J.Sci.Soc.Thailand, 23(1997) 359-369

EXPERIMENTAL STUDIES ON THE EFFECTS OF TRANSITION METAL DOPING IN OVERDOPED "2212" BISMUTH SUPERCONDUCTORS

S. LEELAPRUTE,[a] I.M. TANG[a,b] AND T. OSOTCHAN[a,b]

[a] *Department of Physics, Faculty of Science, Mahidol University, Bangkok 10400, Thailand.*

[b] *Institute of Science & Techology for Research & Development Salaya Campus, Nakorn Pathom 73170, Thailand.*

(Received 28 November 1997)

ABSTRACT

The depression of the T_c's of overdoped "2212" bismuth superconductors due to transition metal (TM) substitution is studied. Single phase $Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2-x}TM_xO_{8+y}$ (TM = Zn, Fe, Ni and Co) superconductors with varying hole concentrations were obtained by quenching in liquid nitrogen, superconducting pellets being annealed at different temperatures. It is seen that the T_c's decrease linearly with increasing substitution (once the influence of the varying hole concentration is taken into consideration) of the TM impurities. The rates of depression of T_c due to non magnetic Zn^{2+} substitution and to magnetic Ni^{2+} substitutions are nearly the same. The magnitudes of the rates of depression dT_c/dx caused by different magnetic TM ion substitutions appear to scale with the square of the magnetic moments formed on the ions. These behaviors are explained in the context of the spin fluctuation induced theory for high temperature superconductors.

I. INTRODUCTION

In conventional superconductors, doping with non magnetic impurities have little or no influence on the superconducting state.[1] Rapid suppression of superconductivity is however seen when magnetic transition metal (TM) impurities are substituted into the host superconductor.[2] The magnetic moments formed on these ions can flip one of the spins in the Cooper pair, thus breaking the pair. It was therefore surprising when it was observed that non magnetic Zn ion substitution into $YBa_2Cu_3O_{7-y}$ lead to a strong decrease of T_c, the rate being dT_c/dx = -17 K/at %.[3] This rate of decrease was greater than those due to magnetic TM ion substitutions. The rates of decreases for Fe, Ni or Co ion substitutions were -(3-5) K/at. %, -3 K/at.% and -1 K/at. %, respectively.[4,5] Usually, only the rates of decrease due to Zn^{2+} and Ni^{2+} ion substitutions are compared with each other since these two ions substitute into the Cu(2) sites in the planar CuO_2 sheets. The other two TM ions substitute preferentially into the Cu(1) sites in the 1D CuO chains in the "123" structure.[6] The cause of the greater suppression by Zn ions over that of Ni ions has been a matter of controversy.

In the spin-fluctuation induced superconductivity theory of Monthoux and Pines (MP),[7] the greater suppression of superconductivity by Zn^{2+} substitutions is due to the more effective way the non magnetic ions affect the superconducting state. Superconductivity in this theory arises from the exchange of spin fluctuations. Due to its complete shell configuration ($3d^{10}$), the substitution of Zn onto a Cu(2) site in the planar CuO_2 layer disrupts the local magnetic ordering and this inturn suppresses the spin fluctuations whose exchange is responsible for the pair formation. The Zn ions also act as potential scatterers, giving rise to non spin flip scattering. Magnetic TM impurities on the other hand do not disrupt the hopping. They only lead to changes in the rate of hopping of the spin between the sites. This would lead to slight modification in the excitation spectrum of the spin fluctuations. Their main effects on the system would arise from their role as scattering centers (for both normal scattering and spin flip scattering). In the anisotropic system, which all HTSC's are, normal scattering behave as a pair breaking parameter.[8]

The MP theory is based on a description of the underlying system as a nearly antiferromagnetic Fermi liquid. Millis, Monien and Pines [9] showed that this description of $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$ ceramic system could account for the observed normal state NMR relaxation rate and the nearly linear temperature dependence of the normal state resistivity. Using the spin susceptibility functions obtained in ref.9, the MP theory predicts a T_c of 90 K for $YBa_2Cu_3O_{6.93}$ and a T_c of 38 K for $La_{1.85}Sr_{0.15}CuO_4$. This theory also leads uniquely to a d-wave symmetry of the order parameter, for which experimental evidences exist for these two HTSC's.[10] Finally, the stronger depression of T_c by non magnetic TM ion doping is accounted for in this theory.

