# Isotope effect in the presence of magnetic and nonmagnetic impurities

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The effect of impurities on the isotope coefficient is studied theoretically in the framework of the Abrikosov-Gor'kov approach generalized to account for both potential and spin-flip scattering in anisotropic superconductors. An expression for the isotope coefficient as a function of the critical temperature is obtained for a superconductor with an arbitrary contribution of spin-flip processes to the total scattering rate and an arbitrary degree of anisotropy of the superconducting order parameter, ranging from an isotropic *s* wave to a *d* wave and including an anisotropic *s* wave and a mixed $(s+d)$ wave as particular cases. It is found that both magnetic and nonmagnetic impurities enhance the isotope coefficient, the enhancement due to magnetic impurities being generally greater than that due to nonmagnetic impurities. From analysis of the experimental results on $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$ high temperature superconductors, it is concluded that the symmetry of the pairing state in this system differs from that of a pure *d* wave.

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The isotope effect has played an important role in the development of the phonon mediated mechanism of electron pairing in superconductors. Its discovery gave rise to this theory developed by Bardeen, Cooper, and Schrieffer.[1] The BCS theory gave the isotope coefficient $\alpha$, defined by the relation $T_c \propto M^{-\alpha}$ or equivalently $\alpha = -\partial \ln T_c / \partial \ln M$, as equal to 1/2, in agreement with experiments for mercury.[2] For simple superconducting metals like Hg, Zn, S, Pb, etc., the values of $\alpha$ 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 discovery of high temperature superconductors (HTSC's) was a serious challenge to the BCS theory, which had firmly established the phonon mediated mechanism of electron pairing as the dominant cause of superconductivity in most previously known superconductors. For conventional superconductors, both theory and experiment agree with the fact that $\alpha$ approaches the BCS value of 1/2 as $T_c$ becomes larger. However, this trend is violated in copper oxide HTSC's, where $\alpha$ has been found to vary with doping in different ways.[5] For the optimum doping, corresponding to the highest critical temperature, the value of $\alpha$ is usually quite small compared to the BCS value of 1/2. For a certain doping level, e.g., in some $La_2CuO_4$ based HTSC's, the value of $\alpha$ becomes greater than 1/2.[5] This behavior of $\alpha$ has been considered as one of the strongest pieces of evidence for a different mechanism of superconductivity in HTSC's. However, this argument is not as strong as it appears. For example, it was shown that, within the BCS picture or within the more realistic Eliashberg approach, these deviations can be understood[6] by considering the effects of anharmonicity, energy dependence of the electronic density of states, pair breaking effects, isotope mass dependence of the carrier concentration, etc.

The presence of impurities strongly affects various characteristics of HTSC's, including the isotope coefficient.[7–9] Earlier theoretical attempts to describe the isotope effect in impure HTSC's were based on either the Abrikosov-Gor'kov formula for $T_c$ of an isotropic *s*-wave superconductor containing magnetic impurities[8,10] or the Abrikosov-Gor'kov-like formula for $T_c$ of an anisotropic superconductor that contains nonmagnetic impurities only.[11,12] An increase in $\alpha$ with increasing impurity concentration was demonstrated, in qualitative agreement with experiment. However, the theory predicted a 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 $\alpha$ and $T_c$ in the absence of impurities. This prediction does not agree with the experimental findings.[7–9] It was shown by Kresin *et al.*[10] that the universal behavior of $\alpha/\alpha_0$ versus $T_c/T_{c0}$ is restricted to the case where 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 $YBa_2Cu_3O_7$ 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:[13]

