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# NUMERICAL SIMULATION OF THE ISOTOPE EFFECT IN THE HIGH-$T_c$ SUPERCONDUCTORS

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## I. INTRODUCTION

The recently synthesized cuprate oxide superconductors having transition temperatures $T_c$ up to 114K [1,2,3] are very interesting research objects both from theoretical and experimental aspects. A major attention herein has been paid to the mechanism(s) of the formation of the superconducting state, in particular, whether it is mediated by phonons or not. It is well known that within the BCS theory the phonon mechanism is supported by the experimental observation of the effect of isotope substitution on the transition temperature $T_c$. The mass dependence of $T_c$ is expressed through $T_c \sim M^{-\alpha}$, where M is the isotopic mass and $\alpha$ is usually around 0.5. Thus, in the light of the new high-$T_c$ superconductors the isotope effect becomes an important issue with respect to testing any theory intending to explain such high $T_c$'s.

Recently, an oxygen isotope effect in both the LaSrCuO and YBaCuO systems has been observed [4,5]. Although the observed shifts in $T_c$ were smaller than one would expect from the BCS theory,( 0.3-1)K for LaSrCuO and (0.3-0.5)K for YBaCuO, they nevertheless indicate that phonons are yet involved in superconductivity.

Structural studies of the high-$T_c$ cuprate oxides have led to the identification of $La_{2-x}Ba_xCuO_4$ as an analogy of $K_2NiF_4$ [7] and $YBa_2Cu_3O_{7-x}$ to be a previously unknown oxygen-deficient perovskite [8].Evidence of structural instabilities and the existence of soft modes in LaSrCuO system have been reported [9-12]. The study of the phonon behaviour of $YBa_2Cu_3O_7$ by neutron inelastic scattering show larger phonon density states in lower frequency modes rather than in high frequency ones [8]. Another interesting feature, namely a possible softening of the high frequency breathing mode was observed [14] in $YBa_2Cu_3O_7$.Thus, these two types of the oxygen vibration,e.g., the high frequency in-plane bond-stretching mode and the low frequency out-of-plane one, the so-called bond-bending mode are of interest within the conventional electron-phonon mechanism. As superconductivity is observed in ceramic and crystalline states, it is practical to apply the cluster approximation method in the theoretical consideration of superconductivity in these compounds. On the

other hand taking into account the sufficient difference in the masses of oxygen and copper, one can make use of a quasi-local mode describing the vibration of the oxygen ion, only. Calculations of the electronic structure[13] demonstrate overlapping of the 3d states of copper with the 2p states of oxygen resulting in strong coovalency which in its turn might cause a strong anharmonicity for the oxygen vibration. Therefore, by considering the electron-phonon interaction in the new high-$T_c$ compounds it is important to take into account the effect of anharmonicity.

## II. MODEL OF THE ANHARMONIC QUASI-LOCAL MODE

We suggest for the vibration of the oxygen ions a double-well anharmonic model potential

$$U(x) = -Ax^2/2 + Bx^4 + A^2/4B, \qquad (1)$$

where A and B are positive and related through

$$U_o = A^2/4B \quad \text{and} \quad x_o = (A/B)^{1/2}$$

to real physical quantities, the central barrier height and it's average width, respectively, thus $2x_o$ being the distance between the two minima of the potential. Units are used where $\hbar = k_B = 1$.

As a matter of fact, several authors[6,15,16] have been using the "Gaussian barrier" type double-well potential function, superposed of a Gaussian and a harmonic oscillator potential function. Although this construction merits attention from a perturbative theoretical point of view, for a good approximation to it the knowledge of three independent properties is required, whereas for the potential (1) only one free parameter

$$\beta = \omega_o / 4U_o , \qquad (2)$$

where $\omega_o = \sqrt{\frac{2A}{m}}$ is a characteristic frequency, and m, the reduced mass of the Cu-O-Cu cluster, thus a complete substitution of $O^{16}$ by $O^{18}$ in the cluster is simulated through decreasing $\beta$ by 5%. In this respect, it is rather advantageous to work with the potential function (1).

