



NON- ADIABATICITY AND NOVEL ISOTOPE EFFECT
IN THE DOPED CUPRATES.

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ABSTRACT

This paper reports a novel isotope effect which is due to a strong non-adiabaticity that manifests itself in the dependence of the carrier concentration on the isotopic mass. The critical temperature in turn depends on the carrier concentration giving rise to a unique and non-phononic isotope shift.

1. Introduction.

This paper describes a novel isotope effect. As we know, the conventional isotope effect is related to the change in the phonon frequency caused by the isotopic substitution. Such a change affects the value of T_C ; and as a result, the isotope effect is always related to the manifestation of phonon-mediated superconductivity.

The goal of this paper is to demonstrate that in the doped materials such as the high T_C oxides, one can observe an entirely different isotope effect. Such an effect is due to strong non-adiabaticity (see below) and is manifested in the dependence of the carrier concentration on isotopic mass. As we know^{1,2}, the critical temperature of the cuprates depends on the carrier concentration, so that $T_C = T_C(n)$. Since the carrier concentration depends on the ionic mass M (see below), so that $n=n(M)$, one can observe the dependence $T_C(M)$ which is not related to the change in the phonon frequency.

Our study was motivated by a peculiar behavior of the isotope coefficient in the high T_C cuprates. It has been observed^{3,4} that a decrease

in the carrier concentration which leads to a decrease in T_c is accompanied by an increase in a value of the oxygen isotope coefficient α . As a result, α has a minimum value at $T_c = T_{c,max}$. We think that the theoretical model described below is directly related to such a peculiar behavior. Our microscopic model was described briefly in⁵. This paper contains a more detailed discussion, and, in addition, we present several new results. One should note also that the dependence $n(M)$ was introduced in a phenomenological way in⁶. Our approach contains a microscopic quantum model which leads to such a dependence.

The structure of the paper is as follows. Sec.2 describes the microscopic model and the derivation of the dependence $n(M)$. Experimental data are discussed in Sec.3. The penetration depth and the pressure coefficient are studied in Sec.4.

2. Theory.

In this section we describe a quantum-mechanical model which contains the dependence of the carrier concentration in doped materials on the isotope mass. At first sight, such a dependence looks strange, because the isotope substitution (e.g. $O^{16} \rightarrow O^{18}$) is not accompanied by change in the nuclear charge and should not affect the charge transfer (doping). However, if we are dealing with a strong non-adiabatic situation (see below) then the electronic and nuclear degrees of freedom can not be separated. As a result, the change in the nuclear subsystem (isotope substitution) affects the electronic degrees of freedom and, consequently, the charge transfer.

As we know, according to the adiabatic theory, the values of the electronic energy depend parametrically on nuclear coordinates, that is $E_n = E_n(\mathbf{R})$. The electronic terms $E_n(\mathbf{R})$ form a potential for the nuclear motion, and their minima correspond to the equilibrium positions.

The intersection of electronic terms crossing (Fig. 1) corresponds to degenerate electronic configurations (Jahn-Teller instability). Near this configuration the total wave function can not be written as a product of the electronic and nuclear wave functions; this reflects a non-separability of

the nuclear and electronic degrees of freedom. Such a case (see Fig. 1) is characterized by two close minima. It is important to emphasize that the situation is similar, but, nevertheless, entirely different from the double-well anharmonic picture. According to the latest model, the electronic and nuclear degrees of freedom are separated, but the potential for the nuclear motion formed by some electronic term $n(\mathbf{R})$ is not harmonic. In our case we are dealing with a non-separability of the motions, and the minima correspond to different terms.

Our approach is based on the diabatic representation⁷ and the quantum transition theory. Consider a non-adiabatic ion; its dynamics corresponds to the intersection of the terms (see Fig. 1).