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

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where $\Psi$ is the digamma function, $\tau_m^{ex}$ is the electron relaxation time due to exchange scattering by magnetic impurities, and $\tau$ 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. Equation (1) was obtained in Ref. 13 in the weak-coupling limit of the BCS model in the framework of the Abrikosov-Gor'kov approach. It generalizes the well-known expressions[14,15] for the critical temperature of impure superconductors to the case of a combined effect of both nonmagnetic and magnetic impurities on the critical temperature of anisotropic superconductors. The coefficient $\chi=1-\langle\Delta(\mathbf{p})\rangle_{FS}^2/\langle\Delta^2(\mathbf{p})\rangle_{FS}$ quantifies the degree of anisotropy of the order parameter $\Delta(\mathbf{p})$ on the Fermi surface (FS), where the angular brackets $\langle\cdots\rangle_{FS}$ stand for a FS average. For isotropic *s*-wave pairing, $\langle\Delta(\mathbf{p})\rangle_{FS}^2=\langle\Delta^2(\mathbf{p})\rangle_{FS}$, and hence $\chi=0$. For a superconductor with *d*-wave pairing we have $\chi=1$ since $\langle\Delta(\mathbf{p})\rangle_{FS}=0$. The range $0<\chi<1$ corresponds to anisotropic *s*-wave or mixed $(d+s)$-wave pairing. The higher the anisotropy of $\Delta(\mathbf{p})$ (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 $\Delta(\mathbf{p})$ ($1/\tau_m^{ex}=0, 0\leqslant\chi\leqslant1$), Eq. (1) reduces to the well-known expressions.[14,15]

It is convenient to specify the relative contribution of the spin-flip scattering rate $1/\tau_m^{ex}$ to the total scattering rate $1/\tau$ by the dimensionless parameter $\gamma$ defined as $1/\tau_m^{ex}=\gamma/\tau$. The greater 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 host material and doping elements, not on the impurity concentration.[13]

Differentiating Eq. (1) for $T_c$ with respect to the isotopic mass *M* under the 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

$$\frac{\alpha}{\alpha_0}=\left[1-(1-\chi)\frac{\gamma}{2\pi T_c\tau}\Psi'\left(\frac{1}{2}+\frac{\gamma}{2\pi T_c\tau}\right)-\chi\frac{1}{4\pi T_c\tau}\Psi'\left(\frac{1}{2}+\frac{1}{4\pi T_c\tau}\right)\right]^{-1}. \quad (2)$$

Equation (2) is obviously more general than equations used previously for the analysis of the pair breaking effect on the isotope coefficient in HTSC's.[8,10–12] 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 HTSC's doped with various chemical elements since, first, there is strong evidence[16] for a dominant *d*-wave (i.e., highly anisotropic) order parameter in HTSC's 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 HTSC's.[18–21]

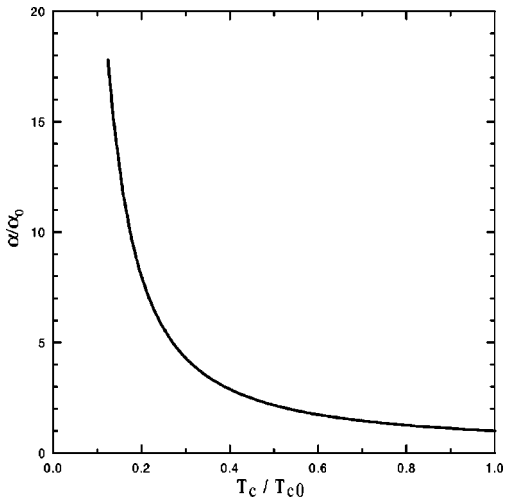


FIG. 1. Universal dependence of the normalized isotope coefficient $\alpha/\alpha_0$ on the normalized critical temperature $T_c/T_{c0}$ in an impure isotropic *s*-wave superconductor ($\chi=0$) with a finite concentration of magnetic scatterers and in an impure *d*-wave superconductor ($\chi=1$) with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

