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# The isotope effect and superconducting oxides

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**Abstract.** We explored standard isotropic three-dimensional theory for the isotope effect with a purely electron–phonon attractive interaction. We find that additional features are necessary to account for the observed values of the isotope effect in the high-$T_c$ superconducting oxides. Some recent proposals for possible explanations of the observed reduced isotope effects are discussed.

## 1. Introduction

Recent discoveries [1] of superconducting materials with transition temperatures $T_c$ of nearly 40 K and above 90 K have led to many new theories [2] of the nature of the interaction responsible for superconductivity in the ceramic oxides. In the past, the magnitude of the isotope effect parameter $\alpha$ ($T_c \propto M^{-\alpha}$) has been cited as evidence both supporting and contradicting the hypothesis that the electron–phonon interaction is responsible for superconductivity in a given material. Hence, recent experiments finding a greatly reduced isotope shift [3] in $La_{1.85}Sr_{0.15}CuO_4$ and almost no shift [4] in $YBa_2Cu_3O_7$ have led to speculation that pairing mechanisms other than the electron–phonon mechanism are needed to explain the properties of the new superconducting oxides.

In 1950 the superconducting transition temperature of mercury was observed [5] to vary with the isotopic mass $M$ as $M^{-1/2}$. This was interpreted as experimental evidence that the phonon modes contributed to superconductivity. The Bardeen–Cooper–Schrieffer (BCS) theory [6] explained the origin of the isotope effect and the BCS model based on a one-square-well phonon attraction yielded $\alpha = 0.5$ for all superconductors. Further experiments on transition metals found a range of values, with several materials obeying the BCS model, but other materials exhibited 'anomalous' isotope effects, i.e. values of $\alpha$ deviating significantly from 0.5. These anomalous values were sometimes cited as 'disproving' the theory of electron–phonon mediation but were later explained through refinements of the BCS model developed in [7, 8] using the two-square-well model described in [9]. The deviations for transition metals were qualitatively explained [8] using a model which took into account the effects of the narrow d bands near the Fermi energy in these materials.

A reversal of the isotope effect was observed [10] in the Pd–H(D) system, where the transition temperature increased on substitution of deuterium for hydrogen. This effect

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was qualitatively explained [11] as resulting from differences in the electronic structure arising from anharmonicity in the zero-point motion of the hydrogen isotopes.

An $\alpha$-value of about $-2$ was found [12] for $\alpha$-uranium and an explanation was proposed [13] in terms of a density-of-states peak near the Fermi energy. At this point, the band structure of uranium is not sufficiently well known to test this possibility. Further anomalous values of $\alpha$ have been reported [14] for compounds containing d- and f-band electrons. Sometimes the results are explained [14] by assuming that only certain phonon modes are important for superconductivity.

For all materials except the new superconducting oxides, an isotope shift $\alpha$ differing substantially from the BCS prediction of 0.5 occurs only in substances with low transition temperatures. Within the two-square-well type of model, this result can be understood since for $\alpha$ to differ significantly from 0.5, the Coulomb repulsion of the electrons must not be too much smaller than the attractive electron–phonon interaction. This leads to a weak net attractive interaction and a corresponding small $T_c$. The superconducting oxides $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ are perhaps the most 'anomalous' materials discovered to date because of the combination of high $T_c$ and greatly reduced or nearly vanishing isotope effect.

In this paper, we briefly examine several previous models of the isotope effect and comment on their applicability. We also present results on the isotope effect for a purely electron–phonon-mediated attractive interaction and discuss its applications to the ceramic oxide superconductors. Some other possible explanations for the observed isotope effects in $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ are discussed.

## 2. Simple models

We examine first several models for the isotope effect in superconductors. The first and simplest model is the BCS one-square-well model, in which the attractive electron–phonon interaction is cut off at the Debye energy $\hbar\omega_D$ and the repulsive Coulomb interaction is neglected. The $T_c$ equation

$$T_c \propto \omega_D \exp[-1/N(0)V]$$

implies that the isotope effect $\alpha = 0.5$ holds in this model. The inclusion of the repulsive Coulomb interaction with the same energy cut-off does not alter the isotope effect, since the only dependence on ionic mass is through the Debye frequency $\omega_D$.