On the other hand (1) is more physical and has been used to describe vibrational effects. Here, we recall the work [17] explaining the infrared spectra of H-bonded solids. Moreover it should be pointed out that this potential was used to describe



structural phase transitions of order-disorder or displacive types[36]. Indeed, if the central barrier height $U_o \gg T_c$ a transition due to ordering takes place, whereas if $U_o \ll T_c$ a displacement of atoms between the two minima occurs. This fact and the observation of structural instabilities and soft modes in the cuprate oxides provide a reasonable background for applying this potential to the new superconducting materials.

By introducing the dimensionless coordinate and energy

$$\xi = x/x_o \quad \text{and} \quad E_n = E'_n / U_o \qquad (3)$$

the Schrödinger equation

$$-(1/2m)\, d^2\varphi(x)/dx^2 + U(x)\varphi(x) = E'_n \varphi(x) \qquad (4)$$

is converted into the following form

$$-d^2\varphi(\xi)/d\xi^2 + 1/\beta^2 [(1-\xi^2)^2 - E_n]\varphi(\xi) = 0 , \qquad (5)$$

which was numerically solved for a broad set of the dimensionless parameter $\beta$, yielding the energy spectrum $E_n$ of the anharmonic oscillator. For the sake of certainty of the results we carried out the calculations by two different methods:

(i) A finite difference approach substituting the differential operator by a series of the central difference operator up to the sixth power, thus transforming the Schrödinger equation into an algebraic eigenvalue problem [18,19];

(ii) Direct numerical integration and shooting method[20,21].

The sufficient reproducibility of the results was demonstrated by the coincidence of the eigenvalues to the 8th figure. The anharmonic eigenfunctions $\varphi_n(x)$ are expanded in terms of the eigenfunctions $u_j(x)$ of the harmonic oscillator

$$\varphi_n(x) = \sum_{j=0}^{N_{max}} a_j u_j(x) , \qquad (6)$$

where $N_{max}$ is fixed by the condition that $\sum_{j=0}^{N_{max}} a_j^2$ be unity within a given accuracy. A study on the convergence accuracy of (6) indicates that it improves from 0.25% to better than 0.0001% when the number of the expansion coefficients is increased from 40 to 100. This demonstrates the strong effect of the anharmonicity on the eigenfunctions and difficulties related to a perturbative treatment of the problem.

In FIG.1 the vibrational frequencies $\varepsilon_{ij}$ given by

$$\Omega_{ij} = \varepsilon_{ij} U_o = (E_j - E_i) U_o \qquad (7)$$

are plotted vs. $\beta$.For large heights of the central barrier, e.g. for small $\beta$'s the transitions are due to tunnelling. Comparing our results with those obtained within the WKB approximation (dashed line in FIG.1)[22] we found a good agreement for $\varepsilon_{01}$ up to the value $\beta$=0.1195 while for higher levels a significant deviation is observed as well as for $\varepsilon_{01}$ at larger $\beta$'s. The vibrational frequency tends to saturate with increasing $\beta$ (smaller $U_o$), which means the oscillator seems not to feel the anharmonicity.

