Here we provide an alternative explanation of how the nonuniversality of the dependence of the critical temperature of a superconductor with anisotropic superconducting order parameter.

Our approach is based on taking into account the combined effect of both nonmagnetic and magnetic scatterers on the $\alpha/\alpha_0$ behavior of $\alpha/\alpha_0$. Our prediction does not agree with the experimental findings [7–9]. It was shown by Kresin et al. that the universal dependence of the normalized isotope coefficient, $\alpha/\alpha_0$, on the normalized critical temperature, $T_c/T_{c0}$, was restricted to the case that magnetic impurities are the only cause for the increase of $\alpha/\alpha_0$, and that other effects like the nonadiabaticity of the apex oxygen in YBa$_2$Cu$_3$O$_y$ could break the universality.

The discovery of high temperature superconductors (HTSCs) brought a serious challenge to the BCS theory which had firmly established the phonon mediated mechanism of electron pairing by Bardeen, Cooper and Schrieffer [1]. The BCS theory gave the isotope coefficient $\alpha_0$, equal to 1/2, in agreement with the experiments for mercury [2]. For simple superconducting metals like Hg, Zn, S, Pb, etc., the values of $\alpha_0$ were found to be very close to the BCS value 1/2. The deviations from the BCS theory found in superconducting transition metals and their compounds were reasonably well explained by taking into account the effects of Coulomb interactions [3], left out in the BCS theory, and by more realistic treatments based on Eliashberg equations [4].

The presence of impurities strongly affects various characteristics of HTSCs, including the isotope coefficient [7–9]. Earlier theoretical attempts to describe the isotope effect in impure HTSCs were based on either the Abrikosov-Gor’kov formula for $T_c$ of an isotropic $s$-wave superconductor containing magnetic impurities [5] or the Abrikosov-Gor’kov-like formula for $T_c$ of an anisotropic superconductor that contains nonmagnetic impurities only [6]. An increase in $\alpha_0$ with impurity concentration has been demonstrated, in qualitative agreement with the experiment. However, the theory predicted the universal dependence of the normalized isotope coefficient, $\alpha/\alpha_0$, on the normalized critical temperature, $T_c/T_{c0}$, where $\alpha_0$ and $T_{c0}$ are, respectively, the values of $\alpha_0$ and $T_c$ in the absence of impurities. This prediction does not agree with the experimental findings [6–8]. It was shown by Kresin et al. that the universal behavior of $\alpha/\alpha_0$ versus $T_c/T_{c0}$ is restricted to the case that magnetic impurities are the only cause for the increase of $\alpha/\alpha_0$, and that other effects like the nonadiabaticity of the apex oxygen in YBa$_2$Cu$_3$O$_7$ could break the universality.

Here we provide an alternative explanation of how the nonuniversality of the dependence of $\alpha/\alpha_0$ on $T_c/T_{c0}$ arises. Our approach is based on taking into account the combined effect of both nonmagnetic and magnetic scatterers on the critical temperature of a superconductor with anisotropic superconducting order parameter.
To derive the expression for the isotope coefficient, we make use of the equation for $T_c$ of an anisotropic superconductor containing both nonmagnetic and magnetic impurities [12]:

$$\ln \left( \frac{T_{c0}}{T_c} \right) = (1 - \chi) \left[ \Psi \left( \frac{1}{2} + \frac{1}{2\pi T_c \tau_{ex}} \right) - \Psi \left( \frac{1}{2} \right) \right] + \chi \left[ \Psi \left( \frac{1}{2} + \frac{1}{4\pi T_c \tau} \right) - \Psi \left( \frac{1}{2} \right) \right],$$  \hspace{1cm} (1)

where $\Psi$ is the digamma function; $\tau_{ex}$ is the electron relaxation time due to exchange scattering by magnetic impurities; $\tau$ is the total electron relaxation time due to potential scattering by both magnetic and nonmagnetic impurities, as well as due to exchange scattering by magnetic impurities. Eq. (1) was obtained in Ref. [13] within the weak-coupling limit of the BCS model in the framework of Abrikosov–Gor’kov approach. It generalizes the well-known expressions [14,15] for the critical temperature of impure superconductors to the case of combined effect of both nonmagnetic and magnetic impurities on the critical temperature of anisotropic superconductors. The coefficient $\chi = 1 - \frac{(\Delta(p))_{FS}^2}{(\Delta^2(p))_{FS}}$ quantifies the degree of anisotropy of the order parameter $\Delta(p)$ on the Fermi surface (FS), where the angular brackets $\langle \ldots \rangle_{FS}$ stand for a FS average. For isotropic s-wave pairing, $\langle \Delta(p) \rangle_{FS}^2 = \langle \Delta^2(p) \rangle_{FS}$, and hence $\chi = 0$. For a superconductor with d-wave pairing we have $\chi = 1$ since $\langle \Delta(p) \rangle_{FS} = 0$. The range $0 < \chi < 1$ corresponds to anisotropic s-wave or mixed (d + s)-wave pairing. The higher the anisotropy of $\Delta(p)$ (e.g., the greater the partial weight of a d-wave in the case of mixed pairing), the closer to unity is the value of $\chi$. Note that in two particular cases of (i) magnetic scattering in an isotropic s-wave superconductor ($\chi = 0$) and (ii) nonmagnetic scattering only in a superconductor with arbitrary in-plane anisotropy of $\Delta(p)$ ($1/\tau_{exm} = 0, 0 \leq \chi \leq 1$), Eq. (1) reduces to the well-known expressions [14,15].

