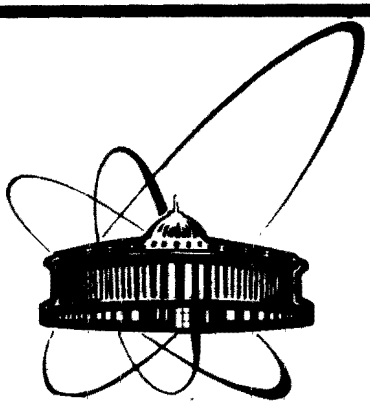

объединенный
институт
ядерных
исследований
дубна

E17-88-624

T.Galbaatar, R.-J.Rakauskas*, J.Sulskus*

Cu-O CHAIN IN $YBa_2Cu_3O_{7-\delta}$ AND THE PHONON MECHANISM OF HIGH-T_c SUPERCONDUCTIVITY

Submitted to "Physics C"

*On leave from Vilnius V.Kapsukas University, Faculty of Physics, Vilnius, USSR

1988

I. Introduction

Since the discovery[1] of high-T_c superconducting $La_{2-x}(Ba,Sr)_xCuO_4$ (hereafter LSCO) quite a few oxides with ever higher Tc have been synthesized[2-4]. Accordingly great and heterogeneous is the number of theoretical papers attempting to explain that phenomenon. However, as emphasized by most of them, the role of oxygen seems to be very important for the superconductivity. Due to a common structural feature of the new superconducting oxides, namely the presence of square Cu-O plane(s) the so-called "breathing" mode involving the in-plane Cu-O bond stretching vibration of oxygen has been considered as critical within the conventional phonon mechanism of superconductivity. Indeed the strong renormalization of this mode at the Brillouine zone boundary is able to produce Tc~40K[5]. However, as has recently been shown[6], in the harmonic approximation this mode cannot help to explain Tc as high as 90K observed in $YBa_2Cu_3O_{7-\delta}$ (YBCO) ceramics. On the other hand, the possibility of enhancing Tc up to 120K was demonstrated in the anharmonic model[7] of high-Tc superconductors. Exact numerical calculations[8], however, show that the soft mode considered in the anharmonic model cannot be held alone responsible for superconductivity in YBCO as it yields deviation from the experimental data concerning the isotope effect whereas quite a good agreement of the experimental observations for LSCO with the predictions of the anharmonic model should be noted. Thus the role of phonons in these superconducting materials ought to be revealed fully including their interactions in order to decide what mechanism underlies the superconductivity in them. The present paper is devoted to the contribution of the Cu-O chain to superconductivity in YBCO focusing on the interplay of two local modes involving the vibration

of oxygen along and across the chain axis, throughout referred as to the bond stretching and bond bending modes, respectively.

II. The bond stretching mode

The vibration of the oxygen atom in the cluster $(Cu_2O)^{2+}$ is considered as antisymmetric vibration of the three-atomic molecule of the symmetry $D_{\infty h}$ ($^1\Sigma_g^+$ electronic term) with the internuclear distance R_{Cu-O}=3.5716a.u[15]. The Schrödinger equation for the antisymmetric stretch vibration can be written as follows :

$$\left[-\frac{h^2}{2M_{aa}}\frac{\partial^2}{\partial Q_a^2} + V(Q_a) \right] \psi_v(Q_a) = E_v \psi_v(Q_a) \quad , \qquad (1)$$

where $V(Q_a)$ is the potential in Born-Oppenheimer approximation,

$M_{a_a} = \frac{m_o m_{Cu}}{2m_{Cu}+m_o}$ is the reduced mass of the cluster.

