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Cu-O CHAIN IN YBa₂Cu₃O_{7-δ} AND THE PHONON MECHANISM OF HIGH-T_c SUPERCONDUCTIVITY

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discovery 11 Since the of high-T superconducting La_ (Ba,Sr) CuO (hereafter LSCO) quite a few oxides with ever higher To have been synthesized 2^{-4} . Accordingly great and beterogeneous 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 T_{-40K} . However, as has recently been shown $^{\prime o \prime}$, in the harmonic approximation this mode cannot help to explain To as high as 90K observed in YBa_Cu_O_s (YBCO) ceramics. On the other hand, the possibility of enhancing up to 120K was demonstrated in the anharmonic model⁷⁷ of high-Te superconductors. Exact numerical calculations . 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 $(Cu_2 0)^{2*}$ is considered as antisymmetric vibration of the three-atomic molecule of the symmetry $D_{och}({}^{4}\Sigma_{g}^{*}$ 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 :

$$\begin{bmatrix} -\frac{\mathbf{h}^{\mathbf{z}} \cdot \boldsymbol{\partial}^{\mathbf{z}}}{---\mathbf{z}} + \nabla(\mathbf{Q}_{a}) \\ 2\mathbf{M}_{aa} \cdot \boldsymbol{\partial}\mathbf{Q}_{a} \end{bmatrix} \boldsymbol{\psi}_{\mathbf{v}}(\mathbf{Q}_{a}) = \mathbf{E}_{\mathbf{v}}\boldsymbol{\psi}_{\mathbf{v}}(\mathbf{Q}_{a}) \quad . \tag{1}$$

where $V(Q_{n})$ is the potential in Born-Oppenheimer approximation,

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

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

$$V(Q_{\alpha}) = Q_{\alpha}^{z} K_{\alpha\alpha} / 2 + Q_{\alpha}^{4} K_{\alpha\alpha\alpha\alpha} / 2 + Q^{6} K_{\alpha\alpha\alpha\alpha\alpha\alpha} / 720 , \qquad (2)$$

where $K_{\alpha,..\alpha}$ denote the force constants and Q_{α} 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 pseudopotential²³, the radial part of which is given by the following analytical expression:

$$r^{z} V_{l}^{eff}(r) = \Sigma A_{lk} r^{n} lk e^{-B_{lk} r^{2}} , \qquad (3)$$

where $n_{lk}=0,1$ or 2, A_{lk} and B_{lk} are fitted from atomic calculations^(P)(Tab.3).The total energy of the linear system $(Cu_20)^{2+}$ is calculated for different values of the oxygen displacement along

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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.): $K_{aa} = 0.333257$; $K_{aaaa} = 0.383826$; $K_{aaaaaa} = 4.547685$; The value of $K_{\alpha\alpha}$ converted into mdyne/Å equals 2.57, which in comparison with force constants given in Ref. 727,287 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 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 100,10 and ⁶³Cu, ⁶⁵Cu we obtained the energy spectra, dipole matrix elements as well as the mean square displacements. The substitution of ⁶⁹Cu by ao 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_{r} (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; $E_1 - E_0 = 138.4 \text{ meV}$; $E_2 - E_1 = 138.7 \text{ meV}$; $E_3 - E_2 = 138.9 \text{ meV}$; $E_4 - E_3 = 139.3$ meV whereby zero-point energy E_=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_2^0 cluster for different isotopes of oxygen and copper

⁶⁵ Cu ₂ ¹⁶ 0	⁶³ Cu ₂ ¹⁶ 0	⁶³ Cu ₂ ¹⁸ 0
138.3meV	138.4meV	131.4meV

lower frequency (60 meV) is assigned to it from TR experiments^{13/}. Frequencies as high as 120meV have been observed hv the neutron inelastic scattering¹⁴, yet they are reported to disappear or decrease down to 90meV in the superconducting state. A similiar picture is seen by IR measurements²⁴ 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 data 15/ linear Cu-O-Cu molecule while the neutron diffraction 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 Cu²⁺ and Cu³⁺ ions preferentially occupy the square pyramidal and square planar sites 26 . As it is known, the electronegativity of Cu^{i+} (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 diffraction²²². The anisotropic Debye-Waller factor changes from 0.15 Å² to 0.40 Å² depending on the sample and temperature. We obtained for ¹⁶O 0.22Å² and for ¹⁸O 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 $\lambda_{g}(^{16}O)=0.3073$ and $\lambda_{g}(^{18}O)=0.3067$ 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 $\eta_{g}=N(O)\langle J_{g}^{2}\rangle$ 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 $x_0=0.1 \text{ Å}^{'15'}$ of oxygen (01) 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^{'10'}. 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^{'0'}. 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 ^{'0'}). The effect of two phonon modes can be studied by means of the following formula for

$$T_{c}:$$

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

derived numerically'''' by assuming the Eliashberg function $S(\omega)$ constructed of two phonon frequencies ω_{a} and ω_{a} .