We wish to report in this paper, the details of our study of the depression of the T_c's in over doped $Bi_{1.55}Pb_{0.45}Sr_2CaCu_2O_{8+y}$ HTSC, caused by the replacement of Cu ions by non magnetic Zn ions and by magnetic Ni, Fe and Co ions. Since there is only one type of Cu sites, in the bismuth compound, we will be able to compare the rates of depression due to all substitutions. In a recent study,[11] the present authors have combined the approach of Millis, Sachdev and Varma[8] to treat the anisotropy in the HTSC's with the spin fluctuation induced theory of Monthoux and Pines[7] to study the effects of both non magnetic TM impurities and magnetic TM impurities on the T_c's of the HTSC's. By making several simple approximations, it was possible to obtain analytic expressions for the effects of the impurities on the T_c's of these superconductors. The results on the decreases in the T_c's of the "123" HTSC due to Zn^{2+} or Ni^{2+} substitutions were obtained in ref. 7 by numerically diagonalizing a matrix eigenvalue equation.

In ref. 11, we obtain expressions for the rates of decrease of the T_c due to both non magnetic TM ion substitution and magnetic TM ion substitutions. We find that the decrease due to non magnetic ion substitution is due to two mechanisms, one due to the pair breaking by the normal scattering process in anisotropic superconductor and another related to the suppression of the spin fluctuations by the non magnetic TM ions. The decrease due to magnetic TM ion substitution was also found to be due to two mechanisms, the pair breaking by the normal scattering process in an anisotropic host and the pair breaking due to the spin flip scattering by the magnetic moment formed on the impurity ion. The latter contribution to the decrease scales with the square of the magnetic moment formed.

We have carefully monitored the hole concentration in the HTSC's fabricated in this study since it is well established that the T_c's depend on the hole concentration. Whangbo and Torardi[12] observed that the T_c's of the $La_{2-x}Sr_xCuO_4$ HTSC exhibit an inverted parabolic dependence on the hole concentration in the planar CuO sheet. Summarizing the data in the literature on the hole dependence of the T_c's of most HTSC's Tallon *et al.*[13] found that the normalized T_c (obtained by dividing the observed T_c by the T_c at optimal doping) fitted an universal inverted parabolic curve. Zhang and Sato[14] gave the ranges of the underdoped, optimal doped and overdoped regions as; $0.06 < N_h < 0.12$, $0.12 < N_h < 0.25$ and $0.25 < N_h < 0.31$, respectively. The reason for this differentiation is that it is now recognized that the underdoped, optimal doped and overdoped specimens behave differently.[14,15] A HTSC is defined to be in the undoped region if its T_c is raised by increasing the hole concentration and similarly, it is defined to be overdoped if the T_c is lowered. We are interested here in the overdoped region. Bernhard *et al.*,[16] has pointed out that in this region, the dynamics of the carriers appears to become more three dimensional and they might be expected to exhibit Fermi liquid behavior. Babushkina *et al.*[17] and Kluge *et al.*,[18] have used the Abrikosov-Gorkov (AG) expression for the suppression of superconductivity due to pair breaking by paramagnetic impurities to analyze their data on $La_{2-y}Sr_yCu_{1-x}M_xO_4$ (M = Fe, Co and Ni; y = 0.15 and 0.20) and on $Bi_2Sr_2Ca_{1-y}Y_y(Cu_{1-x}M_x)_2O_{8+z}$ (M = Fe, Co and Ni; y = 0.0 and 0.30), respectively.

II. EXPERIMENTAL DETAILS AND RESULTS.

Superconducting pellets of the $Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2-x}TM_xO_{8+y}$ (TM = Fe, Co and Ni) composition were obtained using standard ceramic fabrication techniques. Lead was added to facilitate the formation of single phase "2212" specimens. By heating the calcinated pellets at different temperatures (830°C, 835°C, 840°C and 845°C) close to the melting points for over forty hours and then quenching them immediately in liquid nitrogen, the hole concentrations were varied. This quenching freezes in the oxygen content at the level they were at during the annealing.[19] The potentiometric titration method was used to determine the copper valencies since the presence of bismuth iodate prevents the accurate determination of the end point of the standard iodometric titration method. The XRD patterns were obtained on a Philips Analytical Diffractometer with a monochromator using the Cu K_α line. Standard four probe method was used to measure the resistivity, with the T_c defined as the point at which the resistance goes to zero.