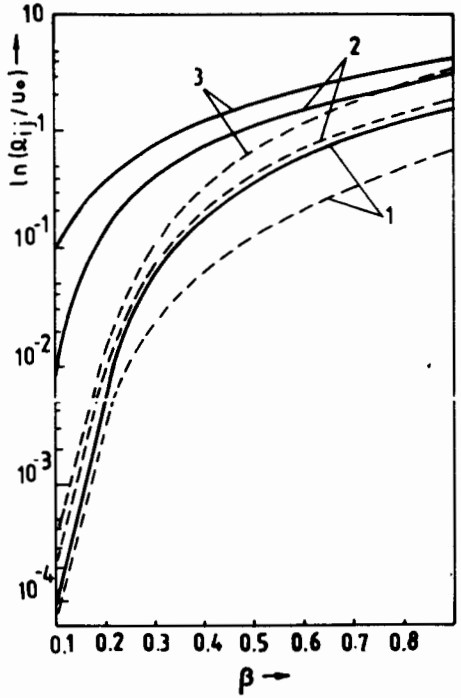


**FIG.1. Vibrational frequencies (transitions) vs. $\beta$ - the dimensionless quantum parameter.**
**1- $\varepsilon_{0,1}=\Omega_{0,1}/U_o$ , 2- $\varepsilon_{2,3}=\Omega_{2,3}/U_o$, 3- $\varepsilon_{4,5}=\Omega_{4,5}/U_o$**
**solid lines- numerical, dashed lines- WKB**

This behaviour of the energy spectrum is illustrated in FIG.2 in terms of

$$\Delta_{i+1,j+1}/\varepsilon_{ij}\,.$$



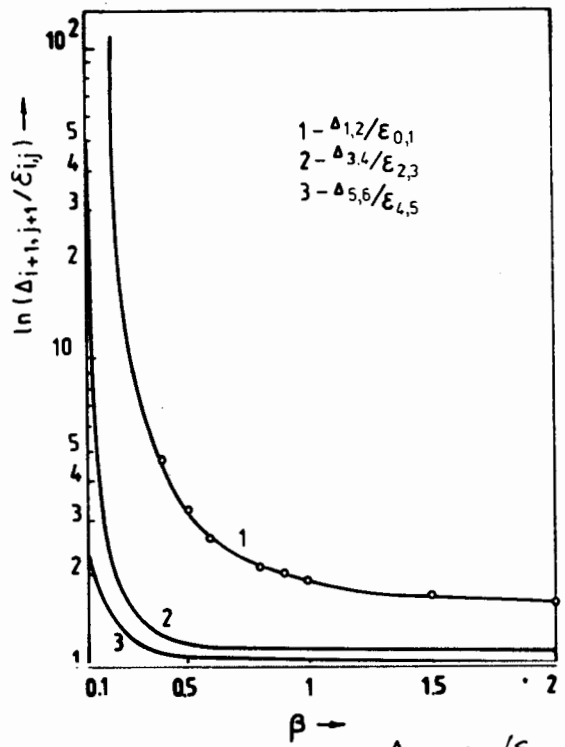


Fig.2. Dependence of the ratio $\Delta_{i+1,j+1}/\varepsilon_{i,j}$ on $\beta$ .

Here is

$$\Delta_{i+1,j+1}=E_{j+1}-E_{i+1}\,. \qquad (8)$$

There, one can see two features of the above ratio,demonstrating for higher levels weak and for lower ones strong anharmonicity.This feature is also observed in the dependence of the mean square amplitude of vibration (Table 1) on the anharmonicity. For the mean square amplitude of vibration calculated by

$$Q^2=\langle 0|\xi^2|1\rangle\,, \qquad (9)$$

we found that while for larger $\beta$ it steadily increases with temperature, for lower values of $\beta$ an oscillating behaviour is observed.

Table 1. The mean-square amplitude of vibration (dimensionless) for different values of $\beta$. Underneath the corresponding eigenvalues $E_n$ (dimensionless) are given. n is the order number of the energy levels.

| $\beta$ \ n | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| .125 | .951 | .932 | .753 | .785 | .452 | .718 | .717 | .815 | .897 |
| En | .242 | .243 | .681 | .689 | .985 | 1.09 | 1.30 | 1.53 | 1.77 |
| .42 | .650 | .922 | .801 | 1.08 | 1.24 | 1.38 | 1.54 | 1.65 | 1.79 |
| En | .631 | .842 | 1.79 | 2.71 | 3.84 | 5.12 | 6.51 | 8.00 | 9.57 |
| .6 | .594 | 1.01 | 1.04 | 1.31 | 1.53 | 1.69 | 1.89 | 2.04 | 2.27 |
| En | .777 | 1.33 | 2.82 | 4.48 | 6.41 | 8.58 | 10.88 | 13.37 | 15.99 |
| .84 | .597 | 1.13 | 1.29 | 1.59 | 1.68 | 2.07 | 2.32 | 2.51 | 2.73 |
| En | .982 | 2.12 | 4.51 | 7.26 | 10.41 | 13.89 | 17.64 | 21.64 | 25.85 |

