Unconventional isotope effects in superconductors

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The value of the isotope coefficient could be greatly affected by a number of factors not related to the lattice dynamics. Among them are magnetic scattering, the presence of a normal film (proximity effect), and nonadiabaticity (dynamic Jahn-Teller effect). The results are in good agreement with existing experimental data for oxygen isotope substitution ($O^{16}\rightarrow O^{18}$) in the $YBa_2Cu_3O_{7-\delta}$, $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ compounds. In addition, we make several predictions related to conventional as well as to high-T_c materials. [S0163-1829(97)04825-X]

INTRODUCTION

This paper is concerned with various aspects of the isotope effect (IE). It will be shown that the value of the isotope coefficient (IC) $\alpha(T_c \propto M^{-\alpha})$ may depend on a number of factors not related to the pairing mechanism. We consider two scenarios. Initially we focus on the situation when the value of the critical temperature is affected by external factors ($T_{c0}\rightarrow T_c$) not related to the lattice dynamics; T_{c0} is the intrinsic value of the critical temperature. A perfectly realistic case is when the relation between T_{c0} and T_c is not linear. For example, we consider the IE in a proximity system *S*-*N* (where *S* and *N* are superconducting and normal films); it will be shown that the value of α depends on the relative thicknesses of the films. The value of α can also be greatly affected by the presence of magnetic impurities and depends strongly on their concentration n_m.

We discuss also a nonadiabatic IE. The Jahn-Teller crossing of electronic terms leads to the carrier concentration (and, hence, T_c) dependence on the isotopic substitution. A general method was described by us in Ref. 4. One can show (see below) that the model allows us to describe the data on the dependence of α on oxygen depletion;[3] the nonadiabatic effect also makes a strong impact on the IE in Pr-substituted $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

Our study was motivated by interesting experimental data.[1–3] We will also make several predictions for conventional superconductors and for the layered cuprates.

ISOTOPE EFFECT IN PROXIMITY SYSTEMS

Consider an *S*-*N* proximity sandwich (e.g., Nb-Ag). One can show that the proximity effect can make a strong impact on the effect of isotope substitution. Indeed, assume that the thickness $L_N \ll \xi_N$, where $\xi_N = h v_{F;N}/2\pi T$ is the coherence length for the *N* film.[5] Then one can use the well-known McMillan tunneling model.[6] According to Ref. 6, the proximity effect is described by the parameter $\Gamma=\Gamma_{SN}+\Gamma_{NS}$, where $\Gamma_{ik}=|T_{ik}|^2\nu_k V_k$, T_{ik} is the tunneling matrix element, ν_k is the density of states (per unit of volume V_k), i, $k=\{S,N\}$, $i\neq k$. The critical temperature, T_c of the whole system differs from T_{c0} (T_{c0} is the critical temperature of the isolated *S* film) and is described[7] by the equation:

$$T_c = T_{c0}(\pi T_{c0}/2\gamma u)^{\rho}; \quad \rho=\nu_N L_N/\nu_S L_S, \tag{1}$$

where $\gamma=0.577$ is Euler's constant. The value of u is determined by the interplay of two parameters, Γ and $\tilde{\Omega}$, where $\tilde{\Omega}=\langle\Omega^2\rangle^{1/2}\approx\Omega_D$ is the average phonon frequency. If $\Gamma\gg\tilde{\Omega}$ (this case corresponds to almost ideal *S*-*N* contact), then $u\approx\tilde{\Omega}$. In the opposite case where $\Gamma\ll\tilde{\Omega}$, which is also perfectly realistic, we obtain $u\approx\Gamma$ (see Ref. 7).