The XRD patterns of specimens exhibit peaks belonging to the two layer phase of the bismuth superconductors. None of them show the presence of a peak at $2\theta = 7.2°$ (indicative of the n = 1 phase) nor at $2\theta = 24°$ and 26° (indicative of the n = 3 phase)). The pattern of one of the specimens fabricated, $Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2.995}Zn_{0.005}O_{8+y}$ annealed at 835 C is shown in Figure 1. The strong peak at $2\theta = 6°$ clearly indicates that the structure is that of the n = 2 layer "2212" bismuth HTSC. The other peaks have been indexed to the orthorhombic structure. A least square best fit of these peaks yield **a** = 5.3812 Å, **b** = 5.3833 Å and **c** = 31.1381 Å. The same best fit of the peaks in the XRD patterns of the other specimens yields the lattice parameters given in TABLE 1. Systemmatic changes are seen in the values of the **c** lattice parameter, but not in the values of the **a** and **b** parameters. Looking at the **c** parameter values for the $Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2-x}Fe_xO_{8+y}$ specimen annealed at 835 C, we find that the values decreasing as the Fe content increases. Since the ionic radius of Fe^{3+} ion is smaller than the radius of Cu^{2+} ion it replaces, the decrease is expected.

The oxygen contents were determined by charge balancing assuming that Bi is in the 3^+ state, Pb is in the 2^+ state and the Cu valency is that determined by potentiometric titration. The levels of substitutions (less then 3%) are low enough to maintain the original structure.[6] The values of the Cu valencies and T_c's of other specimens are given in TABLE 2. The observed T_c's are well below the highest T_c seen in the bismuth "2212" superconductors. Groen *et al.*,[20] reported the maximum T_c seen in the bismuth "2212" superconductors was above 90 K and that their valencies were close to 2.20, the same as those of the 94 K bismuth superconductors previously fabricated in our laboratory.[19] Most of specimens fabricated in this study are in the overdoped regime.

The R versus T curve for the $Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2.995}Zn_{0.005}O_{8+y}$ superconductor annealed at 835 C is shown in Figure 2. By extrapolating the drop to T = 0 K, we obtain a T_c of 89 K. The values of the T_c's of the other specimens were obtained in the same way and are listed

Table 1 Lattice Parameter c, T_c and Oxygen Content of Several Bismuth Superconductors.

Composition c	Annealing Temperature	T_c (K)	Oxygen Content	 (A)
$Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2-x}Fe_xO_{8+y}$				
x = 0.005	840 C	89	8.12	31.1819
x = 0.015	840 C	84	7.92	31.1748
x = 0.020	840 C	79.5	8.06	31.1469
x = 0.030	840 C	< 77	8.02	31.1658
$Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2-x}Co_xO_{8+y}$				
x = 0.005	830 C	86	8.10	31.0920
x = 0.005	835 C	88.5	8.11	31.1211
x = 0.005	840 C	89	8.15	31.1256
x = 0.005	845 C	87	8.14	31.1469

		Lattice Parameters a	 b	 c
$Bi_{1.55}Pb_{0.45}Sr_2CaCu_{1-x}Zn_xO_{8+y}$				
x = .005	830 C	5.3766	5.3850	31.0962
	835 C	5.3812	5.3853	31.1381
	840 C	5.3711	5.3724	31.0014
	845 C	5.3770	5.3841	31.1338
x = .015	845 C	5.3829	5.3771	31.1042
x = .020	835 C	5.3749	5.3783	31.0592
x = .030	835 C	5.3777	5.3863	31.1316
$Bi_{1.55}Pb_{0.45}Sr_2CaCu_{1-x}Ni_xO_{8+y}$				
x = .005	830 C	5.3806	5.3790	31.0998
	840 C	5.3728	5.3692	31.0644
x = .010	845 C	5.3808	5.3779	31.1452
x = .015	845 C	5.3829	5.3771	31.1042
x = .020	835 C	5.3847	5.3783	31.0796
	845 C	5.3824	5.3791	31.1377

Table 2 Copper Valency and Transition Temperatures of the Magnetic Ion Substituted Bismuth Superconductors.