It is convenient to specify the relative contribution of spin-flip scattering rate, $1/\tau_{ex}$, to the total scattering rate, $1/\tau$, by the dimensionless parameter $\gamma$ defined as $\frac{1}{\tau_{ex}} = \gamma \frac{1}{\tau}$. The greater is the relative contribution from exchange scattering by magnetic impurities to $1/\tau$, the higher is the value of $\gamma$ ($\gamma$ ranges from 0 in the absence of exchange scattering to 1 in the absence of non-spin-flip scattering). In general, the value of $\gamma$ depends on the scattering strengths of individual nonmagnetic and magnetic impurities, as well as on their concentrations. At relatively low doping level, one can expect $\gamma$ to depend only on the type of the host material and doping elements, not on the impurity concentration [17].

Differentiating Eq. (1) for $T_c$ with respect to the isotopic mass $M$ under a reasonable assumption that electron relaxation times and the anisotropy coefficient $\chi$ do not depend on $M$, taking the definition of the parameter $\gamma$ into account and using the definition of the isotope coefficient $\alpha$, one has

$$\frac{\alpha}{\alpha_0} = \left[ 1 - (1 - \chi) \frac{\gamma}{2\pi T_c \tau} \psi^\prime \left( \frac{1}{2} + \frac{\gamma}{2\pi T_c \tau} \right) - \chi \frac{1}{4\pi T_c \tau} \psi^\prime \left( \frac{1}{2} + \frac{1}{4\pi T_c \tau} \right) \right]^{-1}. \hspace{1cm} (2)$$

Equation (2) is obviously more general than equations used previously for the analysis of the pair breaking effect on the isotope coefficient in HTSCs [14,15,22]. Indeed, Eq. (2) does not rely on particular assumptions about the symmetry of the superconducting state and the nature of impurities (either magnetic or nonmagnetic). This equation can be used for an impure superconductor with arbitrary anisotropy of the superconducting order parameter and arbitrary relative contributions of potential and spin-flip scattering to the electron relaxation time. Such an approach is of particular importance for HTSCs doped with various chemical elements since, first, there is a strong evidence for a dominant d-wave (i.e., highly anisotropic) order parameter in HTSCs [16] with a subdominant s-wave component [17], and, second, a lot of experiments give evidence for the presence of magnetic scatterers (along with nonmagnetic ones) in doped HTSCs [18,23].

At given values of $\chi$ and $\gamma$, Eqs. (1) and (2) define the dependence of $\alpha/\alpha_0$ on $T_c/T_{c0}$. One can see from Eqs. (1) and (2) that the dependence of $\alpha/\alpha_0$ on $T_c/T_{c0}$ has a universal shape for both an isotropic s-wave superconductor ($\chi = 0$) with nonzero contribution of exchange scattering to the total scattering rate ($0 < \gamma \leq 1$) and a d-wave superconductor ($\chi = 1$) with an arbitrary ratio of spin-flip and potential scattering rates ($0 \leq \gamma \leq 1$), as it is seen from Fig. 1.

Quite a different picture is realized in the case $0 < \chi < 1$, i.e., for a mixed (d + s)-wave or an anisotropic s-wave superconductor. In this case the behaviour of $\alpha/\alpha_0$ as a function of $T_c/T_{c0}$ essentially depends on the value of $\gamma$. As $T_c/T_{c0}$ goes to zero, i.e., in dirty superconductors, the value of $\alpha/\alpha_0$ tends to $1/(1 - \chi)$ in the absence of exchange scattering ($\gamma = 0$), while $\alpha/\alpha_0$ grows as $\alpha/\alpha_0 \propto T_{c0}/T_c$ in the case $\gamma \neq 0$ for all values of $\chi$. Thus, the universality of $\alpha/\alpha_0$ versus $T_c/T_{c0}$ curve breaks down for $0 < \chi < 1$. This is consistent with experimental observations. Indeed, the studies of isotope effect in impure HTSCs [14,3] show that the curves of $\alpha/\alpha_0$ versus $T_c/T_{c0}$ vary with the type of impurities, i.e., with the value of $\gamma$ (since different chemical elements contribute differently to spin-flip and potential scattering rates of charge carriers). So, our results seem to be in a qualitative agreement with the experiment if one

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assumes that the superconducting state in HTSCs differs from a pure \( s \) or \( d \)-wave, i.e., \( \chi \neq 0 \) and \( \chi \neq 1 \), as is also indicated by several experimental observations \(^{17\text{--}23}\).