If we make an isotope substitution $M\rightarrow M^*$ in the isolated *S* film, one can measure the shift in T_{c0} and determine the IC α_0, which is described by the relation

$$\alpha_0=-(M/\Delta M)(\Delta T_{c0}/T_{c0}). \tag{2}$$

Here $\Delta M=M^*-M$, $\Delta T_{c0}=T^*_{c0}-T_{c0}$. The presence of the *N* film leads to a change in T_c and in the IC. One can see directly from Eqs. (1) and (2) that the relative shift in T_{c0} and the new value of the IC

$$\alpha=-(M/\Delta M)(\Delta T_c/T_c) \tag{3}$$

differ from $\Delta T_{c0}/T_{c0}$ and the value of α_0. Indeed, if the superconducting film is covered by the normal film *N*, then the value of T_c is modified by the proximity effect, and the value of the critical temperature for the whole sandwich is described by Eq. (1). Then the value of the shift ΔT_c is determined not only by ΔT_{c0}, but also by the value of the parameter ρ [see Eq. (1)], which reflects the presence of the *N* film.

Consider, for example, the case when $T_c\ll\Gamma\ll\tilde{\Omega}$. Then, $u\approx\Gamma$. The isotope substitution leads to a shift in T_{c0} (ΔT_{c0}). Based on Eq. (1), one obtains

$$\Delta T_c=(\rho+1)(\pi T_{c0}/2\gamma\Gamma)^{\rho}\Delta T_{c0}. \tag{1'}$$

Dividing both sides by T_c, and using Eqs. (1)–(3), we obtain

$$\Delta T_c/T_c=(\Delta T_{c0}/T_{c0})(1+\rho) \tag{4}$$

and, therefore,

$$\alpha=\alpha_0[1+(\nu_N L_N)/(\nu_S L_S)]. \tag{5}$$

One can see that $\alpha>\alpha_0$. Therefore, a decrease in T_c described by Eq. (1), which is a well-known feature of the proximity effect, is accompanied by an increase in the IC. It is interesting that one can modify the value of α by changing the thickness of the films. For example, if $\alpha_0=0.2$, $\nu_N/\nu_S=0.8$, and $L_N/L_S=0.5$, then $\alpha=0.28$. If we increase the thickness of the normal film, so that $L_N=L_S$, then $\alpha=0.36$. Note that the increase of the IC discussed in this section is not related to lattice dynamics; as a result, the value of α can, in principle, exceed, the value of $\alpha^{o}_{\mathrm{ph,\,max}}=0.5$.

In the opposite limit ($u\approx\tilde{\Omega};\Gamma\gg\tilde{\Omega}$) the IC is small, because both T_{c0} and Ω are affected by the isotope substitution. Since the proximity effect leads to a change in the value of the isotope coefficient, it would be interesting to perform experiments aimed at the observation of such effect.

MAGNETIC SCATTERING AND Zn SUBSTITUTION

In this section we focus on another IE which is also not related to lattice dynamics. Let us consider a superconductor which contains magnetic impurities. This case is important, because it is related to recent experiments with high-T_c oxides (see below). It is important to stress, however, that the effect we are discussing, can be observed in conventional superconductors as well.

The presence of magnetic impurities leads to decrease of the critical temperature, T_c relative to the intrinsic value T_{c0}, because of the pair-breaking effect.[9–11] Such a depression is described[9] by a well-known equation:

$$\ln(T_{c0}/T_c)=\Psi[0.5+\gamma_S]-\Psi(0.5). \tag{6}$$

Here Ψ is the digamma function, $\gamma_S=\Gamma_S/2\pi T_c$, $\Gamma_S=\tau_S^{-1}$ is the spin-flip scattering amplitude introduced in Ref. 9; $\Gamma_S=\tilde{\Gamma}_S n_m$, where n_m is the concentration of magnetic impurities and $\tilde{\Gamma}_S=\mathrm{const}$.

Based on Eqs. (2), (3), and (6) one obtains

$$\alpha=\alpha_0[1-\Psi'(0.5+\gamma_S)\gamma_S]^{-1}. \tag{7}$$

Here α is the IC in the presence of magnetic impurities. Equation (7) is valid in a broad range except a very small region near n_{cr} (then T_c is close to $T=0$ K and the condition $\Delta T_c/T_c\ll 1$ is not satisfied). Equation (7) was obtained in Ref. 10, and we will use it to analyze experimental data (see below).

