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ON THE DEPRESSION OF T_c OF $REBa_2Cu_3O_{7-\delta}$ (RE = Y, Er) DUE TO NI^{2+} SUBSTITUTION INTO THE Cu(2) SITES. (s + d)-WAVE MODEL INTERPRETATION

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ABSTRACT

*The depressions of the T_c's of two ç123é $ReBa_2Cu_3O_7$ (Re = Y, Er) HTSC's due to magnetic (Ni^{2+}) transition metal substitution into the Cu(2) layer are studied. Special attention is paid to the difference in the orthorhombicity (**D** = (**b**-**a**)/**a**, where **a** and **b** are the lattice parameters in the basal plane) of the two superconductors. It is observed that the rate of depression dT_c/dx for the çY-123é HTSC is slightly steeper than that for the çEr-123é HTSC. The difference in the rates of depression is explained in terms of a connection between the orthorhombicity and the superconducting state. It is assumed that the orthorhombic distortion induces a change in the pairing interaction. The modification of the pairing interaction leads to a new superconducting state in which order parameter (**OP**) has (**s** + **d**)-wave symmetry.*

I. INTRODUCTION.

Shortly after the discovery of 90 K superconductivity in the $YBa_2Cu_3O_{7-y}$ high temperature superconductor (HTSC),[1] different groups[2] studied the replacement of the Y ions by rare earth (RE) ions. When it was reported that the T_c's did not change in any systematic way, the conclusion was drawn that superconductivity in the HTSC's was two dimensional in nature and that the pair condensation occurred in the planar CuO_2 layer. Since several of the RE ions are magnetic, the absence of any apparent differences between these "RE-123" HTSC's and the $YBa_2Cu_3O_{7-y}$ HTSC was taken as evidence there was not much interaction between the Y or RE ions and the carriers in the CuO_2 layer. Other groups[3] chose to study the replacement of the Cu ions in this ("123") and other HTSC's by other transition metal ions, both magnetic (Ni^{2+}, Fe^{3+} and Co^{3+}) and non magnetic (Zn^{2+} and Al^{2+}) ions. The investigators of refs. 3 found that both the magnetic and non magnetic TM ions substitutions suppress the superconductivity. The suppression of the T_c's by non magnetic Zn^{2+} was surprising since in conventional superconductors, non magnetic ion doping has negligible effects on the superconducting state.[4] The suppression of T_c in the "123" HTSC by Zn^{2+} ion substitution is even greater than that due to Ni^{2+} ion substitution.[5] This was the first indication that the el-ph interaction was not responsible for the pair condensation in the HTSC's.

Another discovery which clearly indicated that pair condensation in the HTSC's was not due to the el-ph interaction was the observation that the order parameters (OP) of the HTSC's exhibited d-wave symmetry.[6,7] This requires a new mechanism be responsible for superconductivity in the HTSC's since the el-ph interaction leads to an OP of s-wave symmetry. This lead Monthoux and Pines[8] (MP) to propose that the pair condensation in the HTSC was due to the exchange of the antiferromagnetic spin fluctuations (SF) which occurs in the 2D CuO_2 plane. The exchange of these SF leads uniquely to a superconducting state of d-wave symmetry. The theory also accounted for the difference in the relative magnitude of the depressions of the T_c's due to Ni^{2+} and to Zn^{2+} substitutions. In this theory, the Zn ions disrupts the propagation of the SF in the 2D plane and thus affects the mechanisms responsible for the pair condensation while the magnetic Ni ions breaks the pairs **after** they are formed. In the first instance, the influence on the superconducting state is a direct one while in the second instance, the influence is an indirect one.

The recent discoveries[9] that the OP of $YBa_2Cu_3O_{7-y}$ HTSC contains a s-wave component requires a change in the SF-induced pairing mechanism in the MP theory. A basic principle in physics is that any potential or interaction existing in a space must be invariant under the group operations which leave the space invariant. One of the reasons for MP to propose the exchange of SF as being the mechanism responsible for superconductivity in the HTSC's is that the SF-induced pairing interaction would have the symmetry of the CuO_2 layer, i.e., tetragonal symmetry. The orthorhombic distortion of the crystal structure occurring in the "123" perovskite ceramics would be expect to induce a change in the symmetry of the pairing interaction so that it remains invariant under the new symmetry operations for the new structure.