Composition	Annealing Temperature	Copper Valency	T_c
$Bi_{1.55}Pb_{0.45}Sr_2CaCu_3O_{8+y}$			
	830 C	+ 2.319	88.5 K
	835 C	+ 2.313	87.5 K
	840 C	+ 2.315	83.5 K
$Bi_{1.55}Pb_{0.45}Sr_2CaCu_{3-x}Fe_xO_{8+y}$			
x = 0.005	830 C	+ 2.311	87.5 K
	835 C	+ 2.222	86.0 K
	840 C	+ 2.345	89.0 K
	845 C	+ 2.254	89.0 K
x = 0.010	830 C	+ 2.409	85.5 K
	835 C	+ 2.168	82.0 K
	840 C	+ 2.173	85.0 K
x = 0.015	830 C	+ 2.229	85.5 K
	835 C	+ 2.311	83.0 K
	840 C	+ 2.139	84.0 K
	845 C	+ 2.158	81.5 K
x = 0.020	830 C	+ 2.204	<77.0 K
	835 C	+ 2.348	<77.0 K
	840 C	+ 2.273	79.5 K
x = 0.030	835 C	+ 2.335	<77.0 K
	840 C	+ 2.230	77.0 K
$Bi_{1.55}Pb_{0.45}Sr_2CaCu_{3-x}Ni_xO_{8+y}$			
x = 0.005	835 C	+ 2.047	87.5 K
	840 C	+ 2.328	85.0 K
x = 0.010	830 C	+ 2.382	85.5 K
	835 C	+ 2.153	86.0 K
	845 C	+ 2.205	86.5 K
x = 0.015	830 C	+ 2.225	84.0 K
	835 C	+ 2.350	84.0 K
	845 C	+ 2.262	86.5 K
x = 0.020	835 C	+ 2.298	81.5 K
	845 C	+ 2.120	86.5 K
x = 0.030	835 C	+ 2.301	80.0 K
	845 C	+ 2.391	85.0 K
$Bi_{1.55}Pb_{0.45}Cu_{3-x}Co_xO_{8+y}$			
x = 0.005	830 C	+ 2.315	86.0 K
	835 C	+ 2.329	88.5 K
	840 C	+ 2.375	89.0 K
	845 C	+ 2.361	87.0 K
x = 0.010	830 C	+ 2.380	85.5 K
	835 C	+ 2.381	86.5 K
	840 C	+ 2.420	83.5 K
x = 0.015	830 C	+ 2.245	82.5 K
	835 C	+ 2.231	85.0 K
	840 C	+ 2.318	82.0 K
	845 C	+ 2.117	83.5 K
x = 0.020	830 C	+ 2.255	79.5 K
	835 C	+ 2.283	83.0 K
	840 C	+ 2.210	83.0 K
x = 0.030	835 C	+ 2.368	<77.0 K
	840 C	+ 2.352	79.5 K

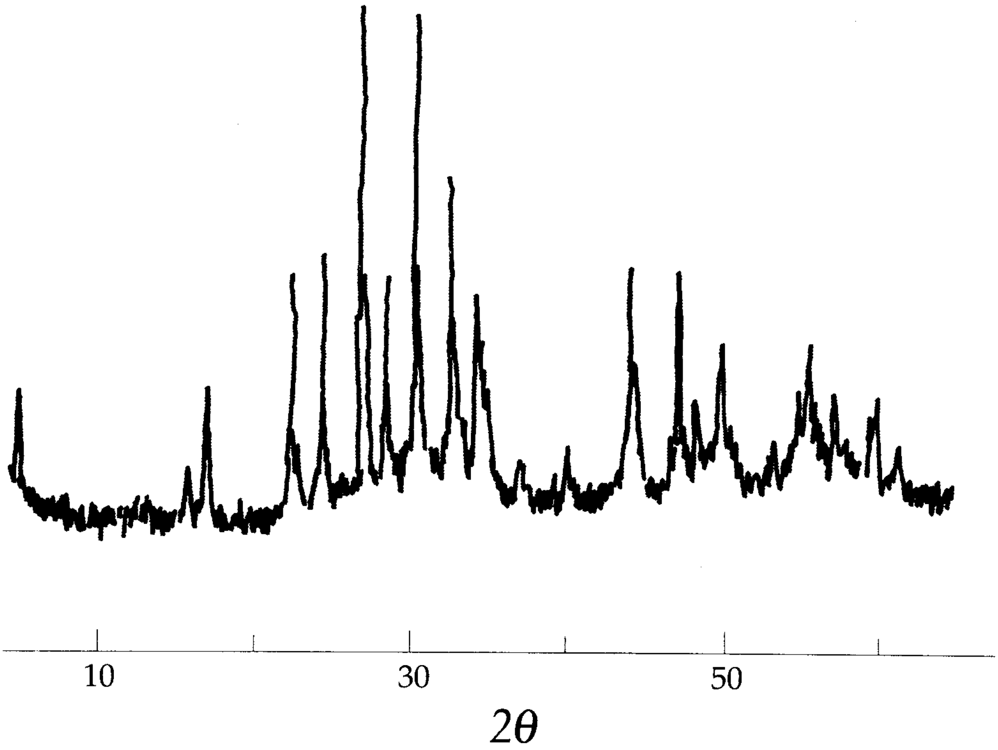

Fig. 1 XRD Pattern of the $Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2.98}Zn_{0.02}O_{+y}$ Specimen Annealed at 835 C. The peak at 2θ = 6° is indicative of the n = 2 layer bismuth superconductor. The other peaks were indexed to the orthorhombic "2212" structure.