Crossing of Terms

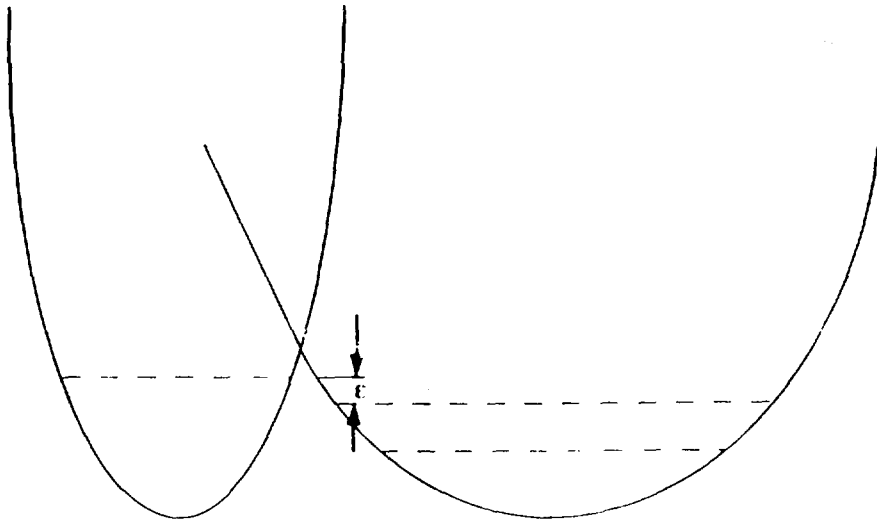


Figure 1

For concreteness one can focus on the apical oxygen in the YBCO compound (see below, Sec.III). The charge transfer correspond to the transitions between the first and second terms. The total wave function can be written in the form

$$\Psi(\vec{r}, \vec{R}, t) = a(t) \Psi_1(\vec{r}, \vec{R}) + b(t) \Psi_2(\vec{r}, \vec{R}) \quad (1)$$

Here

$$\Psi_i(\vec{r}, \vec{R}) = \psi_i(\vec{r}, \vec{R}) \Phi_i(\vec{R}), \quad i = \{1, 2\}$$

$\psi_i(\vec{r}, \vec{R}), \Phi_i(\mathbf{R})$ are the electronic and vibrational wave functions that correspond to two different electronic terms (Fig. 1). Let us separate the non-adiabatic Z-coordinate of the ion, so that $\Phi_i(\vec{R}) = \Phi_i(\mathbf{R}_1) \varphi_i(Z)$, \mathbf{R}_1 corresponds to the other degrees of freedom. We do not assume the electronic terms to be similar. This leads to some splitting \mathcal{E} between the vibrational levels (Fig.1) and the transition of the oxygen ion is not a resonant one. We are using the harmonic approximation for $\varphi_1(Z)$ and $\varphi_2(Z)$. We assume that the ionic motion corresponds to the zero vibrational state of the first term, and v -th level for the second term. Assume also that $b(0) = 0$. The dependence $b(t)$ describes the dynamics of the charge transfer.

In the diabatic representation the transition between the terms are described by the matrix element V_{12} , where $V \equiv \hat{H}_{\vec{r}} = \hat{H}_{el} = \hat{T}_{\vec{r}} + V(\vec{r}, \vec{R})$ (\hat{T} is a kinetic energy operator, $V(\vec{r}, \vec{R})$ is a total potential energy).

One can show that

$$V_{12} \equiv L_0 F_{12} \quad (2)$$

L_0 is the electronic constant, and $F_{12} = \int \varphi_2^*(Z) \varphi_1(Z) dZ$

is the Franck-Condon factor. The presence of the Franck-Condon factor is a key ingredient of our analysis. Its value strongly depends on the ionic mass (see below) and, therefore is affected by the isotope substitution. The probability $[b(t)]^2$ oscillates (see⁸, Sec.40). Its average value \tilde{b}^2 corresponds to the equilibrium doped state. The asymmetry of the potential for the axial oxygen and correspondingly the inequality ϵ not equal to 0 are playing key roles. In the opposite case when $\epsilon = 0$, the value of \tilde{b}^2 is equal; to 0.5 regardless of the value of F_{12} .

Assume a large asymmetry (see Fig 1.) so that $|L_0 F_{12}| \ll \epsilon$. Then the carrier concentration $n \propto \tilde{b}^2 = 2 (L_0 F_{12} / \epsilon)^2$. Since F_{12} and ϵ depend directly on the mass M , the carrier concentration also depends on M .