One of the present authors (IMT) has used this idea to find the dependence of the T_c's of the "RE-123" HTSC's on the orthorhombicity of the RE ions.[10] As mentioned earlier, the first sets of measurements of the T_c's of the "RE-123" HTSC did not reveal any dependence on the size of the RE ions. These measurements were done on specimens for which the hole concentrations was not monitored. Later sets of measurements[11] on specimens for which the oxygen content or hole concentration were kept constant revealed a dependence of the T_c's on the size of the RE ions. The rare earth ion size and the orthorhombicity are related to each other. The orthorhombic distortion in the "123" occur when O^{2-} ions are removed from sites in the **a** direction of the third CuO_2 layer in the triple perovskite $YBa_2Cu_3O_8$. The removal of these ions leaves behind 1D CuO chains in the **b** direction. The chains then collapse towards each other, thus causing the **a** lattice parameter to be smaller than the **b** lattice parameter. Substitution of larger Re ions arrest the collapse of the chains towards each other and thus effect the degree of orthorhombicity.

Tang *et al.*,[12] recently extended the ideas used ref. 10 to find a rare earth ion size dependence of the rates of depression of T_c due to TM ion substitution. That work was motivated in part by a study of Sumana Prabhu and Varadaraju[13] on the suppression of superconductivity in $REBa_2Cu_{3-x}M_xO_7$ (RE = Sm and Dy) by Fe, Ni and Zn substitution. We wish to report our study of the depression of T_c's of $YBa_2Cu_{3-x}M_xO_7$ and $ErBa_2Cu_{3-x}M_xO_7$ due to Ni^{2+} substitution. Only Ni^{2+}substitution is considered here since Co^{3+} and Fe^{3+} ions enter preferentially into the Cu(1) sites in the 1D CuO chain and the special scattering process proposed for Zn^{2+} in the Monthoux and Pines theory is still controversial. We will explain our findings in terms of the modification of the pairing interaction induced by the orhorhombic distortion occurring in the "123" ceramics as oxygen is removed from O sites located in the direction of the **a** lattice.

II. EXPERIMENTAL DETAILS AND RESULTS.

The high temperature superconductors were prepared by the standard ceramic method. Stoichiometric amounts of ER_2O_3, Y_2O_3, $BaCO_3$, CuO and NiO were carefully weight and mixed in a aggate motar to obtain the two series, $YBa_2Cu_{3-x}Ni_xO_7$ and $ErBa_2Cu_{3-x}Ni_xO_7$ (x =

0.0, 0.004, 0.008, 0.010 and 0.015). The mixtures were calcinated at 920 C for 24 hrs. They were then reground and pressed into pellets of approximately one cm in diameter and 2 mm in thickness. These were then sintered in a furnace at 920 C for another 24 hrs., after which they were cooled to room temperature in a flowing O_2 atmosphere at the rate of 1°C/min. The proper hole concentrations were achieved during the slow cooling down cycle. XRD patterns were obtained on each specimens. The temperatures were monitored with a carbon glass thermometer. The resistivities were measured using the standard four probe method. T_c is defined as the temperature at which the resistance extrapolates to zero.

The results of the determination of the lattice parameters **a** and **b** for the specimens are listed in Table 1. As we see, there are small changes in these parameters (at the third decimal place) as the Ni^{2+} ions are initially added. The orthorhombicity were calculated and range from 1.522 to 1.841 (x 10^{-2}) for the (pure and doped) $YBa_2Cu_3O_7$ and from 1.532 to 1.862 for the (pure and doped) $ErBa_2Cu_3O_7$. The averaged orthorhombicities were 1.756 and 1.731, respectively and differ by only 1.4%. Sumana Prabhu and Varadaraju[13] report that the **a** and **b** lattice parameters in the çSm-123é ceramics changed rapidly as Ni^{2+} was added. The orthorhombicity D decreased monotonically, going to zero at x = 0.6. The çDy-123é ceramic remained orthorhombic throughout the entire Ni doping range. For Ni concentrations below 0.04, the orthorhombicities of the "Dy-123" ceramics varied only slightly. Since the impurity concentrations used in our study are very low, we did not expect to see any evidence of any O-T transition, even if one were to occur.