The potential energy has been expressed in a Taylor series expansion up to the sixth power:

$$V(Q_a) = Q_a^2 K_{aa}/2 + Q_a^4 K_{aaaa}/24 + Q^6 K_{aaaaaa}/720 \quad , \qquad (2)$$

where $K_{a..a}$ denote the force constants and Q_a the normal coordinate. The adiabatic potential is calculated in the Hartree-Fock approximation by the LCAO method with a Gaussian basis (Tab.4). They included explicitly only the valence electrons. The effect of ionic cores has been taken into account through the pseudopotential[23], the radial part of which is given by the following analytical expression:

$$r^2 V_l^{eff}(r) = \Sigma A_{lk} r^{n_{lk}} e^{-B_{lk} r^2} \quad , \qquad (3)$$

where n_{lk}=0, 1 or 2, A_{lk} and B_{lk} are fitted from atomic calculations[9] (Tab.3). The total energy of the linear system $(Cu_2O)^{2+}$ is calculated for different values of the oxygen displacement along

the axis from the mass center. It was fixed at five points from 0 (the center) to 1.25a.u.(maximal displacement) with a step of 0.25a.u. At zero displacement of oxygen the total energy is calculated to -403.329961 a.u. The force constants obtained are given below (in a.u.): K_{QQ}= 0.333257 ; K_{QQQQ}= 0.383826 ; K_{QQQQQQ}= 4.547685 ; The value of K_{QQ} converted into mdyne/Å equals 2.57, which in comparison with force constants given in Ref.[27,28] is larger by several times. This might be explained by two factors; (i) the Hartree-Fock approximation usually gives enhanced results (ii) the force constants in above Refs. have been used as fitting parameter and fitted peaks of lower frequency. We also calculated the valence of the copper ions in the Cu-O chain.The total population (charge) of copper at zero and maximal displacements is found to 18.018 and 17.993, respectively.Thereby the dipole moment of the electronic system changes from zero to 0.8052 Debyes. Thus one can argue that the copper ions in the chain are in the 1+ valence state.This is consistent with experiments of positron trapping[16] and the Mössbauer spectroscopy[17].It is reported[25] that the best agreement between X-rayand neutron diffraction results have been obtained proposing 1+ valence for Cu(1) site in the chain. Solving the Schrödinger equation with the potential (2) for ^{16}O,^{18}O and ^{63}Cu, ^{65}Cu we obtained the energy spectra, dipole matrix elements as well as the mean square displacements. The substitution of ^{63}Cu by ^{65}Cu results in a small shift (less than 0.1meV) of the spectrum, thus the copper isotope effect could be neglected, what is in agreement with experimental data[11,12].On the contrary the isotopic substitution of oxygen leads to a noticeable shift in T_c(Table 1).It turned out that the deviation of the energy spectrum from the harmonic case is very small as demonstrated by the differences of energy levels; E_1-E_0=138.4 meV; E_2-E_1=138.7 meV; E_3-E_2=138.9 meV; E_4-E_3=139.3 meV whereby zero-point energy E_0=69.14meV.

The very high frequencies need some discussing.To our knowledge such high frequencies are not yet detected nor published anywhere. Much

Table 1.Vibrational frequencies of the Cu_2O cluster for different isotopes of oxygen and copper

$^{65}Cu_2{}^{16}O$	$^{63}Cu_2{}^{16}O$	$^{63}Cu_2{}^{18}O$
138.3meV	138.4meV	131.4meV

lower frequency (60 meV) is assigned to it from IR experiments[13].Frequencies as high as 120meV have been observed by the neutron inelastic scattering[14], yet they are reported to disappear or decrease down to 90meV in the superconducting state. A similiar picture is seen by IR measurements[24] where a high frequency mode at 1070 cm^{-1} is observed for the lowest oxygen concentration($\delta\approx$ 1), thus in the non-superconducting tetragonal phase. The reason for the discrepancy between our theoretical results and the experimental ones out-lined above might be manyfold. We remind that we considered a linear Cu-O-Cu molecule while the neutron diffraction data[15] indicate some deviation from the linearity of the chain. Another argument might be the fact that this calculation was performed for the simplest cluster without any interaction. Nevertheless, we argue that the frequency of the phonon mode involving the bond stretching vibration in the chain is possibly higher than that of the in-plane "breathing" mode because of various valences of copper in the chain and in the plane, equaling 1+ and 2+, respectively.Actually, structural analysis of the neutron diffraction data leads to the conclusion that in YBCO copper appears in 1+,2+ and 3+ states, whereby the Cu^{2+} and Cu^{3+} ions preferentially occupy the square pyramidal and square planar sites[26]. As it is known, the electronegativity of Cu^{1+} (1.8) is smaller than that of Cu^{2+} (2), thus leading to a stronger bond of the first with oxygen. Thus, we believe a frequency higher than that of the breathing mode, which is in the range (70-80)meV, should be detected.Finally, we calculated and compared the Debye-Waller factor for O(4) parallel to the b-axis (along the chain)