## III. EFFECT OF ANHARMONICITY ON ELECTRON-PHONON INTERACTION

In this section we apply the numerical results to calculate the transition temperature $T_c$ and the isotopic shift $\delta T_c$ of the high-Tc superconductors within a conventional phonon mediated mechanism for the attractive electron-electron interaction. In fact, it was shown [23] that transition temperatures up to 40K can be explained within the phonon mechanism. Moreover, values of Tc as high as 90K are possible [24] provided one gets for the electron-phonon coupling values around 2. However, the pure phonon mechanism in the harmonic approximation fails to explain the experimentally observed 90K in the YBaCuO compound [24].

Our starting point to study the anharmonic effect on the electron-phonon interaction is the anharmonic model of high-Tc superconductors proposed in [25]. In this paper, within a two-level approximation by applying the two-time Green function technique the Eliashberg equation and the following relation for the coupling constant $\lambda_s$ were obtained

$$\lambda_S = N(\omega) \langle J_s^2 \rangle \chi_S , \qquad (10)$$

where $N(\omega)$, $J_s$ and $\chi_s$ denote the density of states at Fermi level $E_F$, the deformation potential and the static susceptibility of the lattice, respectively. The latter is described in a two-level approximation by

$$\chi_S = \frac{2x_o^2 \xi_{o1}^2}{\Omega_{o1}} \operatorname{th}(\Omega_{o1}/2T) , \qquad (11)$$



where $x_{o1}=x_o\xi_{o1}$ is the matrix element of the dipole moment between the states $\varphi_o$ and $\varphi_1$. Expression (11) can be derived from the spectral representation

$$\chi_s = Z^{-1} \sum_{n,m} e^{-T^{-1}E_n} \frac{1 - e^{-T^{-1}(E_m - E_n)}}{(E_m - E_n)/U_o - \omega/U_o} \langle m|\xi|n\rangle^2 , \qquad (12)$$

where $Z=\sum e^{-E_n/T}$, in the static limit $\omega = 0$ by considering the two lowest levels, only [39]. Thus, in accordance with the energetic criterion for the application of the two-level model given in FIG.2 we consider the case $\beta<0.9$, because namely in that region the two lowest levels are separated from the higher levels by a large energy gap relative to the energy difference $(E_1-E_o)$. The lower limit of $\beta$ can be estimated by the relation (7). We reckon the frequency $\Omega_{o1}$, in the case of the soft bond bending mode at range 10-30meV [34,35]. Then, for values of $\beta\sim0.2$ $U_o$ becomes very large (~1000 meV) which is unphysical. In contrast with it in the region $\beta=0.4\div0.8$ $U_o$ takes values between 10-150meV, thus values of $\beta$ in this range can be considered as physically meaningful.

The transition temperature has been calculated by the general relation

$$T_c = \Omega_{o1} f(\lambda_s, \mu^*) , \qquad (13)$$

where $\Omega_{o1}$ is the frequency of the phonon mode under consideration, $f(\lambda_s,\mu^*)$ expresses the dependence of Tc on the coupling constant and the Coulomb pseudopotential and is given for the weak and strong coupling cases by the McMillan [26] and the Allan-Dynes [27] formulas, respectively.

$$f(\lambda_s, \mu^*) = 0{,}83 \exp(-1{,}04(1+\lambda_s)/g) \qquad \text{for } \lambda_s < 1 , \qquad (14)$$

$$f(\lambda_s, \mu^*) = 0{,}83\left(1 + (\lambda_s/\Lambda_1)^{3/2}\right)^{1/3} \exp(-1{,}04(1+\lambda_s)/g) \qquad \text{for } \lambda_s > 1 , \qquad (15)$$

where $\Lambda_1 = 2{,}46(1+3{,}8\mu^*)$ , $g = (\lambda_s - \mu^* - 0{,}62\lambda_s\mu^*)/1{,}04$ .