The presence of magnetic impurities leads to an increase of the IC ($\alpha>\alpha_0$), since $\Psi'>0$. For small γ_S (small values of n_m) $\Delta\alpha\propto n_m$. Therefore, near T_{c0} the critical temperature displays a linear decrease, whereas the IC increases linearly as a function of n_m. In the region $\gamma_S\gg 1$ one can use an asymptotic expression for the digamma function, and we obtain $\Delta\alpha\propto n_m^2$, i.e., the dependence becomes strongly nonlinear. This picture is in very good agreement with experimental data,[1,2] see below.

Note also that $T_c\to 0$ K as n approaches n_{cr}. In the low-temperature region (at $T\cong 1$ K) one should take into account the frustration of the spin-flip scattering caused by the ordering trend of magnetic impurities.[8] As a result, the dependence α on n_m is reduced as $n\to n_{\mathrm{cr}}$.

One can study a more general case combining the proximity effect and pair breaking by magnetic impurities. This case will be described elsewhere.

Note that the effect of magnetic impurities on the value of the IC should be observed for conventional as well as for high-T_c superconductors. To the best of our knowledge, this effect has not been studied experimentally for conventional superconductors, and it would be interesting to carry out these measurements on simple monoatomic superconductors. With regard to the high T_c oxides, we think that the interesting experimental data[1–3] are directly related to the present theory.

The value of the critical temperature for the Y-Ba-Cu-O compound was modified by Zn and Pr substitutions.[1,2] For both types of substitution one can observe a decrease in T_c and an increase in the value of the IC.

Consider first the case of Zn substitution (YBaCuZnO system) which leads to a decrease in T_c. This decrease can be explained by the pair-breaking effect. Indeed, according to Ref. 12, this substitution leads to the appearance of additional magnetic moments on the Cu site in the Cu-O plane. Note that this decrease in T_c is also accompanied by a peculiar temperature dependence of the critical field H_{c2} observed in Ref. 13 (positive curvature, sharp upturn at $T\to 0$ K) and studied in Ref. 8.

The dependence on the IC on T_c is described by Eqs. (7) with $n_m=n_{Zn}$. Equation (6) was used in order to determine the values of γ_S for various T_c; in addition $\alpha_0=0.025$ (see Refs. 1–3). The theoretical curve [Fig. 1(a)] is in a good agreement with experimental data,[1,2] particularly for small and intermediate values of impurity concentration. As for the region near n_{cr} ($T_c\cong 1$ K), there is a large spread of the data and also large error bars (both in α and T_c); this is, probably, due to the sample quality, see Ref. 2. We hope that future experiments provide more reliable data for this region. It is essential to realize that the analysis described above has been carried out without any adjustable parameter.

ISOTOPE EFFECT AND NONADIABATICITY

If we are dealing with a doped superconductor such as a high-T_c cuprate and, in addition, the material is characterized by the crossing of electronic terms [Jahn-Teller (JT) nonadiabaticity], then the superconductor displays an IE.[4] One can show that the isotope substitution affects the doping, and, therefore, the carrier concentration n. Since the critical temperature of cuprates depends strongly on n, this leads to an isotopic dependence of T_c. As was shown in Ref. 4, if the charge transfer is accompanied by the transition between electronic terms (related to the dynamic Jahn-Teller effect), the process of doping depends on the Franck-Condon (FC) factor. The value of the FC factor strongly depends on the ionic mass and, therefore is affected by the isotope substitu-