However, our theoretical consideration doesn’t account for a number of factors that could influence the isotope coefficient in impure superconductors, e.g., the energy dependent electronic density of states, nonadiabaticity, anharmonicity, etc. In particular, the change in the carrier concentration \( n_h \) upon chemical substitution can have a strong influence on \( T_c \) (and hence on \( \chi \)) along with the pair-breaking effect. This is why, to compare our calculations with the experiment, we have taken the data on the isotope effect in the system \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-x}\text{M}_x\text{O}_4 \) (\( \text{M} = \text{Ni, Zn, Co, Fe} \)), see Ref. \(^3\). In this system, the critical temperature decreases rapidly as the impurity content \( x \) increases, and falls down to \( \approx 0.3T_{c0} \) already at \( x = 0.02 - 0.03 \). At such low impurity concentration, the change in \( T_c \) due to the change in \( n_h \) can be neglected in the first approximation (as compared with the pair-breaking effect) since the value of \( T_{c0} \approx 40\text{K} \) in the impurity-free HTSC \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_4 \) corresponds to the maximum on the curve \( T_c(n_h) \), and hence changes insignificantly with \( n_h \) as long as the change in \( n_h \) is small. Note that such an approach (i.e., ignoring the change in the carrier concentration upon doping) may not be appropriate in case of \( \text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7 \) where \( T_c/T_{c0} \approx 0.3 \) at \( x = 0.06 \) and all the more for \( \text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7 \) where \( T_c/T_{c0} \approx 0.3 \) at \( x = 0.5 \), see Ref. \(^4\). A reasonable explanation of the isotope effect in these HTSCs has been given by Kresin et al. \(^{10}\) who considered the interplay between the changes in the carrier concentration and nonadiabaticity of the apex oxygen.

Fig.2 shows the experimental data along with theoretical graphs calculated for \( \chi = 0.5 \) and different values of \( \gamma \), ranging from 0 to 1. One can see that at low impurity content \( x < 0.008 \) (\( T_c/T_{c0} > 0.75 \)) there is a good agreement between the theory and the experiment. However, at higher values of \( x \) (i.e., at lower values of \( T_c/T_{c0} \)) the experimental points lie well above the theoretical curves for all impurity elements, except for \( M = \text{Ni} \). The same is true for other values of \( \chi \) since the upper curve in Fig. 2 (for \( \gamma = 1 \)) changes insignificantly with \( \chi \), at least for \( T_c/T_{c0} > 0.2 \).

To bring the theory closer to the agreement with the experiment, one can assume that the value of \( T_{c0} \) in the impurity-free HTSC \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_4 \) is strongly depressed relative to its ”intrinsic” value \(^{23}\) because of the scattering of charge carriers by inhomogeneities produced by substitution of \( \text{Sr} \) for \( \text{La} \). Recently it was suggested \(^{23}\) that the anomalous response of the anisotropic superconducting state to the development of low energy dynamical charge stripes can also cause the suppression of the ”intrinsic” \( T_{c0} \). Taking \( T_{c0} \) to be equal to its ”intrinsic” value, it is possible to reach a qualitative agreement with the experiment on the isotope effect in impure HTSCs even for heavily doped samples with low \( T_c \). Since the value of ”intrinsic” \( T_{c0} \) in \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_4 \) is not known \( a \ priori \), we take the suggested value \(^{24}\) of 90 K.