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 ($0<\gamma\leqslant1$) and a *d*-wave superconductor ($\chi=1$) with an arbitrary ratio of spin-flip and potential scattering rates ($0\leqslant\gamma\leqslant1$), as 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 behavior 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 $\gamma\neq0$ for all values of $\chi$. Thus, the universality of the $\alpha/\alpha_0$ versus $T_c/T_{c0}$ curve breaks down for $0<\chi<1$. This is consistent with experimental observations. Indeed, studies of the isotope effect in impure HTSC's[7] show that the curves of $\alpha/\alpha_0$ versus $T_c/T_{c0}$ vary with the type of impurity,[7–9] 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 qualitative agreement with experiment if one assumes that the superconducting state in HTSC's differs from a pure *s* or *d* wave, i.e., $\chi\neq0$ and $\chi\neq1$, as is also indicated by several experimental observations.[17,22]

However, our theoretical consideration does not account

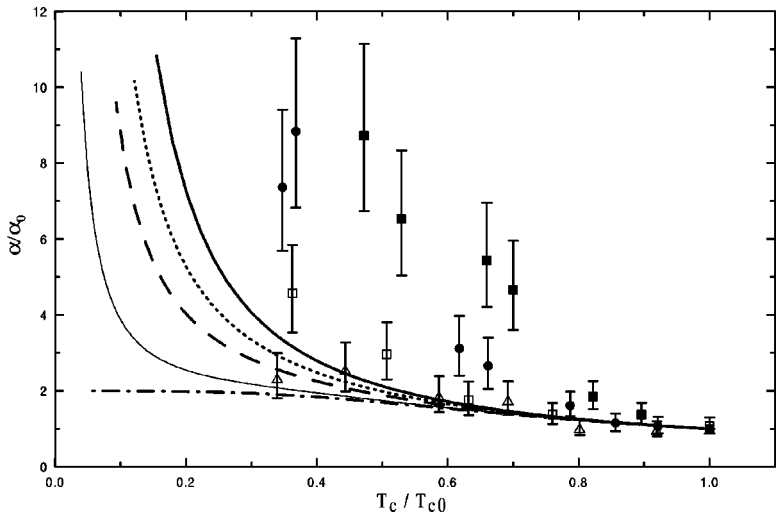


FIG. 2. Same as in Fig. 1 for $\chi=0.5$ (a specific case of anisotropic pairing) for different values of the coefficient $\gamma$ specifying the relative contribution to the total scattering rate from exchange scattering. $\gamma=0$ (dot-dashed curve), 0.01 (thin solid curve), 0.05 (dashed curve), 0.1 (dotted curve), and 1 (thick solid curve). Experimental data from Ref. 8 for isotope effect in $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$ with different $x$ and $M$ = 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 $x=0$.

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 $\alpha$) along with the pair breaking effect. This is why, to compare our calculations with experiment, we have taken the data on the isotope effect in the system $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$ ($M$=Ni, Zn, Co, Fe); see Ref. 8. In this system, the critical temperature decreases rapidly as the impurity content $x$ increases, and falls as low as $\approx 0.3T_{c0}$ 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 $T_{c0}\approx 40$ K in the impurity-free HTSC $La_{1.85}Sr_{0.15}CuO_4$ 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 the case of $YBa_2(Cu_{1-x}Zn_x)_3O_7$ where $T_c/T_{c0}\approx 0.3$ at $x=0.06$ and even less so for $Y_{1-x}Pr_xBa_2Cu_3O_7$ where $T_c/T_{c0}\approx 0.3$ at $x=0.5$ (see Ref. 7). A reasonable explanation of the isotope effect in these HTSC's 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.

Figure 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 $M$=Ni. The same is true for other values of $\chi$ since the top 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 agreement with experiment, one can assume that the value of $T_{c0}$ in the impurity-free HTSC $La_{1.85}Sr_{0.15}CuO_4$ is strongly depressed relative to its ''intrinsic'' value[23] because of the scattering of charge carriers by inhomogeneities produced by substitution of Sr for La. Recently it was suggested[24] 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 qualitative agreement with experiment on the isotope effect in impure HTSC's even for heavily doped samples with low $T_c$. Since the value of intrinsic $T_{c0}$ in $La_{1.85}Sr_{0.15}CuO_4$ is not known *a priori*, we take the suggested value[24] of 90 K.