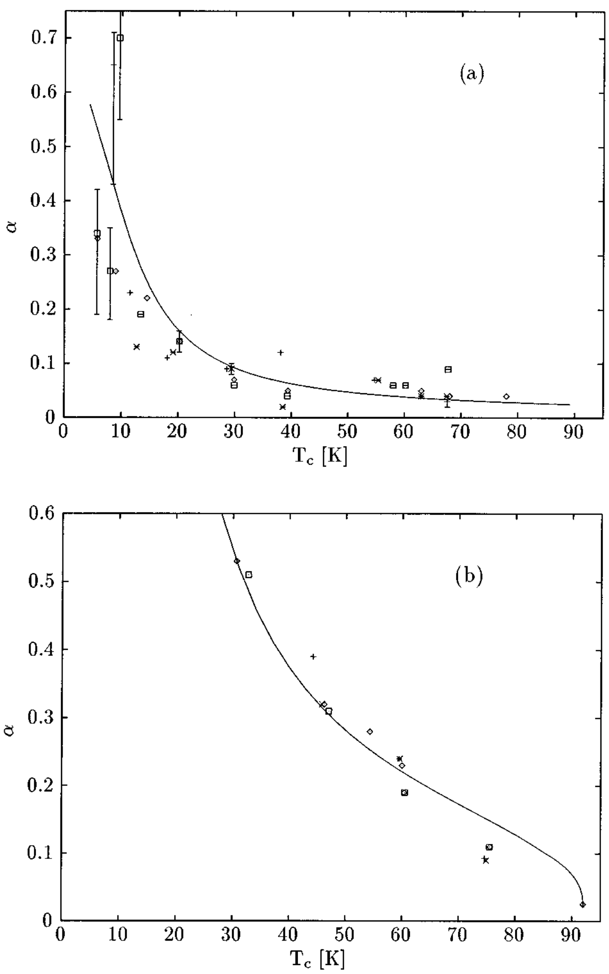

FIG. 1. Dependence of the isotope coefficient α on T_c for (a) $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ and (b) $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. Theory: solid line; experiment: ◇ and + for dc magnetization (Refs. 1 and 2), ⊡ for resistivity (Ref. 2), × for ac susceptibility (Ref. 2).

tion. This leads to the following expression[4] for the nonadiabatic IC:

$$\alpha_{na} = \gamma(n/T_c)(\partial T_c/\partial_n) \tag{8}$$

[γ is a constant, introduced in Ref. 4; do not confuse with Euler's constant, Eq. (1)]. The total IC (in the absence of magnetic impurities and the proximity effect) is a sum $\alpha_t = \alpha_{na} + \alpha_{\text{ph}}$, where α_{ph} is the conventional contribution caused by modification of the phonon spectrum. If, in addition, the sample contains magnetic impurities, the IE is described by Eq. (6) with $\alpha_0 = \alpha_t$.

DISCUSSION

In this section we discuss the experimental data.[1–3] The approach described above cannot be applied to any case, but requires special conditions. The sample should contain local magnetic moments. Another situation occurs when the charge transfer is combined with a JT instability. The presence of these factors can be established by independent experiments. It is interesting that the systems studied in Refs. 1–3 satisfy both of the aforementioned criteria.

Let us first discuss the change of the IC caused by the Pr substitution.[1,2] The Pr substitution occurs on the Y site, that is located between the CuO_2 planes. The value of T_c decreases with increasing Pr content, whereas the value of the IC increases. In fact, the effect is similar to Zn substitution; however, this case is more complicated. Indeed, as we know (see, e.g., Refs. 14 and 15), the effect of Pr on T_c is twofold. First, the presence of Pr leads to a pair-breaking effect, similar to Zn. Secondly, the mixed valence state of Pr leads to depletion of holes from the CuO_2 plane and, correspondingly, to an additional decrease in T_c. This second channel is related to the charge transfer between the CuO_2 plane and Pr and involves dynamics of the in-plane oxygen. Two facts are important regarding the charge transfer. First, note that, indeed, according to the selective study,[16] the main contribution to the oxygen isotope coefficient comes from the in-plane oxygen for $YBa_2Cu_3O_7$. Secondly, the in-plane oxygen is characterized by a Jahn-Teller instability, since the electronic states which determine its equilibrium position, are triple degenerate (see Ref. 17). Therefore, one can expect also a contribution of the nonadiabatic channel to the total oxygen IE. As a whole, the IC is described by Eq. (7), where α_0 is described by Eq. (8). Then the expression for α [see Eqs. (7) and (8) with $\alpha_0 = \alpha_t \equiv \alpha_{\text{na}} + \alpha_{\text{ph}}$, $\alpha_{\text{ph}} = 0.025$ (Ref. 3)] contains two parameters γ and $\tilde{\Gamma}_S$. One can see [Fig. 1(b)] that our calculation is in a good agreement with the experimental data[2] ($\gamma = 0.16$, $\tilde{\Gamma}_S = 123$ K).