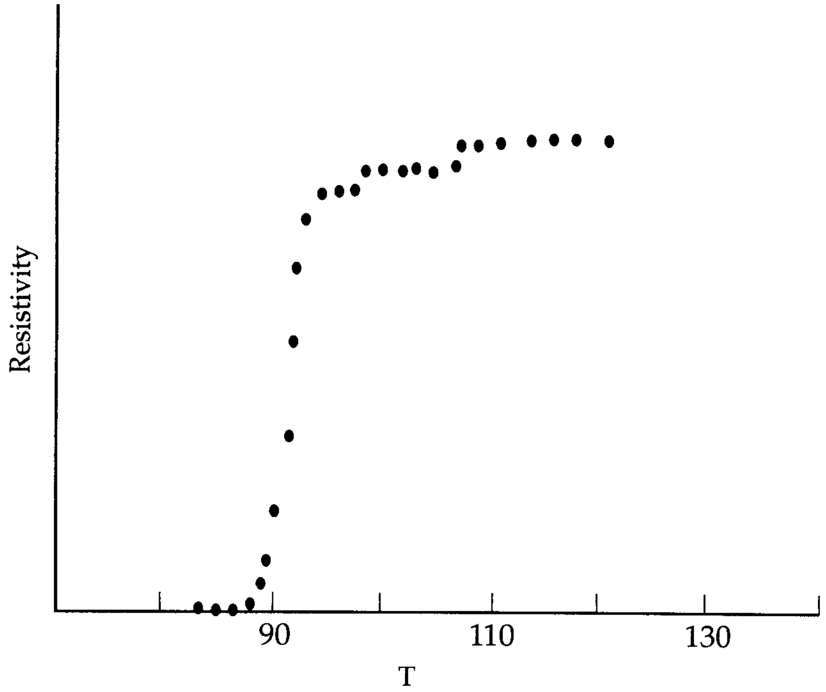

Fig. 2 Resistivity Curve for the $Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2.98}Zn_{0.02}O_{8+y}$ Specimen Annealed at 835 C. The extrapolation of the curve to R = 0 yields a T_c of 81.5 K.

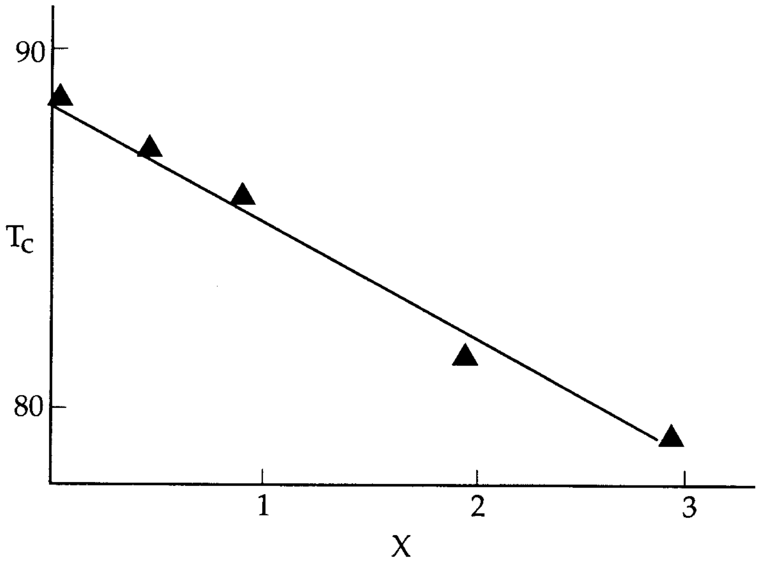

Fig. 3 Normalized Transition Temperature (T_c/T_{c0}) of the Two Lay-er Superconductor $Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2-x}Zn_xO_{8+y}$. The measured values of the T_c's of Zn doped "2212" HTSC having hole concentrations of approximately 2.36 + .02 indicate a rate of supression of T_c, dT_c/dx = - 3.2 K/at. %.

