

Microscopic model for the isotope effect in the high- T_c oxides

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An unconventional microscopic mechanism relating T_c and the isotope substitution for the doped superconductors such as the high- T_c oxides is proposed. Strong nonadiabaticity, when it is impossible, strictly speaking, to separate fully the nuclear and electronic degrees of freedom, leads to a peculiar dependence of the carrier concentration n on the ionic mass M . This case corresponds, for example, to the isotopic substitution of the axial oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Because of the dependence of T_c on n , this leads to the dependence of T_c on M , that is to the isotope effect. The minimum value of the isotope coefficient corresponds to $T_c = T_c^{\text{max}}$.

We present a new microscopic approach to the problem of the isotope shift in the high- T_c oxides. Needless to say, the problem of the isotope shift is important and continues to generate high interest. At present it is firmly established that the value of the isotope coefficient α (see, e.g., Refs. 1–3) for oxygen substitution is correlated with the level of the doping and therefore, with the value of T_c . In fact α has a minimum value at the maximum of T_c . The decrease in carrier concentration, due for example to the oxygen depletion in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO), leads to a decrease in T_c (Refs. 4 and 5) and a concomitant increase in α . In addition, the value of α could, in principle exceed $\alpha_{\text{BCS}} = 0.5$.

As was noted above, we propose a microscopic mechanism relating T_c and isotopic substitution in the doped oxides. The usual manifestation of the isotope substitution is connected with changes in the phonon spectrum and it leads (in the framework at the phonon-mediated superconductivity) to change in T_c . However, a strong nonadiabaticity (e.g., axial oxygen in YBCO is in such state) results in an entirely different isotope effect. Namely, the doping, and therefore, the carrier concentration n , and, correspondingly, T_c are affected by the isotope substitution. Note that a phenomenological description has been introduced in Ref. 6. In this paper we propose a microscopic mechanism which leads to the unusual dependence of α on M .

If the charge transfer occurs in the framework of the usual adiabatic picture, so that only the carrier motion is involved, then the isotope substitution does not affect the forces and therefore does not change the charge transfer dynamics. However, the situation of strong nonadiabaticity is different and does not allow the separation of electronic and nuclear motion; in this case charge transfer appears as a more complex phenomenon which does involve nuclear motion, and this leads to a dependence of the doping on isotopic mass.

Consider the case when the lattice configuration corresponds to the situation when some definite ion (e.g., axial oxygen for YBCO) is in (or near) a degenerate state; this

means that the degree of freedom describing its motion corresponds to electronic terms crossing (see Fig. 1). Then the ion has two close equilibrium positions. Of course, the additional perturbation removes the degeneracy and we have nearly degenerate states; this leads to a dynamic Jahn-Teller effect and a double-well structure. However, here we are going to study the dynamics in the diabatic representation (see, e.g., Refs. 7 and 8); in this representation we are dealing directly with the crossing of electronic terms. The operator $\hat{H}_r = \hat{T}_r + V(\mathbf{r}, \mathbf{R})$ [\hat{T}_r is a kinetic energy operator, $V(\mathbf{r}, \mathbf{R})$ is a total potential energy, \mathbf{r} and \mathbf{R} are the electronic and nuclear coordinates, correspondingly] has nondiagonal terms (unlike the usual adiabatic picture when \hat{H}_r is diagonal).

The charge transfer in this picture is accompanied by the transition to another electronic term. Such a process is analogous to the Landau-Zener effect (see, e.g., Ref. 9).

For concreteness consider the axial oxygen in YBCO; this ion plays a fundamental role in the chain to plane charge transfer process. Unusual dynamic properties of the axial oxygen have been described in many papers (see, e.g., Refs. 10–12).

The total wave function can be written in the form

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

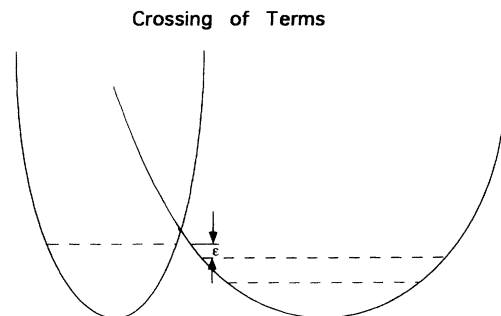


FIG. 1. Electronic terms (diabatic representation).

Here

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

$\Psi_i(\mathbf{r}, \mathbf{R}), \Phi_i(\mathbf{R})$ are the electronic and vibrational wave functions that correspond to two different electronic terms (see Fig. 1). Let us separate the Z coordinate of the axial oxygen (the axis Z has been chosen to be parallel to the c axis), so that $\Phi_i(\mathbf{R}) = \Phi_i(R_i)\varphi_i(Z)$, R_i corresponds to the other degrees of freedom. We do not assume the electronic terms to be similar and, as a result the energy level spacing is different for both of them. This leads to some splitting ϵ between the vibrational levels (see Fig. 1) and the transition of the oxygen ion is not a resonant one. In the harmonic approximation,

$$\varphi_1(Z) = (\pi a_1)^{-1/2} \exp[-(Z - Z_{10})^2 / 2a_1^2]; \quad (2)$$

$$\varphi_2(Z) = (\pi a_2)^{-1/2} \exp[-(Z - Z_{20})^2 / 2a_2^2] \times H_\nu[(Z - Z_{20})/a_2^{01}]. \quad (2')$$

Here $a_i = h/M\Omega_i$ are the vibrational amplitudes, M is the ionic mass and Z_{i0} are the equilibrium positions. We assume that the oxygen motion corresponds to the zero vibrational state of the first term, and ν th level for the second term. Assume that $b(0) = 0$. The dependence $b(t)$ describes the dynamics of the charge transfer chain to plane (1 \rightarrow 2).