In the two-square-well model [9], the Coulomb repulsion $\mu$ is assumed to have a separate energy cut-off $\omega_c \simeq \varepsilon_F$ which is independent of the ion masses. In this model,

$$T_c \propto \omega_D \exp[-1/(\lambda - \mu^*)] \qquad \alpha = \tfrac{1}{2}\{1 - [\mu^*/(\lambda - \mu^*)]^2\}$$

where $1/\mu^* = 1/\mu + \log(\omega_c/\omega_D)$. The isotope effect $\alpha$ is therefore only limited to values of $-\infty < \alpha < 0.5$.

The McMillan [15] equation, which has been refined in [16], is an approximation for strong- and weak-coupling superconductors. It yields

$$k_B T_c = (\hbar\omega_{\log}/1.2) \exp\{-1.04(1 + \lambda)/[\lambda - \mu^*(1 + 0.62\lambda)]\}$$

for the transition temperature and

$$\alpha_{\text{McMillan}} = \tfrac{1}{2}\{1 - 1.04(1 + \lambda)(1 + 0.62\lambda)\mu^{*2}/[\lambda - \mu^*(1 + 0.62\lambda)]^2\}$$

for the isotope effect parameter.

These equations all predict large deviations from the BCS value of $\alpha = 0.5$ at small $\lambda$ for modest $\mu^*$, with the magnitude of the deviations decreasing with increasing $\lambda$. Thus, for elements with large $\lambda$, these models predict an isotope shift close to 0.5 unless very large values of $\mu^*$ occur. [17] contains a tabulation of theoretical predictions of these models and experimental results. For the weak-coupling superconductors, the models generally agree with the calculation in [8] which also qualitatively predicts the values for strong-coupling materials and the transition metals. The large uncertainties in the theoretical values reflect both uncertainties in the available experimental data and the sensitivity of $\alpha$ to changes in $\mu^*$. Unfortunately, the only source for values of $\mu^*$ is from tunnelling experiments, since no *ab initio* method for calculating $\mu^*$ exists.

## 3. Calculations and results

We have calculated transition temperatures and isotope shifts from the electron–phonon interaction spectrum $\alpha^2F(\omega)$ and the Coulomb repulsion parameter $\mu^*$ using the Eliashberg theory [18] in the Matsubara representation [19]. The isotope effect exponent $\alpha$ is not related to the $\alpha$ in $\alpha^2F(\omega)$ which represents the electron–phonon matrix element. We have repeated the calculations using the same physical input parameters but with different energy cut-offs (matrix sizes) and selected a cut-off energy large enough to ensure numerical convergence. In most cases, a matrix size $N$ of 70 corresponding to a cut-off energy of $140\pi k_B T_c$ was found to yield well converged results. A variety of shapes of the electron–phonon interaction spectrum $\alpha^2F(\omega)$ was used, ranging from an Einstein spectrum to a flat 'square-well-like' spectrum and a spectrum modelled after the phonon density of states $F(\omega)$ measured for the superconducting oxides.

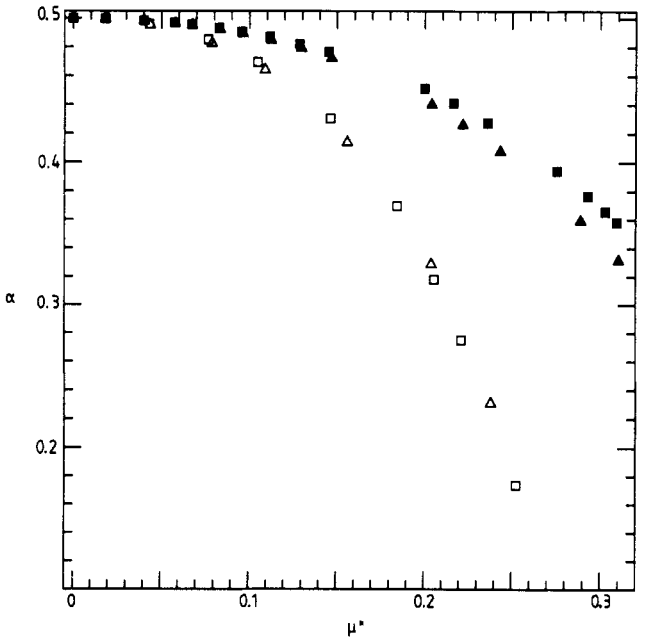


**Figure 1.** Values of $\alpha$ calculated for $\lambda = 1$ (□, △) and $\lambda = 10$ (■, ▲) using an Einstein phonon spectrum (□, ■) and a model $La_{1.85}Sr_{0.15}CuO_4$ spectrum (△, ▲). At constant $\lambda$, the values of $\alpha$ are nearly independent of the shape of the phonon spectrum.