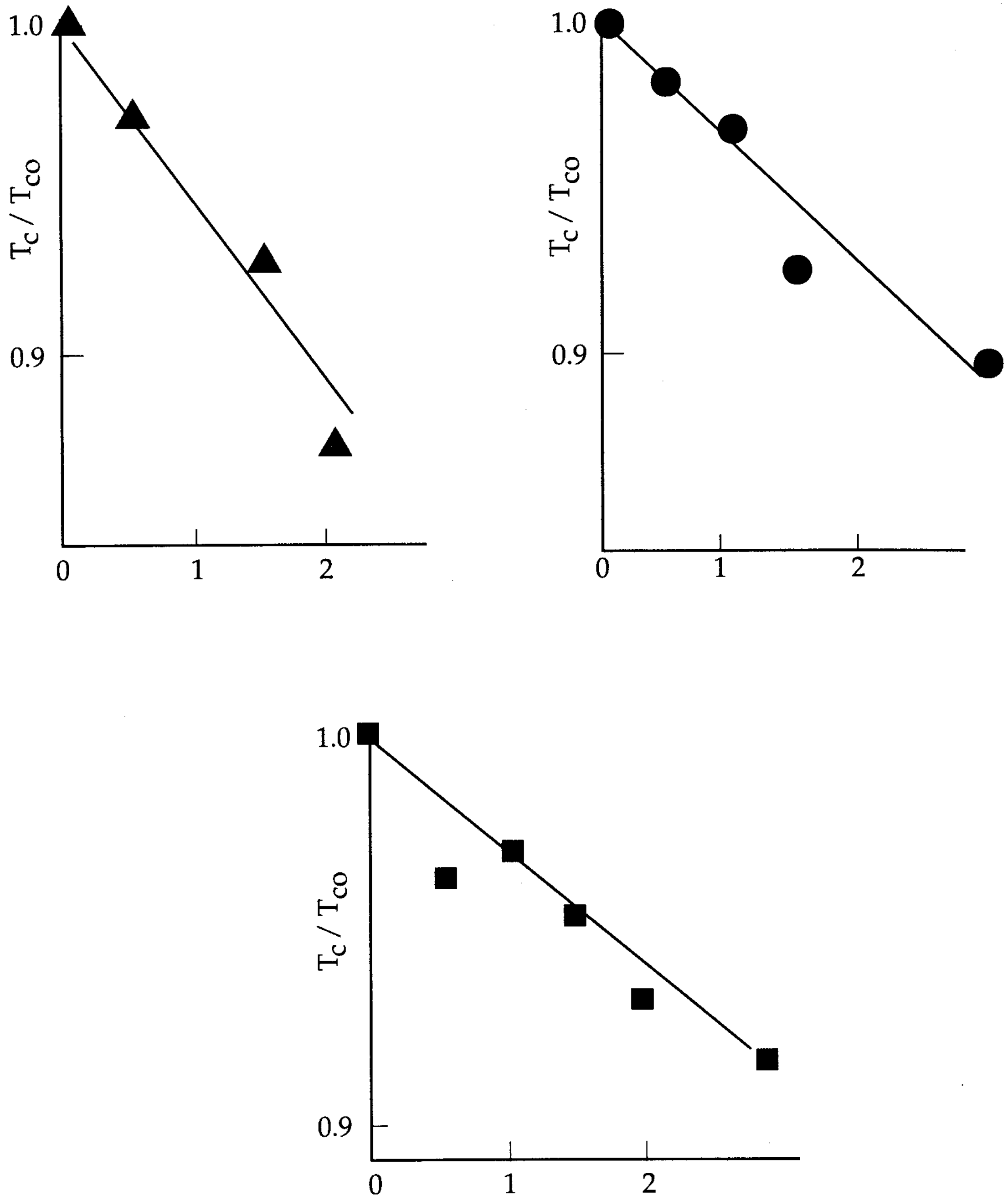

Fig. 4 Normalized Transition Temperature (T_c/T_{c0}) of the Two Lay-er Superconductor $Bi_{1.55}Pb_{0.45}Sr_2CaCu_{2-x}M_xO_{8+y}$ (M = Fe, Co and Ni). 1a. The shaded triangles (▲) are the measured T_c/T_{c0} for the Fe substituted specimens. The initial rate of suppression dT_c/dx due to Fe substitution is - 4.8 K/at. %. **1b.** The shaded circles (●) are the measured values for the Co doped specimens. dT_c/dx due to Co substitution is - 4.0 K/at. %. **1c.** The shaded square (■) are the measured values of Ni doped specimens. dT_c/dx due to NI substitution is - 3.1 K/at.%.

in TABLE 2. We have plotted the T_c's versus the concentration of Zn^{2+} impurities on Figure 3. The values of the copper valencies of the specimens being compared is 2.36 + 0.02. In Figure 4, we have plotted the T_c's versus the concentration of Fe, Co and Ni (values of x) given in TABLE 2. For comparison of the effect of Fe substitution, only specimens having Cu valencies of 2.25 ± 0.02 are considered, for the Co substitution, only specimens having the Cu valencies of 2.35 ± 0.03 are considered, while for the Ni substitution, only specimens having Cu valencies of 2.34 ± 0.04 are considered.