Let us focus now on the isotope coefficient $\alpha = - \frac{M}{T_c} \frac{\partial T_c}{\partial M}$ and

consider the isotope effect which is due to the dependence $n(M)$ described above and also the dependence $T_c(n)$. One should distinguish two contributions, so that $\alpha = \alpha_1 + \alpha_2$, where $\alpha_1 = - (M/T_c) (\partial T_c / \partial \Omega) (\partial \Omega / \partial M)$ describes the usual isotope effect caused by change in the phonon spectrum (Ω is a characteristic phonon frequency for that mass). If some mode in the polyatomic system does not contribute noticeably to the pairing (this is the case for the axial oxygen, see below) then the coefficient α_1 is small. The term α_2 corresponds to a different isotope effect which is due to the dependence $n(M)$ described above and also the dependence $T_c(n)$. Namely:

$$\alpha_2 = - \frac{M}{T_c} \frac{\partial T_c}{\partial n} \frac{\partial n}{\partial M} \quad (3)$$

According to Eq. (2) the function $n(M)$ is determined mainly by the Franck-Condon factor and by the dependence $\epsilon^2 \propto M^{-1}$; after simple calculation we obtain:

$$n \propto M \exp(-sM^{1/2}), \quad (4)$$

$s = \overline{k^{1/2}} c^2 / 2h, (\overline{k^{1/2}})^{-1} = k_1^{-1/2} + k_2^{-1/2}$ where k_i are the elastic constants and c is the distance between the minima; as a result, we obtain the following expression for the isotope coefficient

$$\alpha_2 = \gamma \frac{n}{T_c} \frac{\partial T_c}{\partial n} \quad (5)$$

where γ is a constant. Expression (5) can be compared directly with experimental data (see below).

Eq. (5) contains the derivative $\frac{\partial T_c}{\partial n}$. Since T_c has a maximum at some

value $n = n_0$, the isotope coefficient α_2 is equal to zero if $T_c = T_{c_{\max}}$ (the small value of α actually observed is due to a small contribution from α_1). Therefore, the described mechanism leads to the situation that the maximum value of T_c corresponds to a minimum in isotope coefficient. This phenomenon, indeed has been observed experimentally.

III. Discussion. Experimental data. The axial oxygen in YBCO plays a key role in the chain to plane charge transfer process. This ion displays a non-adiabatic dynamics. Its unusual dynamics properties are described in many papers (see e.g.⁹⁻¹²). We think that the double-wall structure observed in¹⁰ corresponds to the non-adiabaticity, not the anharmonicity (see above). According to neutron data¹¹, the unusual dynamics might correspond to the motion in the a-b plane, and such orientation is consistent with the EXAFS data¹⁰, contrary to the original suggestion in¹⁰ about the c-orientation. Note that the orientation of the non-adiabatic degree of freedom is not essential for our model.

Expression (5) allows us to compare directly with experimental data. We can use the dependence $T_c(n)$ which has been observed in a number of papers (see e.g.^{1,2}) and is well known. One can see from Fig. 2, that there is a good agreement with the data on the isotope effect.

