Doping dependence of T_c and its related isotope effect in high-temperature superconductors

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(Received 27 June 1996; revised manuscript received 26 November 1996)

A structure specific four-band model Hamiltonian is used to investigate the various doping dependences of the superconducting temperature T_c and the related isotope effect for $YBa_2Cu_3O_7$ (YBCO). The model considers explicitly multiphonon-mediated attractive electron (hole) pairing which acts intra- and interband and yields a complicated three-dimensional gap structure. The doping dependence of T_c is calculated by varying the band specific density of states, and from this the corresponding isotope effect is evaluated. Consistent agreement with experimental results is obtained and predictions with respect to site selective doping (including the isotope effect) are given. [S0163-1829(97)05217-X]

Theoretical attempts to model high-temperature superconductors[1] have mainly concentrated on the pseudo-two-dimensionality of the cuprates even though many experimental data show that there is a substantial coupling of the a,b plane to the c axis.[2–5] There are only a few attempts to construct a structure specific attractive pairing interaction which explicitly considers the coupling of the planes in the c direction.[6–8] Recently we have shown[9] that many experiments such as NMR, electromagnetic response, and angle-resolved photoemission spectrocopy results in $YBa_2Cu_3O_7$ (YBCO) can be consistently explained by using an effective Hamiltonian with a minimal set of four bands where *explicitly* attractive phonon-mediated weak-coupling BCS-type electron (hole) pairing is considered intraband *and* interband. It is important to note that four is the minimum number of bands sufficient to represent the different structural elements (in this specific case of YBCO), and also the band-structure-derived Fermi surface. The calculated Fermi surface of YBCO exhibits various interesting features:[10,11] (i) There is not only the extended plane-related van Hove singularity (vHs), but there are also vHs' related to the chains and, interestingly, the apex oxygen ion O(4); (ii) There are large areas on the Fermi surface where bands are strongly hybridized (especially p-d), not only in the plane, but also out of the plane; (iii) There exist various points in k space, where bands cross or are sufficiently close to admit phonon-mediated interband interactions; (iv) The Fermi surface is extremely anisotropic in all directions and inconsistent with a tetragonal symmetry, which would be required for a pure d-wave order parameter.

The four bands considered in the present approach are related to (i) the CuO_2 planes, (ii) the plane-plane coupling through Y, (iii) the apex oxygen, (iv) the CuO chains in YBCO. The gap structures derived from these bands yield a specific energy dependence where (i) and (ii) have a large k-space weight at high energies, while the O(4)-related gap shows up at energies between 0 and 40 cm^{-1} only, and the chains cover the intermediate regime between 100 and 200 cm^{-1}. Each of the four structures considered above plays a distinct role and cannot be neglected if comparison with experimental data is to be made.[12] Thus, the high-energy contributions from (i) and (ii) (between 300 and 340 cm^{-1}) clearly gives rise to the high T_c's. The gap structure from the apex oxygen is crucial for the electromagnetic response and NMR as it only, but substantially, contributes at very small energies and simulates effects which have been interpreted as evidence for d-wave pairing. The chains, even though they yield a rather featureless contribution, are also important in experiments probing low energies, as they do not contribute to the energy region below 100 cm^{-1} and give rise to a gap in the energy distribution of the total gap structure. This gap is not present in a simple d-wave approach but is necessary to achieve quantitative agreement with experimental data. In the following we continue on the basis of this four-band model and calculate the doping dependence of T_c and the corresponding isotope effect.

The already condensed Hamiltonian at an extended BCS level reads

$$H=\sum_{k,i=1}^{4}\epsilon_{ki}c_{ki}^{+}c_{ki}+\text{H.c.}-\sum_{\substack{i=1\\k',k}}^{4}V_{ii}(k,k')c_{ki}^{+}c_{-ki}^{+}c_{-k'i}c_{k'i}$$
$$-\sum_{\substack{i\neq j\\i,j=1,k'k}}^{4}V_{ij}(k,k')(c_{ki}^{+}c_{-ki}^{+}c_{-k'j}c_{k'j}$$
$$+c_{kj}^{+}c_{-kj}^{+}c_{-k'i}c_{k'i}), \tag{1}$$