The measured T_c's of the "Y-123" and "Er-123" HTSC are 94.4 K and 91.3 K, respectively. The relative order of the T_c's of the "Er-123" and "Y-123" HTSC's, i.e., $T_{c,Er\text{-}123} < T_{c,Y\text{-}123}$, is consistent with the observations made in refs. 11. Interestingly, the T_c's of the host "Re-123" HTSC's reported by Sumana Prabhu and Varadaraju[13] (SV) did not exhibit any dependence on the rare earth ions, i.e., they were all the same (about 90 K). We have pointed out this may be due to variability of the hole concentration in the superconductors. On Figs. 1a and 1b, we show the depression of the T_c's of these two HTSC's as Ni^{2+} ions are substituted into the Cu(2) sites. As is seen, the decreases of the T_c's of both the "Y-123" series and the "Er-123" series are characterized by a rapid initial decrease, followed by an almost linear decrease as x (Ni content) is increased from 0.002 to 0.008. In these portions of the curves, the rates of decrease due to Ni^{2+} substitution, dT_c/dx, is 2.29 K/at.% for the "Y-123" series and is 2.16 K/at.% for the"Er-123" series. Our results on the relative magnitudes of the rates of decrease, i.e., $dT_c/dx_Y < dT_c/dx_{Er}$ due to Ni substitutions, are consistent with the results of ref. 13. SV looked at the effects of TM impurity substitution into the $REBa_2Cu_{3-x}M_xO_7$ (RE = Sm and Dy; M = Fe, Ni and Zn) HTSC's. They found that the rates of decrease of the T_c's due to the three TM impurities for the "Sm-123" HTSC were greater than the rates of decrease for the "Dy-123" HTSC. These decreases inturn are less than those of the "Nd-123" HTSC but higher than those for the Y-123. SV quote a value of 3 K/at.% for the rate of depression of T_c due to Ni substitution into the "Y-123" HTSC. (Note: our value is 2.29 K/at.%). The decrease in the ionic radii of Nd, Sm, Dy and Y goes as 1.109 A, 1.079 A, 1.027 A and 1.019 A. The radius of the Er ion is smaller than that of Y and so the relative magnitude of the rate of decrease due to Ni^{2+} fits into the trend seen by SV. Sumana Prabhu and Varadaraju could only conjecture on the reasons for the Re ion size effect of the rates of decreases in the T_c's due to the 3d substitution.

III. THEORETICAL ASPECTS.

As we have pointed out, the orthorhombic distortion which occurs in the "Re-123" HTSC's induces a modification of the tetragonal spin-fluctuation pairing interaction. Such a modification could be[10]

$$V_{pair}(\mathbf{q},\mathbf{q}';\omega) = V_{SF} + \alpha(D)\{ V_{ani}[\eta(\mathbf{q}) + \eta(\mathbf{q}')] + V_{iso} \} - \mu \tag{1}$$

where V_{SF} is the spin fluctuation-induced pairing interaction in the MP theory; V_{ani}, an non separable anisotropic interaction induced by the orhorhombic distortion; V_{iso}, the isotropic pairing interaction also induced by the distortion and which gives rise to the s-wave component of the OP; $\alpha(D)$, a parameter which depends on the orthorhombicity D and which is zero in the absence of the orthorhombic distortion. $\eta(\,)$ is a basis function for a representation of the crystal symmetry group. μ is the Coulomb repulsion term and will be neglected in all further calculations.