We see from Figure 4. that the depression due to Fe substitution is greater than that due to Co substitution, which inturn is greater than that due to Ni. While the relative depression of T_c seen in the figure is only demonstrated for the hole concentrations given, we believe the relative order of depression is true for all hole concentrations in the overdoped regions. Kluge *et al.*,[18] showed that in the overdoped region, the normalized transition temperature $T_c(p,x)/T_c(p,0)$ where p is the hole concentration and x is the amount of TM substitution, depends only on x and is independent of the hole concentration. This (the independence of p) is not true in the underdoped region. Looking at Firgure 4, we see the rate of depression caused by Fe substitution is dT_c/dx = -4.8 K/at. %; that by Co substitution, - 4.0 K/at. %. and that by Ni substitution, -3.1 K/at. %. Comparing Figures 3 and 4, we see that the rate of depression due to non magnetic Zn substitution (-3.2 K/at. %) is almost the same as that due to magnetic Ni substitution.

III. DISCUSSION

As we have mentioned, the present authors have derived expressions for the rate of decrease of the T_c due to non magnetic and magnetic ion substitution within the framework of the spin-fluctuation induced theory for HTSC of Monthoux and Pines.[7] The result obtained in ref. 11 for the rate of depression due to Zn substitution is

$$\left.\frac{dT_C}{dx}\right|_{Zn} = -\frac{\pi}{4}\alpha_N - \frac{T_{CO}}{g_{eff}\chi J C_{cr}} \tag{1}$$

where α_N is the pair breaking parameter due to normal scattering processes in an anisotropic host and is given by

$$\alpha_N = (1-\beta)\frac{1}{2\tau_N}\frac{1}{2+\chi J} \tag{2}$$

with

$$\beta = \iint \frac{dS_p}{8\pi^3 V_F}\frac{dS_k}{8\pi^3 V_F}\eta(p)\left|U(p-k)\right|^2\eta(k)\Big/(1/2\tau_N) \tag{3}$$

$$\frac{1}{2\tau_N} = \frac{1}{N(O)}\iint \frac{dS_p}{8\pi^3 V_F}\frac{dS_k}{8\pi^3 V_F}\left|U(p-k)\right|^2 \tag{4}$$

$$g_{eff} = -g^2\iint \frac{dS_p}{8\pi^3 V_F}\frac{dS_k}{8\pi^3 V_F}\eta(p)\chi(p-k)\eta(k)/\chi \tag{5}$$

and

$$\chi = \frac{1}{N(O)} \iint \frac{dS_p}{8\pi^3 V_F} \frac{dS_k}{8\pi^3 V_F} \chi(p\text{-}k) \tag{6}$$

In the above, $\eta(\mathbf{p})$ is the basis function for the representation of the crystal symmetry group and gives the angular dependence of the order parameter; $\chi(\mathbf{p}\text{-}\mathbf{k})$, the Fourier transform of the spin fluctuation propagator; T_{c0}, the transition temperature of the host HTSC; C_{cr}, the concentration at which the spin fluctuations are suppressed by the Zn impurities; J, the amplitude of the spectra weight of the frequency component of the spin susceptibility function; g, the strength of the spin fluctuation-electron coupling; $U(\mathbf{p}\text{-}\mathbf{k})$, the potential for non spin flip (normal) scattering; N(0), density of states at the Fermi energy and V_F is the Fermi velocity. The result for dT_c/dx due to magnetic TM ion substitution is

$$\left.\frac{dT_C}{dx}\right|_{\text{mag.ion}} = -\frac{\pi}{4}(\alpha_N + \alpha_s) \tag{7}$$

where α_N is still given by eqn. (2) and α_S is the pair breaking parameter due to spin flipping scattering. This second pair breaking parameter is defined as

$$\alpha_s = (1+\beta_1)\frac{1}{2\tau_s}\frac{1}{1+\chi J} \tag{8}$$

where

$$\beta_1 = \iint \frac{dS_p}{8\pi^3 V_F} \frac{dS_k}{8\pi^3 V_F} \eta(p)\left|V(p\text{-}k)\right|^2 \eta(k) \tag{9}$$

with

$$\frac{1}{2\tau_s} = \frac{1}{N(O)} \iint \frac{dS_p}{8\pi^3 V_F} \frac{dS_k}{8\pi^3 V_F} \left|V(p\text{-}k)\right|^2 \tag{10}$$

and where $V(\mathbf{p}\text{-}\mathbf{k})$ is the scattering potential for spin flipping and is equal to $J\,\mathbf{S}\mathbf{s}$ where $\mathbf{S}(\mathbf{s})$ is the spin operator for the ion (electron). The second pair breaking parameter will therefore be proportional to S(S+1) where S is the spin quantum number of the magnetic moment formed on the magnetic TM ion.