where ϵ_{ki} are the band energies of band i with appropriate dispersions, V_{ii} are intraband attractive phonon-mediated interactions, and V_{ij} are the corresponding interband interactions which involve multiphonon contributions and substantially enhance the interband hopping. Both terms, V_{ii} as well as V_{ij}, contain already the screened Coulomb repulsion in an analogous way as in the weak-coupling BCS approach. This

already yields a neglect of electronic correlations, but as all high-temperature superconductor compounds are ''bad'' metals and close to an insulating state, we assume that these effects are not large. As will be shown below, this assumption is also substantiated by the magnitude of the effective dimensionless electron-phonon-couplings which are all smaller than 0.5. The coupled gap structure is derived in the usual manner and reads[9,13]

$$\Delta_i^*[1-V_{ii}N_i(0)F_i]=\sum V_{ij}N_j(0)F_j\Delta_j^*$$

with

$$\Delta_i^*=\Delta_i+\sum_{i\neq j} V_{ii}/V_{ij}\Delta_j$$

and

$$F_i=\int_0^{\omega_i}\frac{1}{E_i}\tanh\frac{E_i}{2kT}d\epsilon, \quad E_i=(\epsilon_i^2+\Delta_i^*)^{1/2}. \tag{2}$$

For simplicity we have omitted the indices due to the k dependence, and $N_i(0)$ corresponds to the density of states in band i at the Fermi level. The gap structure, as derived from Eq. (2) has a highly anisotropic k-space dependence, as has already been discussed in Ref. 9, and thus demands an extension of the BCS ground-state wave function, which corresponds to the special case of zero momentum pairing. This extension can easily be carried out by constructing a ground-state wave function analogous to the BCS ground-state wave function, which explicitly contains the momentum dependence. As has been shown previously, this new ground-state wave function mimimizes the free energy in the same way as the BCS wave function and, in addition, a substantial increase in the available phase space for pairs is obtained. The integrations in Eq. (2) are performed with respect to the frequencies: $\omega_1 = 350\ \mathrm{cm}^{-1}$, $\omega_2 = 210\ \mathrm{cm}^{-1}$, $\omega_3 = 155\ \mathrm{cm}^{-1}$, $\omega_4 = 260\ \mathrm{cm}^{-1}$. These frequencies correspond to lattice modes where large amplitudes in the eigenvectors of the corresponding structural elements are observed, and phonon softening/hardening occurs with the onset of superconductivity.[14] This choice is not unique, but this does not affect the results below. The interaction potentials have been calculated according to the scheme introduced in Ref. 15, where the phonon width γ_q is related to the dimensionless effective electron-phonon interaction λ via

$$\sum_q \frac{\gamma_{qi}}{\omega_q^2}=\frac{1}{4}\pi N(0)\lambda. \tag{3}$$

Inserting in Eq. (9) the densities of states at E_F, as derived from band-structure calculations,[11] the diagonal and off-diagonal $\lambda_{ii},\lambda_{ij}$ are obtained. In accordance with experiment[14] we find that γ_{qi} is largest for the highest frequency mode and decreases with decreasing phonon energy. The choice of our γ_{qi} is such as to fit a value of T_c of 94.1 K. Even though we used here γ_{qi} as parameters, their values correspond very well to the experimental data[14] and to values derived from band-structure calculations. As the off-diagonal interaction potentials include the multiphonon contributions, it is at present theoretically impossible to calculate them. In this case we assumed for simplicity that all λ_{ij} [as defined in Eq. (3)] are 0.45, which yields four additional damping constants γ_{qij}. As expected, these are all very small, but as will be shown elsewhere, crucially influence the phonon mode frequencies and dampings if doping and temperature effects are considered. The diagonal and off-diagonal $\gamma_{qii},\gamma_{qij}$, as well as the densitites of states, which have been taken from band-structure calculations,[11] are given in Table I. The corresponding diagonal λ_{ii} can be calculated with the aid of Eq. (3) and are $\lambda_{11}=0.44$, $\lambda_{22}=0.29$, $\lambda_{33}=0.23$, $\lambda_{44}=0.21$, respectively. All diagonal λ_{ii} are rather small, i.e., are in the weak-coupling limit which justifies the extended BCS approach and also the neglect of electronic correlation effects. T_c is given by the usual condition that the Δ_i^* are zero which corresponds to F_i becoming $F_c=\int_0^{\hbar\omega_i}(1/\epsilon)\tanh(\epsilon/2kT_c)d\epsilon$, where in our case a 4×4 determinant equation has to be solved self-consistently.