Figure 3 shows the results for the set of $T_{c0}=90$ 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.[8] Since the value of $\alpha_0$ at the intrinsic $T_{c0}$ is not known, we assumed for simplicity that the value of $\alpha$ is the same at $T_{c0}\approx 40$ K and 90 K. This assumption might be the reason for the discrepancy between theory and experiment in the region $T_c/T_{c0}=0.3$–$0.4$, (see Fig. 3), since one could expect the value of $\alpha$ at $T_{c0}=90$ K to be somewhat lower than at $T_{c0}\approx 40$ K. It should be noted that in our theory different types of impurity correspond to different values of $\gamma$. The magnetic elements Fe and Co can be thought of as being characterized by $\gamma$ in the range 0.1–1, while Ni, whose magnetic moment is reduced considerably by doping,[8] can be assigned a somewhat lower value of $\gamma\approx 0.01$ (see Fig. 3). Similarly, doping by the nonmagnetic element Zn induces magnetic moments.[18,25] One can see from Fig. 3 that Zn can be assigned a value of $\gamma$ in the range 0.01–0.05, i.e., lower than in the case of Fe and Co but greater than in the case of Ni.

Finally, we note that the agreement between theory and the experiment becomes worse if one takes a value of $\chi$ closer to unity. This implies that the symmetry of the pairing state in La-based HTSC's can differ considerably from that of 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 $La_{1.85}Sr_{0.15}CuO_4$,[26] while phase-sensitive experiments are unknown to us. The value of $\chi\approx 0.5$ is, however, close to that expected for a two-dimensional order parameter of the type $\Delta(\mathbf{k})=\Delta_0[\cos(k_xa)+\cos(k_ya)]$ (see Ref. 27).

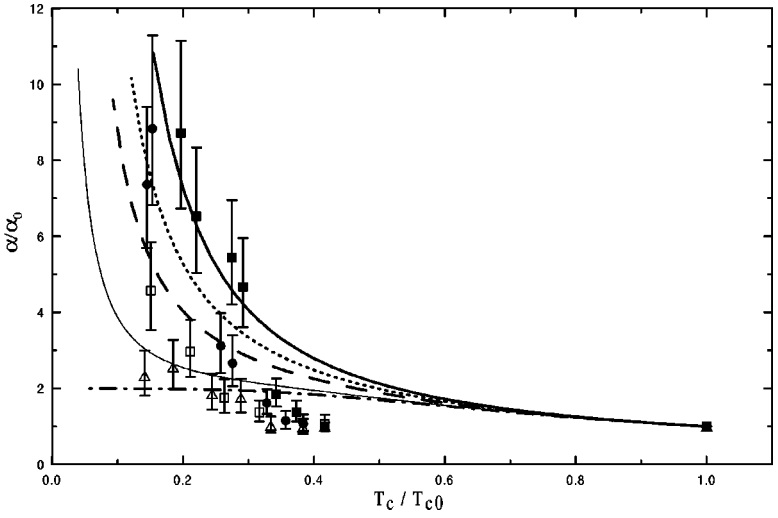


FIG. 3. Same as in Fig. 2 for $T_{c0}=90$ K; see text for details.

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-Gor'kov approach for anisotropic superconductors. We have shown how the interplay between the potential and spin-flip impurity scattering gives rise to a 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 $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$, then the symmetry of the superconducting order parameter in $La_{1.85}Sr_{0.15}CuO_4$ appears to be different from that of 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 would 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 experiment is much more better if one assumes that the intrinsic value of $T_{c0}$ in $La_{1.85}Sr_{0.15}CuO_4$ reaches $\approx 90$ K, more than twice as large as 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 $T_c/T_{c0}$ in $La_{1.85}Sr_{0.15}Cu_{1-x}M_xO_4$ within a pure *d*-wave framework.

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