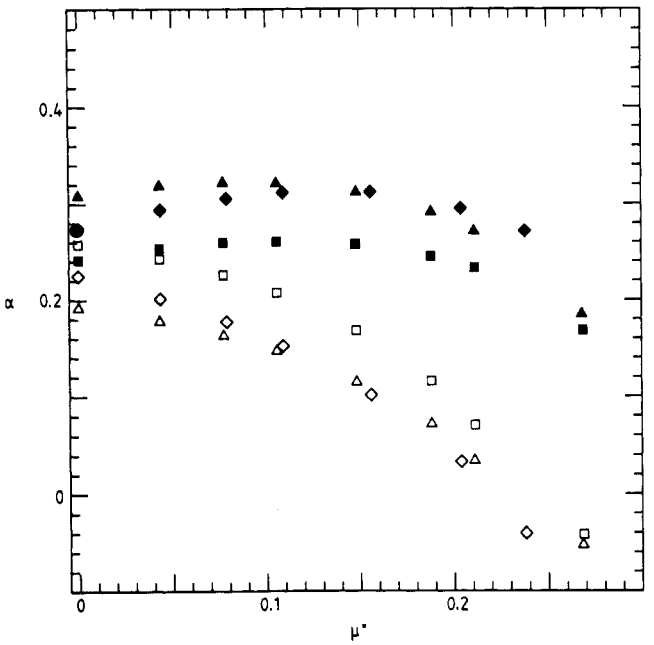


**Figure 2.** Values of $\alpha$ calculated for $\lambda = 1$ on shifting either the low-frequency half (■, ▲, ◆) or the high-frequency half (□, △, ◇) of three model spectra $\alpha^2F(\omega)$. Calculations were made for two-peak Einstein spectra with equal (□, ■) and unequal (△, ▲) weights, as well as for a model $La_{1.85}Sr_{0.15}CuO_4$ spectrum (◇, ◆). At $\lambda = 1$, shifting the low frequencies yields a larger $\alpha$ than shifting the high frequencies.

An important problem in the calculation of the isotope effect in compounds as opposed to elements is the determination of the changes in the spectrum arising from specific isotopic substitutions. Because of the complex structure of the oxide superconductors, it is difficult to determine precisely the changes in $\alpha^2F(\omega)$ or even $F(\omega)$ on substitution of a single element, e.g. oxygen. We have considered a model of oxygen isotope substitution, motivated by the comment in [20] that the high $T_c$ in $La_{1.85}Sr_{0.15}CuO_4$ could be explained if the high-frequency oxygen phonons in that material were primarily responsible for the attractive interaction. In the present calculations, we have assumed that the strength of the repulsive Coulomb interaction $\mu$ was independent of isotopic mass. Hence the calculated isotope effects were obtained by simulating the change in the frequency of the phonons arising from the substitution of one isotope for another. The resulting changes in $\alpha^2F(\omega)$ can be viewed as resulting from changes in either $\alpha^2(\omega)$ or $F(\omega)$.

The isotope shifts resulting from shifting the entire $\alpha^2F(\omega)$ spectrum would be appropriate in the case of an elemental superconductor. We have also calculated the shifts resulting from only shifting the high- and low-frequency halves of $\alpha^2F(\omega)$ as a simple approximation for isotopic substitution of elements in a compound. The division between high and low frequencies was chosen so that half the strength $\lambda$ of the attractive interaction came from each half of $\alpha^2F(\omega)$. Figure 1 shows the calculated isotope effects for shifting the entire $\alpha^2F(\omega)$ spectrum, as would be appropriate for an element. We find that the calculated values of the isotope effect are independent of the shape of $\alpha^2F(\omega)$ for small values of $\mu^*$ and exhibit only a small amount of scatter for extremely