TABLE I. Top row: Density of states for the four bands in the same sequence as (in electrons/eV cell spin) introduced in the text. Following rows: The γ_{qi} matrix (all values in cm^{-1}).

0.85	0.45	0.62	0.62
24	0.69	1.36	0.98
3.8	4.82	1.36	0.98
3.8	0.69	1.3	0.98
3.8	0.69	1.36	4.58

Doping-dependent effects are now considered to affect the individual densities of states, only, while linewidth and phonon frequencies are assumed to be unaffected, i.e., constant. Experimentally, it is known, e.g., that Zn doping replaces the Cu ions in the planes. Thus, the plane-related density of states is varied first, then the interplane density of states, followed by the chains and finally the O(4). Fe doping can have two different effects, depending on sample preparation, as it might either replace the chain Cu ions first, or the Cu ions in the planes. Thus, Fe doping might yield two different T_c dependences which has also been found experimentally.[16–20] The isotope effect has been calculated by varying the four cutoff frequencies only. The total isotope effect is then obtained by averaging the separately obtained isotope-dependent changes in T_c with respect to the specific phonon frequencies. As soon as the individual density of states is reduced, the corresponding isotope effect also decreases. Opposed to this decrease is the isotope effect originating from the other bands, which achieves the BCS value if only one band contributes to the pairing. The present approach thus enables us to calculate the site-selective isotope effect which has recently been investigated experimentally.[21] As has been outlined above, only the densities of states are varied. Through this variation also the diagonal and off-diagonal dimensionless electron-phonon-couplings are varied, as is obvious from Eq. (3). The γ_{qi} and ω_q are assumed to be constant, i.e., independent of doping and given by the values of Table I. This assumption is not fully correct as slight changes in the ω_q are observed upon doping, but clearly this effect is small.

First, we study the doping dependence of T_c for $YBa_2Cu_3O_{7-\delta}$ as a function of δ. We start from the assump-

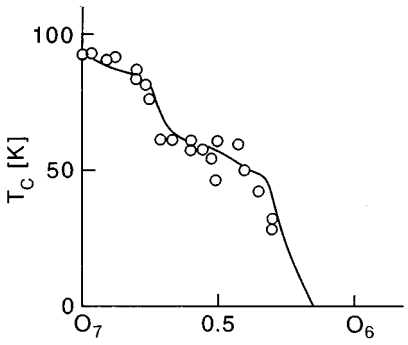

FIG. 1. Doping dependence of T_c for $YBa_2Cu_3O_{7-\delta}$ as a function of δ. Open circles refer to experimental data, (Ref. 22) straight line corresponds to numerical results.

tion that holes are primarily moved from the chains. Then the plane-related density of states is affected but only up to a critical value of hole reduction by 0.125 holes from the value 0.85 given in Table I, which yields the 60-K plateau observed experimentally[22] (Fig. 1). Note that the 60-K plateau results from a nearly commensurate hole reduction of 1 hole/8 unit cells from the fully doped system. Thus, it could be speculated that a charge ordered state is responsible for the occurrence of the plateau.

The interplanar density of states followed by the O(4)-related one are then reduced, and finally, the planes are again affected. As can be seen from Fig. 1, good agreement is obtained between experiment and theory.

The corrresponding isotope effect is shown in Fig. 2, again compared with experimental data.[22] In addition, we insert the site-selective isotope effect (dashed lines) related to the apex oxygen ion and the planes. First it should be noted that from the present investigation the isotope effect reaches the BCS value of $\alpha = 1/2$ at $T_c = 47$ K. This is due to the fact that only the plane gap persists above this T_c. For $T_c < 47$ K it remains constant.

