to reach a complete oxygen-isotope exchange, microcrystals with a volume of $V \approx 150 \times 150 \times 50 \mu$m$^3$ (mass $\approx 10 \mu$g) should be used. In this case, commercial SQUID magnetometers do not have enough sensitivity to measure the magnetization for such tiny crystals especially near $T_c$. Fortunately our highly sensitive torque magnetometer [41] is able to detect the small diamagnetic signal for the tiny crystals.

The superconducting transition was studied by cooling the sample in a magnetic field $B_a = 0.1$ T applied at an angle of 45° with respect to the c-axis [42]. The torque signal was continuously recorded upon cooling the sample at a cooling rate of 0.01 K/s. In order to determine the background signal of the cantilever, the measurement was
repeated in zero field and the data were subtracted from those of the field cooled measurement. The magnetic torque vs temperature data obtained for crystals with \( x = 0.086 \) and 0.080 are shown in Fig. 4. It is clear that \( T_c \) is lower for the \(^{18}O \) exchanged samples. Furthermore, the magnetic signals of the back-exchanged samples (cross symbols) coincide with those of the \(^{16}O \) annealed samples (open circles). We define \( T_c \) as the temperature where the relative changes in \( \tau \) vs \( T \) data obtained for crystals with lower for the \( x = 0.086 \) and 0.080. The measurements were carried out in a magnetic field \( B_a = 0.1 \) T applied at an angle of 45° with respect to the c-axis. After [42].

More interestingly, the in-plane penetration depth \( \lambda_{ab}^{(2)}(T) \) can be extracted from field-dependent measurements [42]. Fig. 4 displays \( \lambda_{ab}^{(2)}(T) \) for the isotope-exchanged crystals with \( x = 0.086 \) and 0.080. The temperature dependence is described by the power law \( \lambda_{ab}^{(2)}(T) = \lambda_{ab}^{(2)}(0)[1 - (T/T_c)^n] \) with an exponent \( n \approx 5 \). From Fig. 4 it is evident that both \( T_c \) and \( \lambda_{ab}^{(2)}(0) \) shift down upon replacing \(^{16}O \) by \(^{18}O \). The shifts are found to be \( \Delta \lambda_{ab}^{(2)}(0)/\lambda_{ab}^{(2)}(0) = -9(3)\% \) and \(-7(1)\% \) for \( x = 0.080 \) and 0.086, respectively. Using \( \Delta n_s = 0 \), we find \( \Delta m_{ab}^{**}/m_{ab}^{**} = 9(3)\% \) for \( x = 0.080 \), and \( 7(1)\% \) for \( x = 0.086 \).

Moreover, a substantial value of \( \Delta m_{ab}^{**}/m_{ab}^{**} = 5-6\% \) was also obtained for several optimally doped cuprates (e.g., \( YBa_2Cu_3O_{6.94} \), \( La_{1.65}Sr_{0.35}CuO_4 \), and \( Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+y} \)) from magnetization measurements [13]. Very recent muon-spin rotation experiments on the oxygen-isotope exchanged \( YBa_2Cu_3O_6 \) have confirmed that \( \Delta m_{ab}^{**}/m_{ab}^{**} \approx 5\% \). Therefore, there is a substantial isotope effect on the in-plane supercarrier mass in optimally doped cuprates, but a very small effect on \( T_c \). Such unusual isotope effects place strong constraints on the pairing mechanism of high-temperature superconductivity.

V. HUGE OXYGEN-ISOTOPE EFFECT ON THE CHARGE STRIPE FORMATION TEMPERATURE

One of the most remarkable findings in the high-temperature copper oxide superconductors is the formation of alternating spin and charge stripes below a characteristic temperature [43][44]. Various x-ray absorption spectroscopic measurements [16] suggest that the local structures in the alternating stripes are different, forming an incommensurate superlattice. Such a stripe phase is believed to be important to the understanding of the pairing mechanism of high-temperature superconductivity [47]. 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, 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 stripes (or charge ordering), as inferred from a very large oxygen-isotope shift of the charge-ordering temperature observed in both Nd_{0.5}Sr_{0.5}MnO_{3} and La_{0.5}Ca_{0.5}MnO_{3} systems. Therefore it seems natural to seek for an isotope effect on the stripe formation temperature in cuprates.