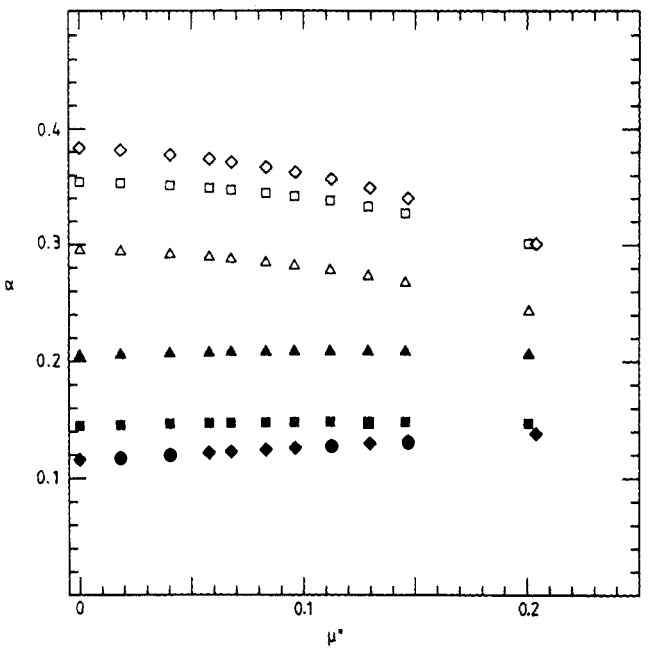


**Figure 3.** Values of $\alpha$ calculated for $\lambda = 10$ on shifting either the low-frequency half (■, ▲, ◆) or the high-frequency half (□, △, ◇) of three model spectra $\alpha^2F(\omega)$. Calculations were made for two-peak Einstein spectra with equal (□, ■) and unequal (△, ▲) weights, as well as for a model $La_{1.85}Sr_{0.15}CuO_4$ spectrum (◇, ◆). At $\lambda = 10$, shifting the high frequencies yields a larger $\alpha$ than shifting the low frequencies.

large values of $\mu^*$, where $\mu^*$ is the renormalised Coulomb interaction evaluated at the root-mean-square phonon frequency. This is not too surprising in view of the known weak dependence of the ratio $T_c/\omega_{log}$ on the shape of $\alpha^2F(\omega)$ reported earlier [15].

Figures 2 and 3 show the calculated isotope effects for a simulated oxygen substitution in the oxide superconductors at $\lambda = 1$ and 10, respectively. In these calculations the high-frequency modes were shifted, while the low-frequency half of $\alpha^2F(\omega)$ was left unchanged. The isotope effects resulting from shifting only the low-frequency modes are also shown. These calculations reveal the dependence of $\alpha$ on the shape of the electron–phonon interaction spectrum $\alpha^2F(\omega)$.

For all the spectra studied, shifting only half of the spectrum results in reduced isotope effects as expected, and greatly reduced isotope effects at large $\mu^*$. In the case of large $\lambda$, shifting the high-frequency modes is seen to lead to a greater isotope shift than for small $\lambda$. This can be understood if one notes that the renormalisation included in the strong-coupling model grows more rapidly with increasing $\lambda$ for low frequencies than it does for high frequencies, increasing the importance of high-frequency modes relative to the low-frequency modes.

## 4. Application to high $T_c$

Using electron–phonon spectra similar to those presented in experimental data, we have calculated the isotope effect in $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$ with the goal of

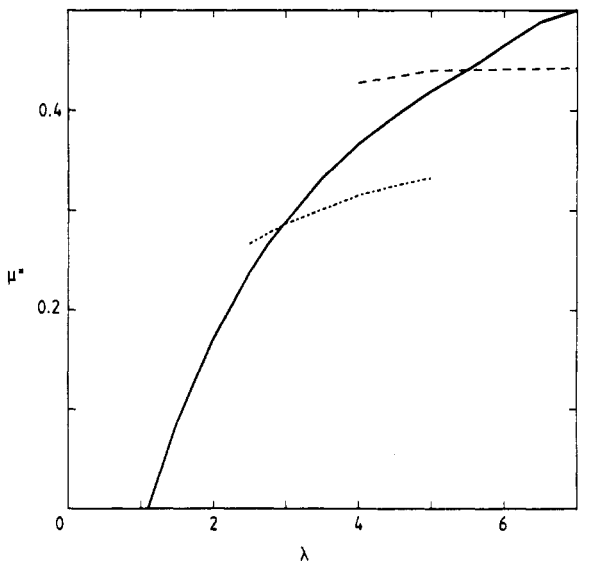


**Figure 4.** Values of $\lambda$ and $\mu^*$ for which $T_c = 37$ K from numerical solutions of the Eliashberg equation (——). Solutions with $\alpha = 0.14$ for shifting the entire phonon spectrum (– – –) and shifting only the phonon spectrum peaks corresponding to oxygen vibrations (- - - - -) are given. The intersections of the $T_c$ curve with the broken curves give the solutions consistent with phonon-mediated superconductivity in $La_{1.85}Sr_{0.15}CuO_4$.