In the diabatic representation the transition between the terms is described by the matrix element V_{12} , where $V \equiv \hat{H}_r$. One can show that

$$V_{12} \simeq L_0 F_{12}, \quad (3)$$

where

$$L_0 = \int d\mathbf{r} \psi_2^*(\mathbf{r}, \mathbf{R}) \hat{H}_r \Psi_1(\mathbf{r}, \mathbf{R})|_{R_0} \quad (3')$$

is the electronic constant (R_0 correspond to the crossing configuration), and

$$F_{12} = \int \varphi_2^*(Z) \varphi_1(Z) dZ \quad (4)$$

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 function $b(t)$ is equal to (see Ref. 9, Ch. 6)

$$|b(t)|^2 = \bar{b}^2 \{1 - \cos 2[(\epsilon^2/4) + (\hat{H}_{r|12})^2]^{1/2} t\}, \quad (5)$$

where

$$\bar{b}^2 = \frac{L_0^2 F_{12}^2}{2[(\epsilon^2/4) + L_0^2 F_{12}^2]}. \quad (5')$$

The probability $[b(t)]^2$ oscillates according to Eq. (5). Its average value which corresponds to equilibrium doped state is equal to \bar{b}^2 [see Eq. (5)]. The asymmetry of the potential for the axial oxygen and correspondingly the inequality $\epsilon \neq 0$ are playing key roles. This is due to the asymmetry of the local field for the ion. In the opposite case when $\epsilon = 0$, the value of \bar{b}^2 is equal to 0.5 regardless of the value of F_{12} .

We assume a large asymmetry (see Fig. 1), so that $|L_0 F_{12}| \ll \epsilon$. Then the carrier concentration

$$n_{\text{pl}} \propto \bar{b}^2 = 2L_0^2 |F_{12}|^2 / \epsilon^2. \quad (6)$$

Since the matrix element $\hat{H}_{r|12} \propto F_{12}$ and the value of ϵ depends directly on the mass M , the carrier concentration also depends on M .

Let us focus now on the isotope coefficient $\alpha = -(M/T_c)(\partial T_c / \partial M)$. 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 Ref. 13) 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,

$$\alpha_2 = -\frac{M}{T_c} \frac{\partial T_c}{\partial n} \frac{\partial n}{\partial M}. \quad (7)$$

According to Eqs. (3) and (6) the dependence $n(M)$ is determined mainly by the Franck-Condon factor. Based on Eqs. (3), (4), and (7), and the dependence $\epsilon^2 \propto M^{-1}$ [therefore $n \propto M \exp(-sM^{1/2})$, $s = k^{1/2}c^2/2\hbar, (k^{1/2})^{-1} = k_1^{1/2} + k_2^{-1/2}$ where k_i are the elastic constants and c is the distance between the minima] we obtain the following expression for the isotope coefficient

$$\alpha_2 = \gamma \frac{n}{T_c} \frac{\partial T_c}{\partial n}, \quad (8)$$

where γ has a weak logarithmic dependence on M . Expression (8) 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., Refs. 4 and 5) and is well known. One can see from Fig. 2 that there is a good agreement with the data on the isotope

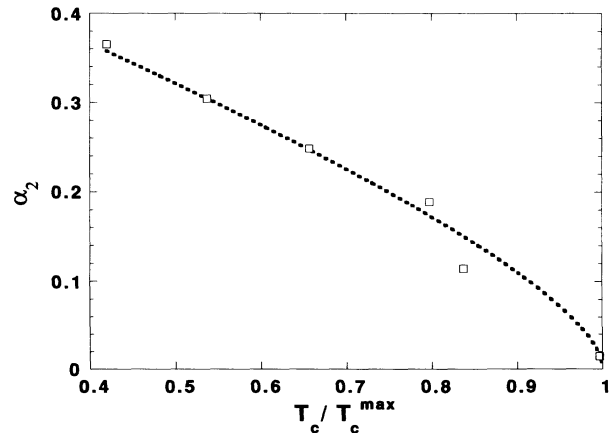


FIG. 2. The isotope coefficient α_2 plotted vs T_c/T_c^{max} . The dotted line is the theoretical curve [see Eq. (8)] with γ equal to 0.13 and the open squares are the experimental data from Ref. 3.

effect.

Equation (8) contains the derivative $\partial T_c / \partial n$. Since T_c has a maximum at some value $n = n_{\max}$, 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.

Let us make several comments. Continuous doping leads not only to an increase in concentration n , but to a change in electronic terms; the structure of the terms becomes less asymmetric. This is reflected in the movement of the average position of the axial oxygen towards the plane. This motion is experimentally observed.¹⁴ Such an evolution leads to an additional decrease in the value of α . We will discuss this question in more detail elsewhere.

The second comment is related to the overdoped region. Our analysis described above is applicable to a single phase system, that is for the underdoped region of the phase diagram. Structural transitions can drastically modify this picture. If the overdoped region corresponds to the same phase as the underdoped region (probably, this is the case for Bi-Pb-Ca-Sr-Cu-O), then in the region $n > n_{\max}$, the isotope coefficient should become negative; such an effect indeed, has been observed in Ref. 3. How-

ever, if the region $n > n_{\max}$ is a multiphase compound, then the picture described above can be used for $n < n_{\max}$ only. Finally one should note that according to our model the values of α are not limited by a maximum of 0.5 and may exceed this value. The unusually large isotope effect observed in 2:1:4 compounds^{1,3} for O and Cu can also be due to nonadiabaticity of the ionic motion and the consequent dependence of n on M .

In summary, we describe an effect of the isotopic substitution on T_c . It is interesting that this effect is not related directly to the mechanism of the pairing. A strong nonadiabaticity 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 nonadiabaticity 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.

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