Differentiating (13) with respect to the isotopic mass one obtains the following relation for the relative shift in $T_c$

$$\delta T_c = dT_c/T_c = -\alpha\, dm/m , \qquad (16)$$

where

$$\alpha = 0{,}5\left(1 + \frac{\beta}{\varepsilon}\frac{d\varepsilon}{d\beta}\right)\left(1 - \frac{\lambda}{f}\frac{df}{d\lambda} - \frac{\mu^{*2}}{f}\frac{df}{d\mu^*}\right) . \qquad (17)$$

The isotope effect thus depends on $\lambda_s$ and $\mu^*$ through the second term while the first term gives the effect of the anharmonicity on

the value of $\alpha$. The modification of the frequency $\Delta\varepsilon_i$ due to the variation $\Delta\beta$ is plotted in FIG.3 showing a saturation for the weak and almost vanishing for the strongly anharmonic case.

To calculate the coupling constant we estimate $x_o$, No and $J_s^2$ in following ranges [28-30]:

$x_o = (0.1 \div 0.3)\text{Å}$ ,

$N(o) = (1 \div 3)$ states/eV,

$J_s^2 = (0.5 \div 1)(\text{eV}/\text{Å})^2$.

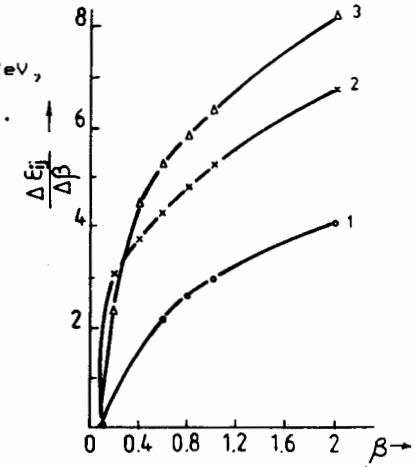


**FIG.3. The change of the vibrational frequency due to variation of $\beta$.** 1- $\varepsilon_{0,1}$; 2- $\varepsilon_{2,3}$; 3- $\varepsilon_{4,5}$;

As for $\Omega_{01}$ the choice of the mode at present cannot take place unambiguously. Actually the high-frequency bond-stretching mode has so far been considered by many authors [31,23,24], to be responsible for high $T_c$'s. Nevertheless, bond-bending-type interactions are able to produce large coupling constants because of the high polarizability [24,30]. This idea has been backed up by the observation of unusual large Debye-Waller factors in $YBa_2Cu_3O_7$ [28,32]. By an appropriate combination of the structural and electronic data it is possible to obtain transition temperatures in the region of 90K, even for the soft bond-bending mode, the frequency of which is assumed to be in the range 10-30 meV [23,24,35] within the anharmonic model. Concerning the isotope effect we state that it is much more complicated than in the harmonic limit. As is shown in FIG.4 even an inverse isotope effect is possible for $T_c$<33K, while in the narrow region 34-35K a



nearly zero or heavily suppressed one is observed. At $T_c$ slightly above 36K $\alpha$ lies in the range 0.1-0.2, depending on $\beta$; thus, it is in agreement with experimental observation for the LaSrCuO system. However, for higher $T_c$ we found normal isotope effect with a trend of $\alpha$ to increase with temperature and then to saturate at 0.3-0.4, which is in contradiction with the up-to-date observed trend of $\alpha$ to decrease [34].