determining whether or not standard phonon-mediated pairing in three dimensions can be responsible for superconductivity in the ceramic oxides. We assume the following data: for $La_{1.85}Sr_{0.15}CuO_4$, $\alpha = 0.14$ and $T_c \simeq 37$ K [3]; for $YBa_2Cu_3O_7$, $\alpha \simeq 0.02$ and $T_c \simeq 93$ K [4].

We find that for $La_{1.85}Sr_{0.15}CuO_4$, phonon-mediated pairing is still possible, but for values of the parameters $\lambda$ and $\mu^*$ that are larger than previously estimated [20]. The results of our calculations are shown in figure 4. In this figure, the shape of $\alpha^2F(\omega)$ is held fixed while its amplitude is scaled to yield different values of $\lambda$, and the Coulomb parameter $\mu^*$ is also varied. The $T_c = 37$ K isotherm represents those values of $(\lambda, \mu^*)$ that yield a transition temperature of 37 K. The upper broken line represents $(\lambda, \mu^*)$ values with constant $\alpha = 0.14$ when the entire spectrum is shifted. The lower broken line represents $(\lambda, \mu^*)$ values with constant $\alpha = 0.14$ for simulated oxygen substitution, when only the high-frequency modes are shifted. Phonon-mediated superconductivity is possible at the parameter values indicated by the intersection of the $T_c$ isotherm and the constant-$\alpha$ lines. Experimental determinations of $\lambda$ from resistivity measurements have yielded results supporting both strong [21] and weak [22] coupling. If conclusive experimental evidence for weak coupling in $La_{1.85}Sr_{0.15}CuO_4$ were found, however, it would indicate that the simple phonon-based coupling model would fail, since the range of possible $\lambda$ here clearly identifies $La_{1.85}Sr_{0.15}CuO_4$ as a strong-coupling superconductor.

For $YBa_2Cu_3O_7$, we find it nearly impossible to explain the observed experimental values within a solely phonon-mediated isotropic three-dimensional model. Figure 5 shows the results for $YBa_2Cu_3O_7$, with the $T_c = 93$ K isotherm and the lines of constant $\alpha \simeq 0 \pm 0.02$. For the case where the entire spectrum is shifted, no values of the parameters will yield the necessary values of $\alpha$ and $T_c$. When only the high-frequency

phonon modes are shifted, we find that the intersection of the $T_c$ isotherm and the constant-$\alpha$ line occurs for $\lambda > 30$. Such a value of $\lambda$ would be unphysical owing to the onset of lattice instabilities and/or electron localisation at extremely strong electron–phonon coupling. These conclusions also hold for values of $\alpha$ from 0.02 to 0.05 as have been recently reported [23]. Calculations based on measurements of $\alpha$ in $YBa_2Cu_3O_7$ for copper or barium isotopic substitution [24] yield less restrictive bounds on the values of $\lambda$ and $\mu^*$ than the limits imposed by simulated oxygen substitution. We therefore conclude that superconductivity in $YBa_2Cu_3O_7$ cannot be explained within our simple three-dimensional phonon-mediated model and that additional features are necessary for the model to explain the observed experimental values.

Several attempts have been made to explain the experimental results by adding an attractive non-phonon interaction with a higher energy to the phonons and then calculating $T_c$ and $\alpha$. In [25], strong-coupling calculations of the isotope effect for simulated oxygen substitution were carried out, and $\mu^*$ was made negative to simulate an attractive Coulomb interaction. It was found that $\alpha \simeq 0.08$ within this model for oxygen substitution for both $T_c = 91$ K and $T_c = 35$ K. In [26] a combined phonon–exciton model for $La_{1.85}Sr_{0.15}CuO_4$ was proposed and many properties within the framework of the Eliashberg strong-coupling theory were calculated. Within their model, they find that their calculated $T_c$, $\alpha$ and critical field fall within the range of experimental results. In [27] a three-square-well model with renormalisation was used to calculate $T_c$ and $\alpha$. With the inclusion of higher-energy non-phonon attractive interactions, possible agreement was found with the observed $T_c$ and $\alpha$ for $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$. They speculate that the differences in $T_c$ and $\alpha$ between the two materials could be accounted for solely by changing the strength of the non-phonon interaction. An interesting possibility is that the previously known oxide superconductor Pb–Bi–Ba–O could