It is well known that a decrease in T_c in the Y-Ba-Cu-O compound as well as in other cuprates, can also be provided by oxygen depletion. This process is accompanied by an increase in the IC; see Ref. 3. Oxygen depletion from the chains affects the doping of the CuO_2 planes and the carrier concentration. The charge transfer from chains to planes occurs via the apical oxygen, and this manifests itself in the nonadiabatic IE which plays a key role here (see Ref. 4). According to various experimental data (x-rays and Raman spectroscopy, transport data, see, e.g., Ref. 18 and recent ion-channeling measurements[19]), the apical oxygen position has two close minima, and this leads to the IE described by Eq. (8). The analysis carried out in Ref. 3 supports this picture [see also their Fig. 1(b)]. Note, that unlike the Pr-substitution case, this process should be sensitive to the isotope substitution of the apical oxygen, and the IC caused by its substitution should increase upon oxygen depletion and the associated decrease in T_c. The method of selective isotope measurements developed in Ref. 16, which was applied only to optimally doped Y-Ba-Cu-O, should demonstrate the growing effect of the apical oxygen contribution. It would be interesting to perform such measurements.

As can be seen on Fig. 2 calculations done with Eq. (7), where $\alpha_0 = \alpha_t$, $\alpha_{\text{ph}} = 0.025$, and α_{na} is given by Eq. (8) ($\gamma = 0.28$, $\tilde{\Gamma}_S = 123$ K) provide a good description of the experimental data (Ref. 3). Note also that the dependence $T_c(n)$ (see Ref. 3) is characterized by a jump in $\partial T_c/\partial_n$ at some value of $n = n_1$. This corresponds to the well-known 60 K plateau and leads to the peak for α at $n = n_1$. It would be interesting to perform measurements of α for the oxygen-depleted sample in the region $n \cong n_1$. Note that such peak has been observed in Ref. 20 for the La-Sr-Cu-O compound. We will describe a detailed analysis for this material elsewhere. Note also that the system studied recently in Ref. 3 differs

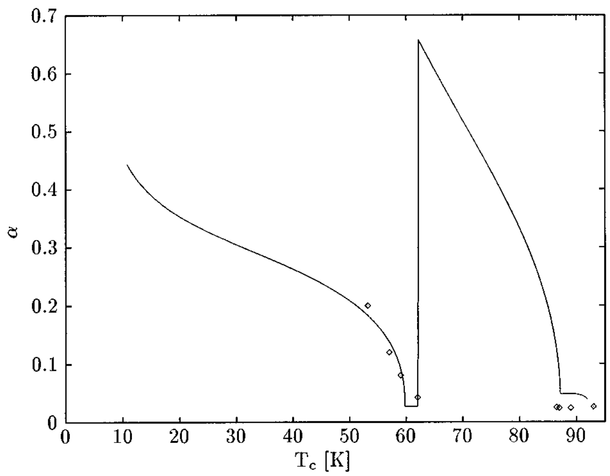

FIG. 2. The dependence α (T_c) for $YBa_2Cu_3O_{6+x}$. Theory: solid line; experiment: ◇ for dc magnetization (Ref. 3).

from those described in Ref. 21 and discussed in our paper.[4] Indeed, the YBaLaCuO compound was studied in Ref. 21, whereas direct oxygen depletion is described in Ref. 3. Such depletion is accompanied by the formation of magnetic moments (see Refs. 18,22), and this leads to a different picture.

In summary, it has been shown that the proximity effect (S-N sandwich) leads not only to depression in T_c, but to a noticeable increase in the value of the isotope coefficient. The value of α depends on the relative thicknesses of the S and N films. The presence of magnetic impurities also greatly affects the value of the IC. These effects can be observed for conventional as well as for the high-T_c superconductors. It would be interesting to carry out direct experiments aimed at the observation of these effects.

In addition, the carrier concentration, and, subsequently, T_c of doped superconductors, such as the cuprates, can be greatly affected by the isotope substitution of an ion, whose dynamics is characterized by the Jahn-Teller crossing and, therefore, by two close minima. This process also leads to an isotope effect. The calculations show that our approach provides a very good description of the experimental data presented in Refs. 1–3.

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