At $T_c = 94$ K the site-selective isotope effect is $\approx 6\times$ larger for the planes than for the O(4). With decreasing T_c both components increase until $T_c = 63$ K below which the O(4)-related isotope effect monotonically approaches zero, while the plane-related isotope effect increases to the BCS value ($\alpha = 1/2$). Our findings concerning the site-selective

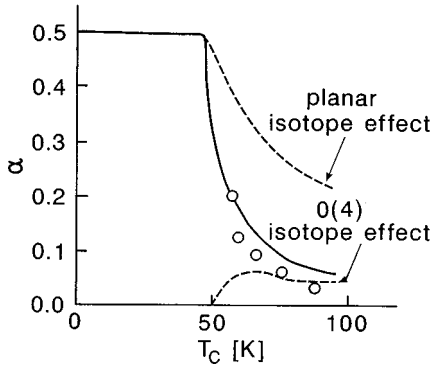

FIG. 2. Comparison of calculated (full line) full isotope effect with experimental data[22] (open circles). Dashed lines show the calculated site selective isotope effect.

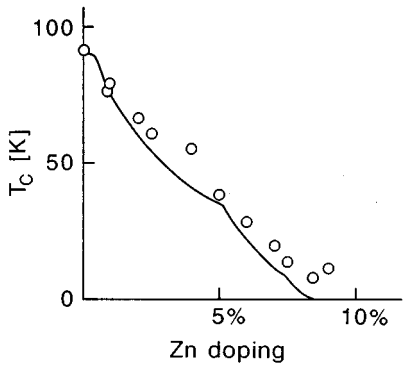

FIG. 3. Comparison of calculated doping dependence of T_c (full line) to experimental data[20] (open dots) for $YBa_2(Cu_{1-x}Zn_x)_3O_7$.

isotope effect is in good qualitative agreement with experimental data.[21]

Zn doping of YBCO is known to primarily replace the Cu ions in the plane. In order to calculate this T_c dependence we first reduced the plane-related density of states followed by the chains, the interplanar, and finally the O(4) densities. The results are shown in Fig. 3 in comparison with experimental data. When our phase diagram is scaled to the experiment, 10% Zn doping obviously has the effect of removing one oxygen atom from the unit cell. The isotope effect of this system is shown in Fig. 4 again compared with experiment. Due to the strong effect of Zn on the plane-related density of states, α remains less than 0.1 until $T_c \approx 40$ K below which it smoothly increases.

Finally, we have investigated three model systems: For the first we started from the assumption that doping affects all densities of states proportionally the same (Fig. 5, straight line). In this case T_c drops nearly linearly to zero with increased doping. The isotope effect (Fig. 6, straight line) does not exceed 0.1 even in the limit $T_c \to 0$ as contributions from all gaps are always present.

The second model considers doping of the chains first, followed by the interplane, the plane, and finally the O(4)-related densities of states. This case applies to Fe doping in the chains, but there is not sufficient data available for direct comparison. This model system exhibits rather high T_c's up to $\approx$ 63% doping followed by a rapid drop in T_c (Fig. 5, dashed line). The corresponding isotope effect (Fig. 6, dashed line) rather rapidly increases to a maximum of $\alpha \approx$

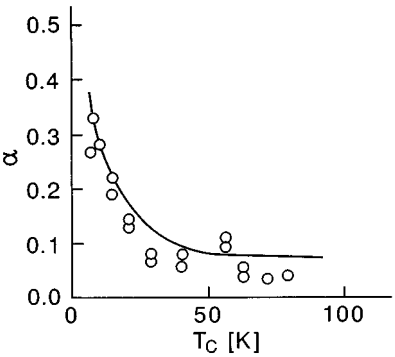

FIG. 4. Isotope effect related to Fig. 3. Full line corresponds to theoretical results, open dots refer to experimental data.[20]

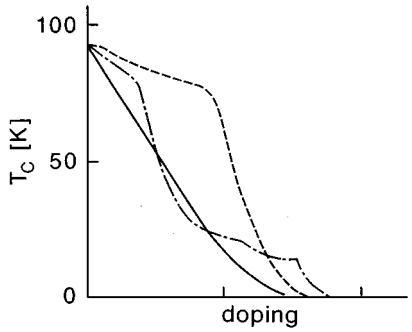

FIG. 5. Calculated doping dependence of T_c for three different model systems, as explained in text.