For the colossal magnetoresistive manganites, a strong electron-phonon interaction plays an essential role in the formation of the stripe phase. From the XANES data, two characteristic peaks denoted by \( \Gamma(1) \) and \( \Gamma(2) \) have been determined by other techniques. In Fig. 11, we show the temperature dependence of the parameter \( R \) for the oxygen isotope mass. Upon replacing \(^{16}\text{O}\) with \(^{18}\text{O}\), the charge-stripe formation temperature \( T^* \) in this cuprate increases from about 110 K to 180 K. Such a large negative isotope effect on charge ordering can be explained in terms of electron-phonon coupling beyond the Migdal approximation.

VI. OXYGEN-ISOTOPE EFFECTS ON THE PSEUDOGAP FORMATION TEMPERATURE

Recently, a neutron spectroscopic investigation of the isotope effect on the relaxation rate of crystal field excitations of Ho\(^{3+}\) in HoBa\(_2\)Cu\(_4\)O\(_8\) has been carried out. In Fig. 12, we plot the temperature dependence of the intrinsic linewidth \( \Gamma(T) \) (corresponding to the \( \Gamma_3 \) \( \rightarrow \) \( \Gamma_4 \) transition of Ho\(^{3+}\)) for the \(^{16}\text{O}\) and \(^{18}\text{O}\) samples. In the high temperature range, the linewidth appears to exhibit a linear temperature dependence. Cooling down to a characteristic temperature \( T^p \), the linewidth suddenly gets narrower. Of particular interest is the characteristic temperature \( T^p \) which strongly depends on the oxygen-isotope mass. Upon replacing \(^{16}\text{O}\) by \(^{18}\text{O}\), \( T^p \) changes from 170 K to 220 K, i.e., there is a large oxygen-isotope effect.

![Fig. 11. The temperature dependence of the parameter \( R \) for the oxygen-isotope exchanged La\(_{1.94}\)Sr\(_{0.06}\)CuO\(_4\). See text for the definition of the parameter \( R \). After Ref. 50.](image1.png)

![Fig. 12. Temperature dependence of the intrinsic linewidth \( \Gamma(T) \) of the \( \Gamma_3 \) \( \rightarrow \) \( \Gamma_4 \) transition of Ho\(^{3+}\) for the \(^{16}\text{O}\) and \(^{18}\text{O}\) samples of HoBa\(_2\)Cu\(_4\)O\(_8\). After Ref. 52.](image2.png)
effect on $T^p$ ($\approx 50$ K). Similarly, a large copper-isotope effect on $T^p$ has been found in the same compound \cite{53}. The huge oxygen-isotope effects on $T^p$ and on $T^p$ \cite{52} indicate that a strong electron-phonon interaction plays an essential role in the charge dynamics and superconductivity \cite{18}. Although the authors of Ref. \cite{52} attributed the characteristic temperature $T^p$ to a pseudogap formation temperature, one cannot rule out the possibility that $T^p$ may be related to a dynamical charge ordering. We would like to mention that a small positive oxygen-isotope effect on the spin pseudogap has been observed in YBa$_2$Cu$_4$O$_8$ \cite{54}.

VII. OXYGEN-ISOTOPE EFFECT ON THE EPR LINEWIDTH

![Graph](image)

FIG. 13. (a) Temperature dependence of the EPR linewidth $\Delta H_{pp}$ for $^{16}$O isotope samples of La$_{2-x}$Sr$_x$CuO$_{4}$ with $x = 0.03$, 0.06, and 0.10; (b) The oxygen-isotope effect on the EPR linewidth $\Delta H_{pp}$ in La$_{1.97}$Sr$_{0.03}$CuO$_{4.02}$O$_4$. After Ref. \cite{58,59}.

The Electron Paramagnetic Resonance (EPR) is a powerful technique to probe and understand various phenomena in solid state physics. Unfortunately, the intrinsic Cu$^{2+}$ signals in the cuprate superconductors have not been observed except for those of chain fragments in YBa$_2$Cu$_3$O$_{6+\delta}$ (0.7 < $\delta$ < 0.9) \cite{75}, and three-spin polarons \cite{56}. The EPR silence has been attributed by many researchers to the very fast relaxation time of the Cu$^{2+}$ spins. In order to test this possibility, one needs to dope the material with a paramagnetic S-state ion (e.g., Mn$^{2+}$). Its relaxation occurs via the fast relaxing carriers. This is called bottleneck effect, which has indeed been observed in Mn$^{2+}$ doped La$_{2-x}$Sr$_x$CuO$_4$ \cite{55}.