with experimental data from neutron diffraction[22]. The anisotropic Debye-Waller factor changes from 0.15 Å² to 0.40 Å² depending on the sample and temperature. We obtained for ^{16}O 0.22Å² and for ^{18}O 0.21Å², thus they are in good agreement with above figures. The evaluation of the contribution of the bond-stretching mode to superconductivity in a standard manner yields coupling constants $\lambda_s(^{16}O)=0.3073$ and $\lambda_s(^{18}O)=0.3067$ and transition temperatures $T_c(^{16}O)=0.73K$ and $T_c(^{18}O)=0.68K$ for a value $\mu^*=0.1$. Hereby the Hopfield parameter $\eta_s=N(0)\langle J_s^2\rangle$ is estimated at 10 ev/Å². Thus it is obvious that this mode is not able to produce the experimentally observed high T_c's. As for the isotope, effect one obtains $\alpha=0.56$ with a small deviation from the harmonic value $\alpha=0.5$. The calculations including vectorized codes have been performed on the array processor EC 2706 at JINR.

III. Interplay of two modes

As has been mentioned above, the Cu-O chain has a zig-zag form with a characteristic length of the displacement $x_o=0.1$ Å[15] of oxygen (O1) from the chain axis. It is well known that structural phase transitions of such a displacive type can be described by a double-well anharmonic potential[18]. Thus, the contribution of this bond bending mode can be studied within the anharmonic model of high-T_c superconductors[7] and we take over the results of our numerical simulation[8]. The frequency of this mode is estimated in the range (20-30)meV. The figures taken over correspond to a value of $\beta=0.42$ (for its description and other details dealing with the double-well potential see [8]). The effect of two phonon modes can be studied by means of the following formula for T_c:

$$T_c = 1.14\ \tilde{\omega}\ \exp\left[-\frac{1+\lambda}{\lambda-\mu^*(1+\alpha)}\right] , \qquad (4)$$

derived numerically[19] by assuming the Eliashberg function $S(\omega)$ constructed of two phonon frequencies ω_1 and ω_2.

$\tilde{\omega} = \omega_1^{\lambda_1/\lambda}\omega_2^{\lambda_2/\lambda}\exp(-A)$, where $\lambda=\lambda_1+\lambda_2$ and $\alpha = \lambda A/(1+\lambda)$

$$A = 0.5 - \frac{\lambda_1\lambda_2}{2\lambda^2}\left[1 + \ln\frac{\omega_2}{\omega_1}\,\frac{\omega_1^2+\omega_2^2}{\omega_1^2-\omega_2^2}\right] , \qquad (5)$$

In Table 2 the values of T_c produced by each mode separately are compared with those resulting from their interplay.

Table 2

$h\omega_o$=138.4meV	Ω=30meV			ω_{log}		
	x_o= 0.1;	0.15;	0.25	57.49;	43.82;	35.28
Tc=0.73K	1.33K	21.59K	64.24K	24.95K	45.39K	68.27K

Ω is the frequency of the bond bending mode and $\omega_{log} = \tilde{\omega}/e^{-A}$.

The three different values of ω_{log} correspond to three different displacement amplitudes x_o given in Å. One can see a considerable enhancement of T_c due to the interplay of the two modes, whereby $T_c(\Omega)$ and $T_c(\omega_{log})$ apparently aim at a common asymptotic value due to some saturation effects of the exponential part of (4). This leads to the idea that the Cu-O chains are not the only participants on superconductivity in the YBCO compounds. The isotope effect is presented in FIG.1 by α of the relation $T_c \sim M^{-\alpha}$ vs. $\lambda=\lambda_1+\lambda_2$. One has to expect a large normal isotope effect. For T_c~90K a value of α~0.7 is predicted.