Fig. 3 shows the results for the set of \( T_{c0} = 90\text{K} \) and \( \chi = 0.5 \). For such a choice of the values of \( T_{c0} \) and \( \chi \), the theoretical curves for \( \gamma = 0 - 1 \) are closer to the experimental data \(^3\). Since the value of \( \alpha_0 \) at ”intrinsic” \( T_{c0} \) is not known, we assumed for simplicity that the value of \( \alpha \) is the same at \( T_{c0} \approx 40\text{K} \) and 90 K. This assumption can be the reason for a discrepancy between the theory and the experiment in the region \( T_c/T_{c0} = 0.3 - 0.4 \), see Fig. 3, since one could expect the value of \( \alpha \) at \( T_{c0} \approx 90\text{K} \) to be somewhat lower than at \( T_{c0} \approx 40\text{K} \). It should be noted that in our theory different types of impurities correspond to different values of \( \gamma \). The magnetic elements \( \text{Fe and Co} \) can be thought of being characterized by \( \gamma \) in the range 0.1 - 1, while \( \text{Ni} \), whose magnetic moment is reduced considerably by doping \(^3\), can be assigned somewhat lower value of \( \gamma \approx 0.01 \), see Fig. 3. Similarly, the doping by the nonmagnetic element \( \text{Zn} \) induces magnetic moments \(^{18,23}\). One can see from Fig. 3 that \( \text{Zn} \) can be assigned the value of \( \gamma \) in the range 0.01 - 0.05, i.e. lower than in the case of \( \text{Fe and Co} \) but greater than in the case of \( \text{Ni} \).

Finally, we note that the agreement between the theory and the experiment becomes worse if one takes the value of \( \chi \) closer to unity. This implies that the symmetry of the pairing state in \( \text{La}-\)based HTSCs can differ considerably from a pure \( d \)-wave. As far as we know, up to now there were only indirect arguments in favor of \( d \)-wave symmetry of the superconducting state in \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_4 \) \(^{24}\) while phase-sensitive experiments are unknown to us. The value of \( \chi \approx 0.5 \) is however close to that expected for the two-dimensional order parameter of the type \( \Delta(k) = \Delta_0 [\cos(k_x\alpha) + \cos(k_y\alpha)] \), see Ref. \(^{27}\).

In conclusion, we have studied theoretically the effect of both magnetic and nonmagnetic impurities on the isotope coefficient in the framework of a generalized Abrikosov-Gorkov approach for the anisotropic superconductors. We have shown how the interplay between the potential and spin-flip impurity scattering gives rise to the nonuniversal dependence of \( \alpha/\alpha_0 \) versus \( T_c/T_{c0} \) in mixed \( (d + s) \) wave or anisotropic \( s \) wave superconductors. Our main result is that if the impurities are viewed as the only cause for the increase in the isotope coefficient in \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-x}\text{M}_x\text{O}_4 \), then the symmetry of the superconducting order parameter in \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_4 \) appears to be different from a pure \( d \)-wave. Indeed, even if one takes into account relatively large experimental errors in the values of \( \alpha \), it is clearly seen that experimental points do not lie on a single ”universal” curve of \( \alpha/\alpha_0 \) versus \( T_c/T_{c0} \) as one could expect in the case of a pure \( d \)-wave symmetry of the superconducting state. According to our calculations, the difference in \( \alpha/\alpha_0 \) versus \( T_{c0}/T_c \) curves for different impurity elements can be attributed to different contributions from the exchange scattering to the total scattering rate of charge carriers in the mixed \( (d + s)\)-wave or anisotropic \( s \)-wave
superconducting state. The agreement with the experiment is much more better if one assumes that the "intrinsic" value of $T_c$ in La$_{1.85}$Sr$_{0.15}$CuO$_4$ reaches $\approx 90$ K, more than twice greater than the experimental value $\approx 40$ K. It would be interesting to check if it is possible to explain the nonuniversality of $\alpha/\alpha_0$ versus $T_c/T_c^0$ in La$_{1.85}$Sr$_{0.15}$Cu$_{1-x}$M$_x$O$_4$ within a pure $d$-wave framework.

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FIGURE CAPTIONS

Fig. 1. Universal dependence of the normalized isotope coefficient $\alpha/\alpha_0$ on the normalized critical temperature $T_c/T_{c0}$ in an impure isotropic $s$-wave superconductor ($\chi = 0$) with a finite concentration of magnetic scatterers and an impure $d$-wave superconductor ($\chi = 1$) with an arbitrary ratio of spin-flip and potential scattering rates.

Fig. 2. Same as in Fig. 1 for $\chi = 0.5$ (a specific case of anisotropic pairing) for different values of the coefficient $\gamma$ specifying the relative contribution to the total scattering rate from exchange scattering. $\gamma = 0$ (dot-dashed curve), 0.01 (thin solid curve), 0.05 (dashed curve), 0.1 (dotted curve), 1 (thick solid curve). Experimental data from Ref. 5 for isotope effect in La$_{1.85}$Sr$_{0.15}$Cu$_{1-x}$M$_x$O$_4$ with different $x$ and $M = \text{Ni}$ (triangles), Zn (open squares); Co (closed circles); Fe (closed squares). Experimental values of $T_c$ as a function of $x$ are normalized to the value of $T_{c0} = 37.5$ K at $x = 0$.

Fig. 3. Same as in Fig. 2 for $T_{c0} = 90$ K, see text for details.