Here we focus on the oxygen-isotope effect on the EPR linewidth in the Mn$^{2+}$ doped La$_{2-x}$Sr$_x$CuO$_4$ \cite{58,59}. In Fig. 13, we show the temperature dependence of the EPR linewidth $\Delta H_{pp}$ for $^{18}$O isotope samples of La$_{2-x}$Sr$_x$CuO$_{4+\alpha}$ with $x = 0.03$, 0.06, and 0.10 (Fig. 13a), as well as the isotope effect on the EPR linewidth $\Delta H_{pp}$ in La$_{1.97}$Sr$_{0.03}$Cu$_{0.98}$Mn$_{0.02}$O$_4$ (Fig. 13b). It is remarkable that the EPR linewidth at 100 K for the $^{16}$O sample is about half the one for the $^{18}$O sample. Such a large oxygen-isotope effect on the linewidth indicates that the dynamics of the oxygen atoms play a key role in the Cu$^{2+}$ relaxation. Interestingly, the temperature dependencies of the linewidth for both isotope samples are in good agreement with theoretical calculations (see solid and dashed lines) \cite{58,59}.

VIII. LARGE OXYGEN-ISOTOPE EFFECT ON SPIN-GLASS FREEZING TEMPERATURE

![Graph](image)

FIG. 14. Temperature dependence of the internal magnetic fields $B_\mu$ (probed by muon-spin-rotation) for the $^{16}$O and $^{18}$O samples of La$_{1.97}$Sr$_{0.03}$Cu$_{0.98}$Mn$_{0.02}$O$_4$. After \cite{53}.

The parent compounds of the cuprate superconductors exhibit long-range 3D antiferromagnetic (AF) order, which is rapidly destroyed as holes are doped into the CuO$_2$ planes. A short range ordered AF state exists at doping of 0.02 < $x$ < 0.06 in La$_{2-x}$Sr$_x$CuO$_4$. Early $\mu$SR and neutron scattering experiments found that this magnetic state resembles a spin glass \cite{30}. More detailed studies using $^{139}$La nuclear quadrupole resonance \cite{63} showed that the magnetic state in this doping regime is not a conventional spin glass, but a cluster spin glass (CSG). The understanding of how the short-range or-
dered AF state affects superconductivity and how it is influenced by lattice vibrations will help to clarify the pairing mechanism of high-$T_c$ superconductivity.

It is well known that conventional theories of magnetism neglect atomic vibrations; the atoms are mostly considered as being infinitely heavy in theoretical descriptions of magnetic phenomena, which rules out the existence of an isotope effect on magnetism. However, there is an exceptional example. In the ferromagnetic manganites, a giant oxygen-isotope effect on the Curie temperature has been observed \[62\]. The question is whether such an isotope effect also exists in cuprates.

In Fig. 4, we show the temperature dependence of the internal magnetic fields $B_y$ (probed by muon-spin rotation) for the $^{16}$O and $^{18}$O samples of La$_{1.95}$Sr$_{0.05}$CuO$_{2.98}$Mn$_{0.02}$O$_4$. It is remarkable that the spin-glass freezing temperature $T_g$ almost doubles upon replacing $^{16}$O by $^{18}$O. Such a huge isotope effect on the spin-glass freezing temperature suggests that spin dynamics in cuprates is ultimately correlated with lattice vibrations.

IX. OXYGEN-ISOTOPE EFFECT ON THE AF ORDERING TEMPERATURE

The antiferromagnetic order observed in the parent insulating compounds like La$_2$CuO$_4$ signals a strong electron-electron Coulomb correlation. On the other hand, the large isotope effects found in the underdoped cuprate superconductors indicate a strong electron-phonon interaction. Now a question arises: can the strong electron-phonon interaction modify the antiferromagnetic exchange energy and thus the AF ordering temperature in the parent insulating compounds? Studies of the isotope effect on the AF ordering temperature could clarify this issue \[64\].