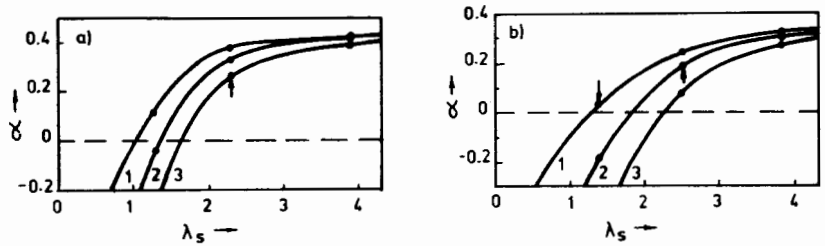


**FIG.4. The dependence of the constant of the isotope effect $\alpha$ on the electron-phonon coupling.** a) $\beta$=0.84; b) $\beta$=0.4 ; 1- $\mu^*$=0; 2- $\mu^*$=0.1; 3- $\mu^*$=0.2; The arrows -values of $\alpha$ at $T_c$=36K.

We conclude from our numerical calculation that in the anharmonic model the phonon mechanism permits one to obtain an agreement with the experimentally observed isotope effect in the LaSrCuO system ( $\alpha \sim$ 0.1-0.2 ) whereas it is not the case for the YBaCuO system. This may be an indication that higher energy levels have to be taken into account, the more so as we have found an oscillating behaviour of the mean square amplitude of vibration (Table 1), otherwise a nonphonon mechanism should be considered. It is interesting to note that there is a qualitative agreement between our numerical calculations and the estimation of the isotope effect with the "Gaussian barrier" type potential [33]. Our main conclusion is that the two-level approximation is applicable in that region of $\beta$ where the energy spectrum of the anharmonic oscillator has the feature that $E_o$ is under the central barrier while the next level $E_1$ is above it confirming the suggestion for the applicability of a two-level model [38]. This is consistent with the behaviour of the static susceptibility $\chi$. We studied the convergence of (12) taking into account up to four levels. As one

can see from Table 2. it is convergent,thus the application of the two-level approximation is justified. A more detailed study of the tunneling effect in a double-well potential e.g., region with small $\beta$ was reported elsewhere [37].

Table 2.The static susceptibility $\chi$ (dimensionless) calculated by taking into account 2,3 and 4 levels,respectively for three different values of $\beta$ at T=92K.

| $\beta$ | $\chi_s$ | | |
|---|---|---|---|
| | n=2 | n=3 | n=4 |
| .2 | 262.191 | 262.199 | 262.208 |
| .5 | 3.236 | 3.249 | 3.251 |
| 1.0 | .711 | .719 | .720 |

Finally, we would like to express our gratitude to Dr.N.M.Plakida for pointing out the problem and helpful discussions and Prof.M.G.Meshcheryakov for supporting the work.

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Галбаатар Т., Ракаускас Р-И., Шулскус Ю.К.
E17-88-382

Численное моделирование изотопического эффекта в высокотемпературных сверхпроводниках

Представлены результаты моделирования кислородного изотопического эффекта в высокотемпературных сверхпроводниках, полученные численным решением уравнения Шредингера для квазилокальной моды движения атомов $O^{16}$, $O^{18}$ с потенциалом вида $Ax^2/2 + Bx^4/4$. Обсуждаются особенности энергетического спектра, матричных элементов дипольного и квадрупольного операторов. Определена область применимости двухуровневой модели для описания электрон-фононного взаимодействия. В рамках данной модели изучено влияние изотопического замещения на $T_c$.

Работа выполнена в Лаборатории теоретической физики и Лаборатории вычислительной техники и автоматизации ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1988

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E17-88-382

Numerical Simulation of the Isotope Effect in the High-$T_c$ Superconductors

The results of a numerical simulation are presented for the oxygen isotope effect in the high-$T_c$ oxides by solving the Schrödinger equation for a local vibrational mode of oxygen ions in a double well anharmonic potential of the form $-Ax^2/2+Bx^4/4$. The features of the anharmonic energy spectrum, eigenfunctions and the matrix elements of the dipole and quadrupole moments are discussed. The applicability region of a two-level approximation to describe the electron-phonon interaction is given. The effect of isotope substitution on $T_c$ in the new high-$T_c$ superconductors is studied.

The investigation has been performed at the Laboratory of Theoretical Physics and the Laboratory of Computing Techniques and Automation, JINR.

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