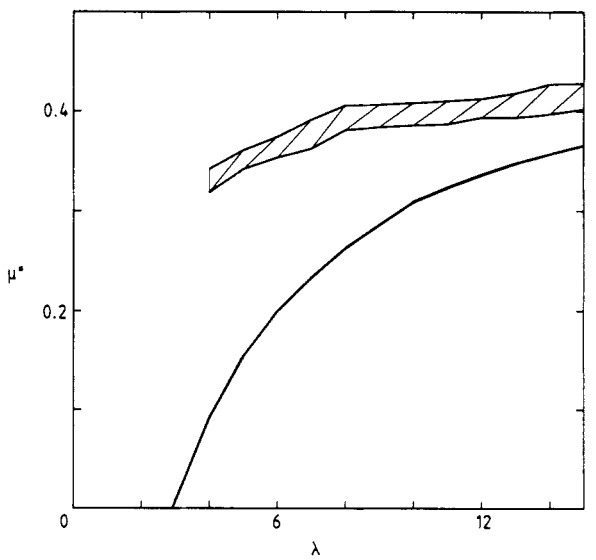


**Figure 5.** Values of $\lambda$ and $\mu^*$ for which $T_c = 90$ K from numerical calculations (——). The shaded area represents solutions with $\alpha = 0 \pm 0.02$ found numerically by shifting only the phonon spectrum peaks corresponding to oxygen vibrations. An intersection of the full curve with the shaded area indicates values of $\lambda$ and $\mu^*$ consistent with phonon-mediated superconductivity in $YBa_2Cu_3O_7$.

be described similarly. From their model, the predicted value of the isotope shift corresponding to the known $T_c = 13$ K would be $0.26 < \alpha < 0.30$. The oxygen isotope shift in Pb–Bi–Ba–O has recently been measured [28] and a value of $\alpha$ of $0.22 \pm 0.03$, which is nearly in agreement with the prediction reported in [27].

Other theories have been advanced to explain the size of the observed isotope effects in $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ without introducing a new attractive interaction. These include a two-dimensional theory proposed in [29], a model proposed in [30] in which the change in zero-point motion yields an isotope effect, and a quasi-two-dimensional bond-asymmetry model in [31].

$La_{1.85}Sr_{0.15}CuO_4$ was treated in [29] as having a two-dimensional electronic structure with an electronic density of states which diverges logarithmically at a Van Hove singularity. This divergence is assumed to fall near the Fermi energy, so that the width of the peak in the density of states is the important energy scale. Hence the transition temperature depends weakly on the phonon frequency $\omega_D$ and a small $\alpha$ results. It was proposed in [30] that the change in zero-point motion (and therefore in the volume of the unit cell and the Cu–O hopping parameter) combined with the large value of the pressure derivative of $T_c$ in $La_{1.85}Sr_{0.15}CuO_4$ could account for the observed isotope effect without any phonon contribution at all. It was proposed in [31] that within a quasi-two-dimensional model, bond asymmetry due to orthorhombic distortions causes a rapid variation in the electronic density of states, resulting in a power-law dependence of $T_c$ and a reduced isotope effect.

## 5. Summary

We have found that the isotope effect in elemental superconductors is nearly independent of the shape of the phonon spectrum, while in compounds it depends on which subset of the phonon modes is affected by the isotopic substitution. We find that the superconductivity in $La_{1.85}Sr_{0.15}CuO_4$ may be explained within our model for certain values of the parameters $\lambda$ and $\mu^*$, while the model appears to fail to account for the parameters of the 93 K superconductor $YBa_2Cu_3O_7$. We emphasise that our results do not necessitate a phonon-based mechanism for superconductivity in $La_{1.85}Sr_{0.15}CuO_4$ but rather admit the possibility that such a mechanism exists in $La_{1.85}Sr_{0.15}CuO_4$.

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