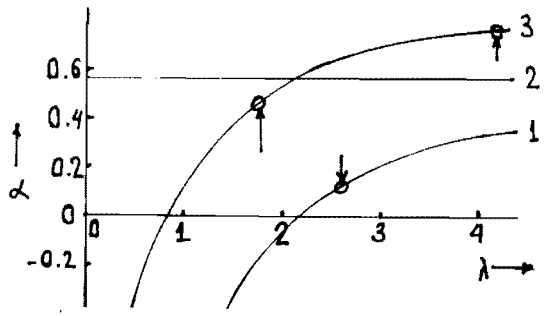

Fig. 1. o - LSCO, T_c ≈ 38 K; □ - YBCO, T_c ≈ 92 K; 1 - bond bending mode; 2 - bond stretching mode; 3 - interplay of 1 and 2; μ^* = 0.1; ω_1/ω_2=4.61.

Table 3.Effective potentials used for the calculations

Atom	Potentials	A_{lk}	n_{lk}	B_{lk}
O	V_p	- 0.9255	1	16.11718
	V_{s-p}	1.96069	0	5.05348
		29.13442	2	15.95333
Cu	V_d	-10.0	1	511.9951763
		-72.5548282	2	93.2801074
		-12.7450232	2	23.2206669
	V_{s-d}	3.0	0	173.1180854
		23.8351825	1	185.2419886
		473.8930488	2	73.1517847
		157.6345823	2	14.6884157
	V_{p-d}	5.0	0	100.7191369
		6.4990936	1	130.8345665
		351.4605395	2	53.868372
		85.5016036	2	14.0989469

Table 4. Gaussian basis functions of the valence electrons of oxygen and copper atoms

Atom	Exponent	Coefficients	
		s	p
O			
	8.519	-0.14551	0.11007
	2.073	-0.08286	0.34969
	0.6471	0.74325	0.48093
	0.2	0.28472	0.30727
Cu		3s	4s
	8.176	-0.419145	0.089201
	2.568	0.735292	-0.179247
	0.9587	0.5501	-0.234761
	0.1153	0.012726	0.539268
	0.0396	-0.004027	0.575271
		3p	
		25.63	-0.048802
		3.166	0.625804
		1.023	0.470505
		0.086	0.018172
		0.024	-0.006569
		3d	
		41.34	0.040754
		11.42	0.195077
		3.839	0.397458
		1.23	0.465382
		0.3102	0.288097

IV.Discussion

An attempt to reveal the role of the Cu-O chain for the superconductivity in YBCO has been made. Based on cluster calculations for the bond stretching and bond bending modes the possibility of enhancing of the superconducting transition temperature T_c is shown within the conventional phonon mechanism. Our results, however, could be applied to the LSCO system,too, as in its parent compound La_2CuO_4 besides the breathing mode the existence of soft modes [10,20,21] is proposed, which is supported by the observation of unusually large, strongly anisotropic Debye-Waller factors[22].Our calculations demonstrate that at T_c around 38K an isotopic shift of δT_c=2K should be detected, what is not the case, at least now .On the contrary, recalling our previous work[8], where we obtained α=0.16 at 36K being in agreement with experiments, we suppose that for the LSCO system the soft tilting mode may be decisive. As for YBCO, the interplay of two modes involving the longitudinal and transversal vibrations of oxygen can produce T_c higher than that of LSCO resulting in a large isotope effect.It is possible that an additional mechanism of non-phononic nature suppressing the isotope effect has to be considered. In conclusion, we deduce from our results that the Cu-O chains in YBCO play an important role, but not the crucial role for the superconductivity. The authors would like to thank Dr.N.M.Plakida, Prof.V.G.Makhankov and Prof.E.P.Zhidkov for supporting and helpful discussions.

References

1 Bednorz J.G. and Müller K.A. Z.Phys.B64,189(1986)
2 Wu M.K.et.al. Phys.Rev.Lett.58, 908(1987)
3 Chu C.W. et.al. Phys.Rev.Lett.60,941(1988)
4 Sheng Z.Z. et.al. Phys.Rev.Lett.60,937(1988)
5 Weber W. Phys.Rev.Lett.58, 1371(1987)
6 Weber W.and L.Mattheiss Phys.Rev.B37, 599(1988)
7 Plakida N.M., Aksenov V.L. and Drechsler S-L. Intern.J.Mod.Phys.B1,1071(1987)