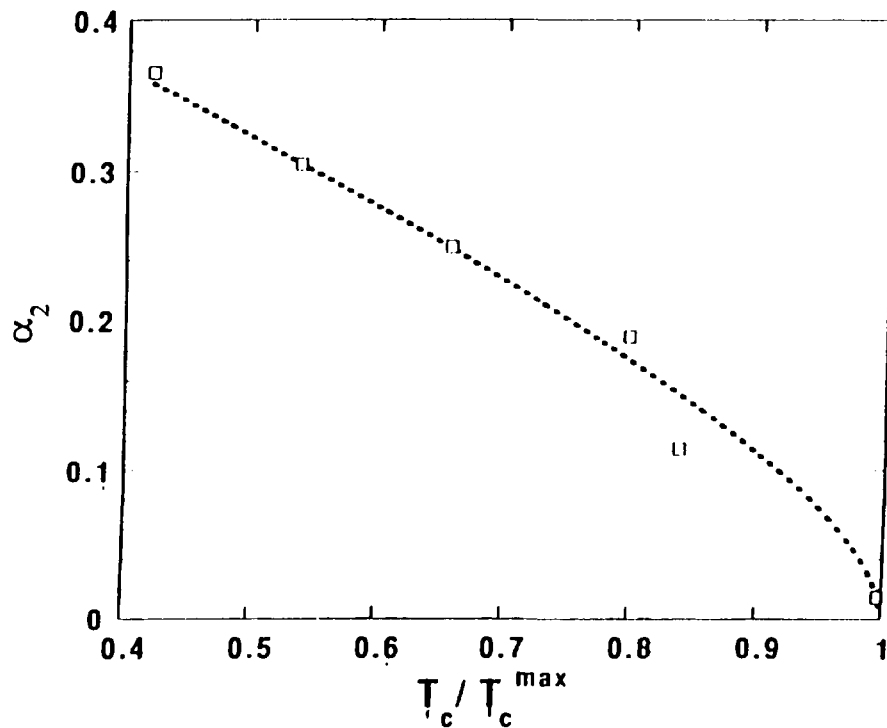


Figure 2

As was noted above, the coefficient α has a minimum value at $T_c = T_{c,\max}$. The small but measurable isotope shift at this point has recently been shown to be due to phonons associated with the plane

oxygens. In fact the axial oxygens at this point contribute little to the conventional isotopic shift¹³. In addition, one should note that if the overdoped region corresponds to the same phase as the underdoped region (probably, this is the case for BiPbCaSrCuO), then in the region $n > n_0$, the isotope coefficient should become negative; such an effect indeed, has been observed in⁴. Note also that according to our model the values of α are not limited by a maximum of 0.5 and may exceed this value.

A strong non-adiabaticity of the ions in the doped superconductors, such as the high T_c oxides leads to the dependence of the carrier concentration on M , and this factor affects the value of T_c . Qualitatively the charge transfer for such non-adiabaticity can be visualized as a multistep process; first the carrier makes a transition from the chain site to the axial oxygen O(4), then the axial oxygen transfers to another term, and this is finally followed by the transition of the carriers to the plane. The second step is affected by the isotope substitution. This mechanism provides a good description of the experimental data.

3. Penetration depth ; pressure coefficient

As was shown in Sec.2, non-adiabaticity leads to the dependence of the carrier concentration on M . The dependence of T_c on n leads to the isotope effect (5). However, the value of n affects not only T_c , but a number of other parameters as well. One of them is the London penetration depth $\delta = (m/4\pi e^2 n)^{1/2}$. Note that the correlation between the doping and the value of δ has been observed recently in¹⁴. The substitution $M \rightarrow M^*$ leads to change in n , and to the dependence $\delta(M)$. One can arrive to the following relation:

$$\delta = M^\beta; \beta = (M/\delta) (\partial\lambda/\partial n) (\partial n/\partial M) = -0.5 (M/n)(\partial n/\partial M) \quad (6)$$

One can see that $\beta = \gamma/2$. Note that the paper¹⁵ contains an observation of the isotopic dependence of the Meissner fraction; we think that this observation is related to the dependence $\delta(M)$. It would be interesting to perform a direct measurements of the penetration depth in YBCO as a

function of the isotope oxygen substitution.

The pressure coefficient $r = -T_C^{-1}(\partial T_C / \partial p)$ also displays the dependence on n , similar to α (see Eq.(5), see also ⁶). This can also be understood in the framework of the model described in Sec.2. Indeed, the pressure affects the width of the barrier "c". As a result, the doping, and, therefore n , is affected by the pressure. Since

$r = T_C^{-1}(\partial T_C / \partial n)(\partial n / \partial c)(\partial c / \partial p)$, one can use the relation (4), $s \propto c^2$ and we obtain $r \propto \alpha$, that is a dependence similar to (5).