Looking at eqns. (1) and (7), we find that the pair breaking due to the normal scattering process is common to both. However, the pre-sence of (1 - β) in this parameter would diminish its value and thus reduces its influence (Note: This mechanism goes to zero as the anisotropy of the host HTSC becomes small, i.e., β →1). Accordingly, the main influence on the suppression of T_c would be due to the second terms in the two expressions. These terms arise from mechanisms which are not related to each other. Thus the nearly identical values for the rates of depression of the T_c's of the bismuth superconductors due to non magnetic Zn^{2+} substitution and to magnetic Ni^{2+} substitution (-3.2 K/at.% versus -3.1 K/at.%) may be coincidental. Koike *et al.*,[21] report that magnetic Ni^{2+} substitution into $Pb_2Sr_2Y_{1-y}Ca_y(Cu_{1-x}M_x)_3O_8$, produces a larger depression than is produced by non magnetic Zn^{2+} substitution. Similar behaviors are seen in $YBa_2Cu_{4-x}M_xO_8$ ("124") where the depression due Zn is less than that due to Ni.[22] The rate of depression of T_c due to non magnetic Zn^{2+} substitution can be greater (the case for the "123" HTSC), equal to (the present findings for the bismuth HTSC), or less than (the two just mention HTSC's) that due to magnetic Ni^{2+} substitution, depending on the HTSC.

Returning to the case of magnetic TM impurities, their substitution into a single type of Cu sites, allows their behavior to be compared with each other. As we have pointed out, the second term in eqn. 7 is proportional to S(S+1). Since the effective magnetic moments formed on these ions are proportional to the square root of S(S+1), the depression due to magnetic TM ion substitution should scale with the square of the magnetic moment. Thus the rates of depression due Fe, Co and Ni substitution should scale in the ratio 1 to 0.79 to 0.35 (taking the values of the moments of Fe^{3+}, Co^{3+} and Ni^{2+} to be 5.4, 4.8 and 3.2 Bohr magnetons, respectively). The rates of depression measured in the present study scale in the ratio 1 to 0.83 to 0.65. The differences between the predicted and observed scalings of the rates of depression could be an indication that the pair breaking by the normal scattering is not small and can not be neglected.

IV. ACKNOWLEDGEMENT

Two of the authors (IMT and SL) would like to thank the Thailand Research Fund for providing financial support to conduct this research.

REFERENCES

1. P.W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
2. A. Abrikosov and L.P. Gorkov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960)
3. Y. Zhao et al., J. Phys. Condens. Mat. **5**, 3623 (1993).
4. C. Xiao et al., Phys. Rev. B **35**, 8782 (1987).
5. N. Peng and W.Y. Liang, Physica C **233**, 61 (1994).
6. T.J. Kistenmacher, Phys. Rev. B **38**, 8862 (1988).
7. P. Monthoux and D. Pines, Phys. Rev. B **47**, 6069 (1993); *ibid* **49**, 4261 (1994).
8. A.J. Millis, S. Sachdev and C.M. Varma, Phys. Rev. B **37**, 4975 (1988).
9. A.J. Millis, H. Monien and D. Pines, Phys. Rev. B **42**, 167 (1990).
10. D.A. Wollman et al., Phys. Rev. Lett. **71**, 2134 (1993): C.C. Tsuei et al., Science **271**, 329 (1996).
11. I.M. Tang, S. Leelaprute and T. Ostchan, submitted.
12. M.H. Whangbo and C.C. Torardi, Science **249**, 1143 (1990).
13. J.L. Tallon et al., Phys. Rev. B **51**, 12 911 (1995).
14. H. Zhang and H. Sato, Phys. Rev. Lett. **70**, 1697 (1996).
15. K. Kishio, in *Coherence in Superconductors,* edited by G. Deutsch and A. Revcolevischi (World Scientific, Singapore) (1995).
16. C. Bernhard et al., Phys. Rev. Lett. **77**, 2304 (1996).
17. N.A. Babushkina et al., Physica C **272**, 257 (1996).
18. T. Kluge et al., Phys. Rev. B **52**, R727 (1995).
19. I.M. Tang, S. Leelaprute and P. Setsuwan, Physica C **177**, 57 (1991)
20. W.A. Groen, D.M. de Leeuw and L.F. Feiner, Physica C **165**, 55 (1990)
21. Y. Koike et al., Physica C **211**, 409 (1993).
22. R. Lai et al., Phys. Rev. B **49**, 6382 (1994).