The order parameter (**OP**) as in any theory of superconductivity is defined as

$$\Delta(\mathbf{k},\omega_n) = 2\pi T\Sigma\int \frac{dS\mathbf{p}}{8\pi^3 V_F} \; V_{pair}(\mathbf{k}\text{-}\mathbf{p};\omega_n\text{-}\omega_m) \; \frac{\Omega\,(\mathbf{p},\omega_m)}{\sqrt{(|\omega_m|^2 + |\Omega|^2)}} \tag{2}$$

with Ω being the renormalized energy gap and dS_p denoting an integration over the Fermi surface. To obtain an (**s** + **d**)-wave symmetry state, we assume that the order parameter and energy gap can be written in the form

$$\Delta(\mathbf{k},\omega_n) = \Delta_s(\omega) + \Delta_d(\omega)\eta(\mathbf{k}) \tag{3a}$$

and

$$\Omega(\mathbf{q},\omega) = \Omega_s(\omega) + \Omega_d(\omega)\eta(\mathbf{q}). \tag{3b}$$

Substituting the pairing interaction given by eqn. (1) and the above two eqns. (3a) and (3b) into eqn. (2), we obtain a set of coupled equations for Δ_s and Δ_d, which can be solved. Joynt and coworkers[14] showed that in the absence of the orthorhombic distortion, the (**s** + **d**)-wave state was an unstable one and that the stable state was the (**s** + **id**)-wave state. Beal-Monod and Maki[15] showed at both the microscopic and macroscopic level that the (**s** + **d**)-wave state is possible in the presence of an orthorhombic distortion. The question of which mixed wave symmetry state best describes the HTSC is now the object of much current interests. Recently, Modre *et al.*,[16] suggested that an investigation of the low temperature behavior of the London penetration depth λ_L might be a possible way to differentiate between an orthorhombic distorted HTSC having an (**s** + **id**)-wave symmetry OP and one having an (**s** + **d**)-wave symmetry OP.

The effects of the spin flip scattering off the magnetic moments formed on the Ni^{2+} ions can be easily incorporated into the Eliashberg Equations by writing out the one-loop corrections to the off diagonal energy

$$W(\mathbf{q},\omega) = Z(\omega)\Omega(\mathbf{q},\omega) = \Delta(\mathbf{q},\omega) + n_i \int \frac{dS_{\mathbf{k}}}{8\pi^3 V_f} \{ |U_n(\mathbf{q}\text{-}\mathbf{k})|^2 - |U_s(\mathbf{q}\text{-}\mathbf{k})|^2 \} \frac{\Omega(\mathbf{q},\omega)}{|\omega_n|} \,. \tag{5}$$

where $U_{n(s)}$ are the normal (spin flip) scattering potential and n_i is the concentration of the magnetic impurities. The corrections to the diagonal energy yields

$$Z(\omega) = 1 + \alpha(D)V_{iso} + n_{2i}\tau_n \{\frac{1}{2\tau_n} + \frac{1}{2\tau_s}\} \frac{1}{|\omega|} \,. \tag{6}$$

where the two scattering life times are defined as

$$\frac{1}{2\tau_{n(s)}} = \iint \frac{dS\mathbf{p}}{8\pi^3 V_f}\,\frac{dS\mathbf{k}}{8\pi^3 V_f}\,|U_{n(s)}(\mathbf{p}-\mathbf{k})|^2 \tag{7}$$

Following the steps in ref. 10, we arrive at the following expression for the rate of depression of T_c of an (**s** + **d**)-wave HTSC due to substitution of magnetic ions into the Cu(2) sites

$$\frac{dT_c}{dx} = \frac{\pi}{4} C^{-1}\{(\frac{g_{sf}\chi J}{1+\chi J})\, a_d - \alpha(D)\, B\} \tag{8}$$