$$\widetilde{\omega} = \omega_{1}^{\lambda_{1}/\lambda} \omega_{2}^{\lambda_{2}/\lambda} \exp(-A), \text{ where } \lambda = \lambda_{1} + \lambda_{2} \text{ and } \alpha = \lambda A/(1+\lambda)$$

$$A = 0.5 - \frac{\lambda_{1}\lambda_{2}}{2\lambda^{2}} \left[1 + \ln \frac{\omega_{2}}{\omega_{1}} - \frac{\omega_{1}^{2} + \omega_{2}^{2}}{\omega_{1}^{2} - \omega_{2}^{2}} \right], \quad (5)$$

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

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$\mathbf{x}_{0} = 0.1; 0.15; 0.25 57.49;$	42 82.	
	43.02;	35.28
To=0.73K 1.33K 21.59K 64.24K 24.95K	45.39K	68.27K

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

The three different values of ω_{\log} correspond to three different displacement amplitudes x_ogiven in \mathbf{A} . One can see a considerable enhancement of T_c due to the interplay of the two modes, whereby T_c(Ω) and T_c(ω_{\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^{-M^{- $\alpha}} vs. <math>\lambda = \lambda_i + \lambda_z$. One has to expect a large normal isotope effect. For T_c-90K a value of α -0.7 is predicted.</sup></sup>



Fig. 1. o - LSCO, $T_c \approx 38$ K; D - YBCO, $T_c \approx 92$ K; 1 - bond bending mode; 2 - bond stretching mode; 3 - interplay of 1 and 2; $\mu^* = 0.1$; $\omega_1/\omega_2 = 4.61$.

Atom	Potentials	Alk	n _{lk}	B _{1 k}
0	V_	- 0.9255	1	16.11718
	v	1.96069	0	5.05348
Cu	v,	29.13442 -10.0	2 1	15.95333 511.9951763
	TZ	-72.5548282 -12.7450232	2 2 0	93.2801074 23.2206669 173.1180854
	vs-d	23.8351825 473.8930488	1 2 2	185.2419886 73.1517847 14.6884157
	V p-d	5,0	ດ້	100.7191369
	, -	6.4990936 351.4605395 85.5016036	1 2 2	130.8345665 53.868372 14.0989469

Table 3.Effective potentials used for the calculations

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

Atom	Exponent	Coeffic	cients
		ß	P
0	0 610	0 14551	0 11007
	0.519	-0,14001	0.11007
	2.013	-0.00200	0.048003
	0.64/1	0.74020	0.40033
	0.2	0.204/2	0.30121
u	0 170	-0 410145	0 080201
	0.1/0	0.735303	-0.179247
	2.000	0.100202	-0.234761
	0.9007	0.0001	0.539268
	0.1155	-0.004027	0.535200
	0.0398	-0.004027	3n
		25 63	-0 048802
		3 166	0.625804
		1 023	0.470505
		0.086	0.018172
		0.000	-0.006569
		0.024	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 ${\rm T_{c}}$ is shown within the conventional phonon mechanism. Our results, however, could be applied to the LSCO system, too, as in its parent compound La_CuO, besides the breathing mode the existence of soft modes $\overset{\scriptstyle \times 10,20,21\prime}{}$ is proposed, which is supported by the observation of unusually large, strongly anisotropic Debye-Waller factors 22. Our calculations demonstrate that at T around 38K an isotopic shift of $\delta T_z=2K$ should be detected, what is not the case, at least now .On the contrary, recalling our previous work '8', where we obtained a=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 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 Muller	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	\mathbf{L} . and Drechsler S-L.
	Intern.J.Mod.Phys.B1.10'	71(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-M²S 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. Juned 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 CBFF-NF-046/87, Centro Brasil. de Fesquisas 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)

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Цепочки Сu-О в YBa₂Cu₈O_{7-б} 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 $_2$ Cu $_3$ O $_7$ $_8$. 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-O-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.

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Cu-O Chains in $YBa_gCu_gO_{7-\delta}$ and the Phonon Mechanism of High-T_ 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 YBa₂Cu₃O_{7-δ} is studied. The possibility of enhancing T_e 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 $(Cu-O-Cu)^{2+}$ 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.

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