8 Galbaatar T.,Rakauskas R-J. and Sulskus J.
JINR preprint, E17-88-382

9 Walter J. Bash H. and Krauss M. J.Chem.Phys. 81, 6026(1984)

10 Flemming R.M. et.al. Phys.Rev.B35,7191(1987)

11 Vasiliev B.V.,Lushchikov V.I. and Sikolenko V.V.
JINR Rapid Comm. No.2[28]-88

12 Lin Quan et.al. Sol.state comm: vol.65,869 (1988)

13 Klamut J. et.al Proceedings of HTSC-M^{2}S Intern.
Interlaken,Feb.1988 ,Physica C 153-155,288(1988)

14 Ruan Jinghui et.al. Intern.J.Mod.Phys. B, v.1,409(1987)

15 Francois M.,Junod A.,Yvon K. and Hewat A.W.
Nature 286(1988)

16 Smedskjaer L.C. et.al. Physica B 150, 56(1988)

17 Alp E.E. et al. Physica B 150, 74(1988)

18 Muller K.A. and Thomas H. Structural Phase Transitions I.
Topics in current physics series
Springer-Verlag,Berlin Heidelberg
New York, 1981

19 Maksimov E.G.,Karakozov A.E. and Mashkov S.A.
Zh.Eksp.Theor.Fiz. 68, 1937(1975)

20 Jorgensen J.D. et.al. Phys.Rev.Lett. 58, 1024(1987)

21 Cava R.J. et.al. Phys.Rev. B35,6716(1987)

22 Capponi J.J. et.al. Europhys.Lett. 3,1301(1987)

23 Heine V. Solid State Physics,Advances in Research
and Applications series,vol.24
Academic press,New York .

24 Taylor K.N.R. et.al. J.Phys. C:Sol.stat.phys. 21, L489(1988)

25 Roth G. et.al. Physica C: 152, 329(1988)

26 Danon J. Report CBPF-NF-046/87, Centro Brasil. de
Pesquisas Fisicas, Rio de Janeiro

27. Yasuda T. and Mase S. JJAP Series 1,Superconducting materials
265-267(1988)

28 Bruesch P. and Buhrer W. Z.Phys. B 70, 1(1988)

Received by Publishing Department
on July 11, 1988.

Галбаатар Т., Ракаускас Р.И., Шулкус Ю.К. E17-88-624

Цепочки Cu-O в $YBa_2Cu_3O_{7-\delta}$ и фононный механизм ВТСП

В рамках фононного механизма сверхпроводимости рассмотрено влияние взаимодействия высокочастотной и низкочастотной квазилокальных мод, связанных с продольными и поперечными колебаниями атома кислорода в цепочках Cu-O в $YBa_2Cu_3O_{7-\delta}$. Показано, что учет взаимодействия этих мод приводит к повышению критической температуры T_c, а при этом изотопическое замещение кислорода в цепочке - к сильному нормальному эффекту. Адиабатический потенциал для высокочастотной моды получен, рассматривая кластер $(Cu\text{-}O\text{-}Cu)^{2+}$, методом Хартри-Фока с псевдопотенциалом. Показано, что валентность меди близка к 1. В работе для проведения расчетов применены алгоритмы параллельных вычислений и был использован матричный процессор ЕС 2706 ЦВК ОИЯИ.

Работа выполнена в Лаборатории вычислительной техники и автоматизации ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1988

Galbaatar T., Rakauskas R.-J., Sulskus J. E17-88-624

Cu-O Chains in $YBa_2Cu_3O_{7-\delta}$ and the Phonon Mechanism of High-T_c Superconductors

Within the phonon mechanism the effect of the interplay of high and low frequency quasi-local modes, involving the longitudinal and transversal vibrations of oxygen atoms in the Cu-O chains on the superconductivity in $YBa_2Cu_3O_{7-\delta}$ is studied. The possibility of enhancing T_c due to this interplay is demonstrated numerically. A strong normal isotope effect is predicted. The adiabatic potential for the high frequency mode is obtained by considering the cluster $(Cu\text{-}O\text{-}Cu)^{2+}$ by the Hartree-Fock method with pseudopotential. It is shown that the in-chain copper ions are 1^+ valence state. The calculations including vectorized codes have been performed on the array processor EC 2706.

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

Preprint of the Joint Institute for Nuclear Research. Dubna 1988