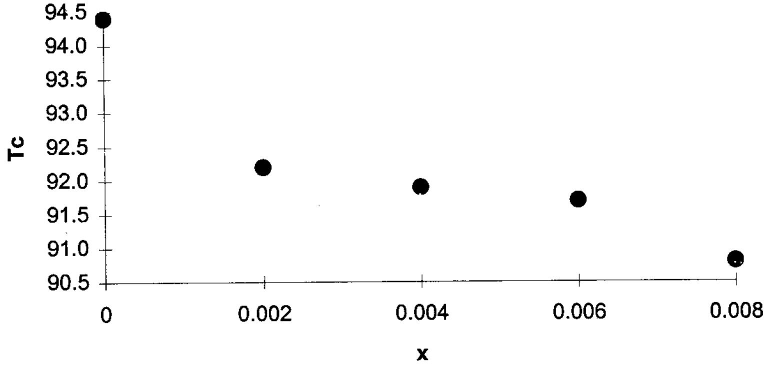
where the constants C and B depend on the various parameters which characterize the SF-mediated HTSC and which are given in refs. 10 and 12. a_d is the pair breaking parameter which appears in the Abrikosov-Gorkov theory. The exact forms of C and B are not important for the present analysis other than to say that in the limit that (D) →0, eqn. (8) reduces to the standard expression for the depression of T_c due to pair breaking.

IV. DISCUSSION.

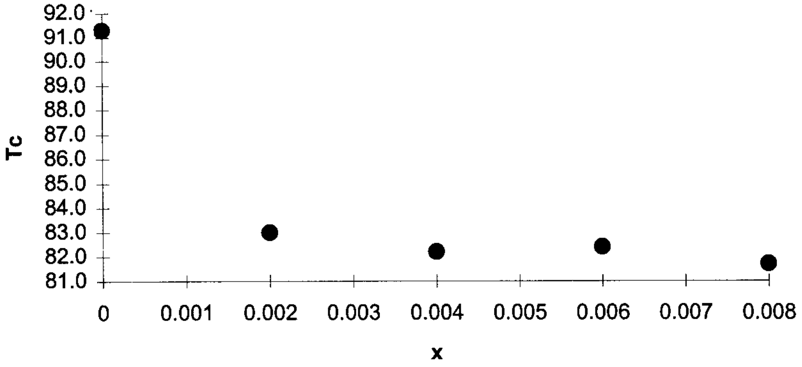
In their study, Sumana Prahbu and Varadaraju[13] state "*it appears at the outset that superconductivity is independent of the R ion*" yet go on to say that the suppression rate due to a given impurity "*ion depend on the ionic size of the rare earth (R), higher for larger R ions.*" They then go on and mention several possible causes of the rare earth size dependences. However, they did not come to any definte conclusions about the causes. Looking at eqn. (8), we note that the slope predicted by eqn. (8) is lowered by increasing the value of the orthorhombicity parameter (D). If our assumption that the substitution of larger rare earth ions into the layer inbetween the double CuO_2 retards the collapse of the CuO chains towards each other is correct, then our results from ref. 10 explains the rare earth size effect in the T_c's of the "RE-123" HTSC's and eqn. (10) of this work explains the rate earth size effect in the suppression rates dT_c/dx due to magnetic ion substitution in the Cu(2) sites of the "RE-123" HTSC's.

Table 1 Lattice Parameters.

$YBa_2Cu_{3-x}Ni_xO_{7-\delta}$	**a(A)**	**b(A)**	**(b-a)/a (10^{-2})**
x = 0.000	3.8076	3.8772	1.828
0.002	3.8071	3.8772	1.841
0.004	3.8170	3.8751	1.522
0.006	3.8133	3.8812	1.781
0.008	3.8235	3.8929	1.807
$ErBa_2Cu_{3-x}Ni_xO_{7-\delta}$			
x = 0.000	3.8179	3.8808	1.655
0.002	3.8125	3.8804	1.784
0.004	3.8076	3.8785	1.862
0.006	3.8102	3.8797	1.824
0.008	3.8250	3.8836	1.532



1a.



1b.

Fig.1 Depression of T_c. 1a. Of $Yba_2Cu_3O_{7-\delta}$ due to Ni^{2+} substitution into Cu (2) sites. 1b. Of $ErBa_2Cu_3O_{7-\delta}$ due to Ni^{2+} substitution.

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