Fig. 13 shows the temperature dependence of the susceptibility for the $^{16}$O and $^{18}$O samples of underdoped La$_2$CuO$_4$ (upper panel), and of oxygen doped La$_2$CuO$_{4+y}$ (lower panel). One can see that the AF ordering temperature $T_N$ for the $^{18}$O sample is lower than the $^{16}$O sample by about 1.9 K in the case of the undoped samples. For the oxygen-doped samples, there is a negligible isotope effect.

It is known that the antiferromagnetic properties of La$_2$CuO$_{4+y}$ can be well understood within mean-field theory which leads to a $T_N$ formula \[64\]:

$$k_BT_N = J'[\xi(T_N)/a]^2,$$ \hspace{1cm} (5)

where $J'$ is the interlayer coupling energy, $\xi(T_N)$ is the in-plane AF correlation length at $T_N$ with $\xi(T_N) \propto \exp(J/T_N)$ for $y = 0$ ($J$ is the in-plane exchange energy). When $T_N$ is reduced to about 250 K by oxygen doping, a mesoscopic phase separation has taken place so that $\xi(T_N) = L$ (Ref. \[17\]), where $L$ is the size of the antiferromagnetically correlated clusters, and depends only on the extra oxygen content $y$. In this case, we have

$$T_N = J'(L/a)^2.$$

Since $L$ is independent of the isotope mass, a negligible isotope shift of $T_N$ in the oxygen-doped La$_2$CuO$_{4+y}$ suggests that $J'$ is independent of the isotope mass. Then we easily find for undoped compounds

$$\Delta T_N/T_N = (\Delta J/J)B/(1+B),$$ \hspace{1cm} (6)

where $B = 2J/T_N \simeq 10$. From the measured isotope shift of $T_N$ for the undoped samples, we obtain $\Delta J/J \simeq -0.6%$.

![Fig. 15. The temperature dependence of the susceptibility for the $^{16}$O and $^{18}$O samples of undoped La$_2$CuO$_4$ (upper panel), and of the oxygen-doped La$_2$CuO$_{4+y}$ (lower panel). After \[64\].](image)

Theoretically, Kugel and Khomski \[68\] considered the Jahn-Teller effect in a single-band Hubbard model. They showed that, for $U >> E_p$, $\hbar\omega$,

$$J = \frac{2t^2}{U} \left(1 + \frac{2E_p\hbar\omega}{U^2}\right).$$ \hspace{1cm} (7)

On the other hand, when $U << \hbar\omega$,

$$J = \frac{2t^2}{U} \exp\left(-\frac{2E_p}{\hbar\omega}\right).$$ \hspace{1cm} (8)

Here $U$ is the onsite Coulomb repulsion, $t$ is the bare
hopping integral, $E_p$ is the Jahn-Teller stabilization energy, and $\omega$ is the vibration frequency of the Jahn-Teller mode. Assuming $t = 0.5 \text{ eV}$, $J = 0.13 \text{ eV}$, we obtain $U = 3.8 \text{ eV}$. With $\hbar \omega = 0.1 \text{ eV}$, $E_p = 1.2 \text{ eV}$, we obtain $\Delta J/J \simeq -0.1\%$ from Eq. 3, which is about a factor of 6 smaller than the measured value. The discrepancy might be due to the fact that the single-band Hubbard model is oversimplified for the parent cuprates.

X. CONCLUDING REMARKS

In summary, the unconventional isotope effects observed in cuprates clearly demonstrate that the electron-phonon interaction plays an important role in the physics of cuprates. Our results also show that the phonon modes related to both oxygen and copper vibrations are important to the pairing.

Interestingly, the concept of enhancing the electron-phonon coupling was the original motivation for the high-$T_c$ discovery. Bednorz and Müller argued that there should be a strong electron-phonon interaction in perovskites with strong Jahn-Teller centers. Indeed, the stretching vibration mode, which is related to the $Q_2$-type Jahn-Teller distortion, has proved to couple strongly to the doped holes. This high-energy $Q_2$-type mode may couple to the low-energy tilting mode ($Q_4/Q_5$-like Jahn-Teller mode) if the Cu-O-Cu bonding angle is less than 180°. Thus both stretching and tilting modes are important to high-$T_c$ superconductivity.

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