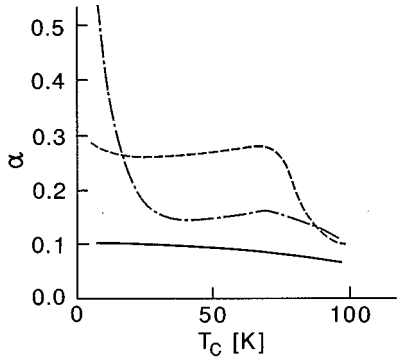

FIG. 6. Calculated isotope effect related to Fig. 5 (see text).

0.38, then decreases slightly and increases again to the same value for small T_c's. Finally, we started by doping the O(4) site, followed by the planes, the interplane, and lastly, the chain-related N_i's (Fig. 5, dashed-dotted line). T_c initially drops smoothly, then experiences a rapid decrease, which always occurs when the plane density of states is reduced, and falls off smoothly again upon further doping. Note that in all cases, including the two where comparison to experiment is made, cusplike dependences of T_c are observed. These are due to the fact that when the individual densities of state are sufficiently small, a further reduction of them does not induce much change in T_c, while reducing high densities of state by the same amount yields much larger decreases in T_c. This feature is of course not present in the first model system above. The isotope effect arising from the last model is shown in Fig. 6 (dashed-dotted line). It increases smoothly with decreasing T_c, to exhibit a maximum value of $\alpha = 0.11$ at $T_c = 70$ K, drops slightly with decreasing T_c and finally α rapidly increases to the BCS value of 0.5 at low T_c's.

The above results are derived for optimally und underdoped systems. Overdoped systems which seem to have a small positive isotope effect will be discussed elsewhere. The present approach does not extend to $\alpha > 0.5$ as the anharmonic phonon-phonon interaction has been treated here on a mean-field level. It has been shown by Crespi and Cohen,[23] and Kresin and Wolf[24] that highly anharmonic systems may easily exceed the BCS value of 0.5.

The above model is conducive to similar ideas where also the variation in density of states near the Fermi energy is considered to be related to the isotope effect[25–28] as we not only concentrate on the large density of states at the vHs in the CuO_2 planes, but also explicitly include other structural elements. Due to this procedure the isotope effect is substantially different for the same T_c's in different systems. A serious limitation of the present model is certainly that the Coulomb repulsion is only effectively included in the pairing interactions V_{ii}, V_{ij}, and electronic correlations are neglected. Yet from the values of $\lambda_{ii}, \lambda_{ij}$ which yield the optimum T_c of 94 K, this weak-coupling approach seems to be justified. It should be noted that the rather small values of the electron-phonon interactions result from the fact that we start from a multiband model where the contribution from each band (with its proper k-space weight) acts to increase T_c through the interband interaction. These findings have also been emphasized previously[25] from the study of a two-band model. The inclusion of Coulomb correlations on our model will be given elsewhere and has already, in a different context, been studied in detail by Kim and Tesanovic.[29]

In conclusion, we have presented results on the doping dependence of T_c and the related isotope effect starting from a four-band model Hamiltonian with attractive phonon-mediated pairing interactions. The individual densities of states attributed to the four bands have been varied in order to simulate site-selective doping. We find that the 60-K plateau observed in $YBCO_{7-\delta}$ is due to a critical doping of 0.125 holes/CuO_2 unit hole concentration. The agreement with experiment is good, and the same holds for the corresponding isotope effect, the total one as well as the site-selective isotope effect. Zn doping is consistently described if first the CuO_2 plane-related density of states is reduced followed by changes in the chains and then the two other structural elements. The corresponding isotope effect is again in good agreement with experimental data but differs distinctly from the previous case. The three model systems we investigated are intended to stimulate experimental work on high-T_c materials, as specific site-selective doping can be correlated with a specific dependence of α on T_c. We have shown that α may vary substantially for the same T_c's if doping affects structural elements differently.

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