4. Conclusion.

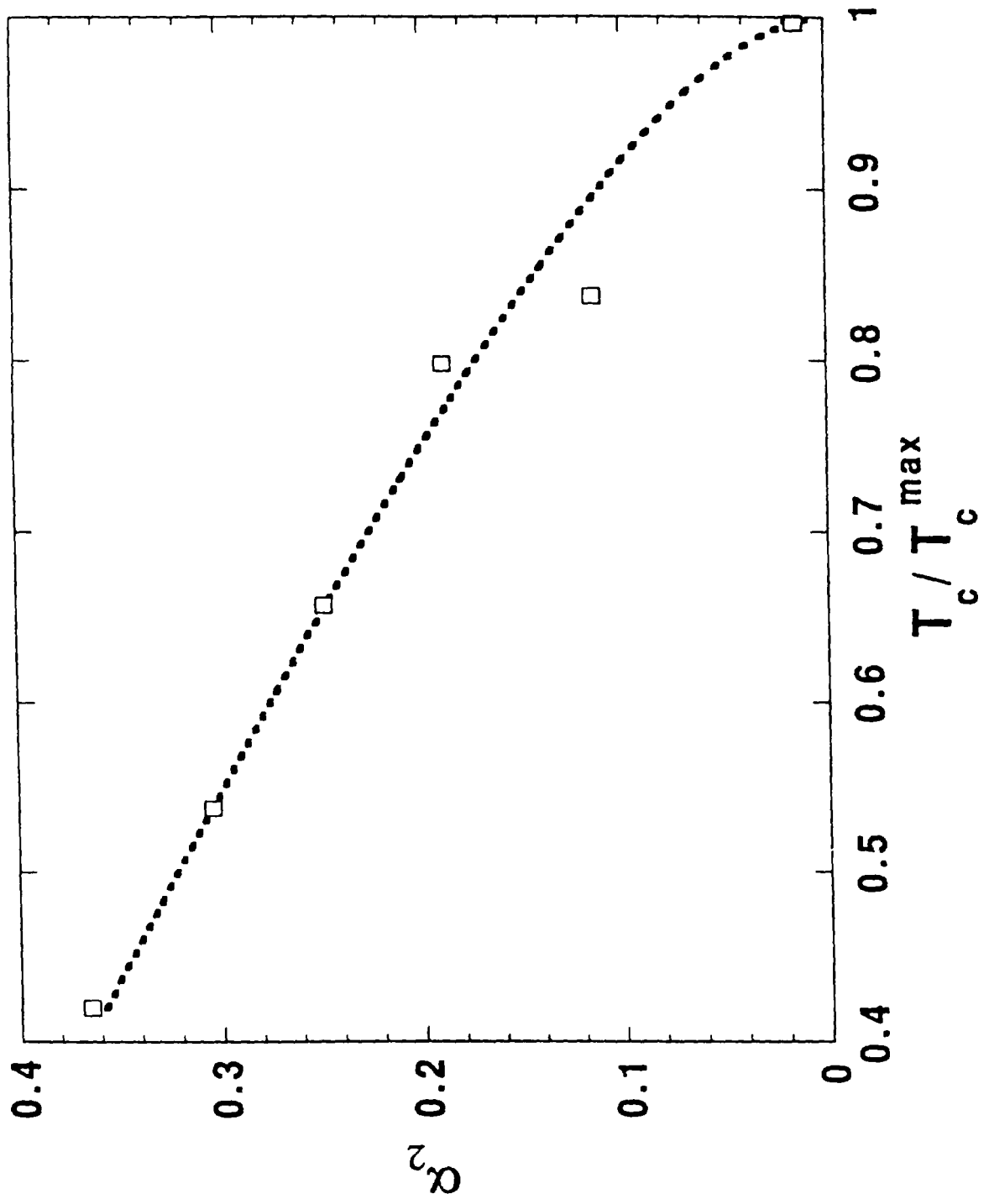
In Summary, we describe a novel effect of the isotopic substitution on T_C . It is interesting that this effect is not directly related to the mechanism of the pairing, but reflects system dynamics that are complicated and non-adiabatic. A strong non-adiabaticity of the ions in the doped superconductors, such as the high T_C oxides leads to an unusual dependence of the carrier concentration on M , and this factor affects the value of T_C . The non-adiabaticity may affect a number of various properties of the cuprates, and this problem deserves a more detailed study.

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5. References

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Crossing of Terms

