EFFECTS OF DIFFERENT ALKALI METAL SUBSTITUTION ON THE INTERLAYER COUPLING IN "2212" BISMUTH SUPERCONDUCTORS

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ABSTRACT

The effects of systematic (non isovalent) substitutions of alkali metal ions (Li, Na, K and Rb) on the T_{co}'s of the two layer bismuth superconductor $Bi_2Sr_2CaCu_2O_z$ are studied. It is found that the decrease in the optimal T_c (occurring at some optimal level of substitution) for each type of substitution correlates with the increase in the ionic size of the alkali metal. The results are interpreted within a framework of a model for high temperature superconductivity in which interlayer coupling of the order parameters in adjacent CuO_2 layers plays an important role in enhancing the transition temperatures.

INTRODUCTION

It is generally accepted that most high temperature superconductors exhibit a maximum T_c's at some optimal hole concentration[1]. The necessary holes can be doped into the systems by inserting excess oxygen ions into the interstitial sites in the perovskite structure or by replacing ions of one valency by ions of another valency. Other changes, such as the size of the unit cell, may occur with the chemical substitutions. It is known that the addition of impurities to ceramic mixtures leads to a lowering of the melting temperature T_m. This inturn, could facilitate the formation of the sought after phase or cause a change in the amount of oxygen being absorbed by the ceramic. If the impurities are alkali metals, the lowering of T_m is drastic. Kawai *et al.*[2], report that the addition of Li causes T_m to drop from 840 K to below 770 K. Some of our results with other alkali metals indicate that the drop can be much greater.

Recently, we reported on the effects of lithium and rubidium substitution in the "2212" bismuth superconductors[3,4]. It was seen that the main effect of the Li^+ and Rb^+ on superconductivity was through their influence on the copper valency in the ceramics, which inturn led to changes in the transition temperature. This paper reports on our study on the effects of systematic replacement of some Sr^{2+} ions in the two layer bismuth superconductors with other alkali metal ions. Other alkali metal substitution studies have

been carried out by Kanai *et al.*[5], Horiuchi *et al.*[6], Goncalves *et al.*[7], and by Sampathkumaran *et al.*[8], Horiuchi *et al.*, raised the possibility that the alkali metal substitution might influence superconductivity through its effect on the two dimensional CuO layer. Our interests is to see whether the changes in some superconducting properties depend on the type of alkali metal used and if so, why?

EXPERIMENT

Stoichiometric amounts of $SrCO_3$, Bi_2O_3, $CaCO_3$, CuO, Li_2CO_3, K_2CO_3, Rb_2CO_3, and Cs_2CO_3, were weighed to yield $Bi_2(Sr_{1-x}A_x)_2CaCu_2O_{8+y}$ (A = Li, K, Rb and Cs ; x = 0, 0.1, 0.2 and 0.3). The chemicals were mixed in an agate mortar and pressed into pellets. Most of the pellets were then heated at various temperatures for 48 hours. Kawai *et al.*[2], reported that the melting temperatures of $Bi_2(Sr_{0.7}A_{0.3})_2CaCu_2O_{8+y}$ were drastically reduced from that of the undoped bismuth compounds. Since optimal quality superconductors are achieved when the ceramics are sintered close to their melting temperatures, each series had to be sintered at different temperatures. The Li-doped specimens were heated to 700° C for 47 hrs. The other three doped series underwent a two step fabrication process. The Cs-doped specimens were calcinated at 800° C for 12 hrs, reground, pressed and sintered for 48 hrs at 820°C; the K-doped specimens were calcinated at 780°C for 12 hrs, reground, pressed and sintered for 48 hrs at 800°C; the Rb-doped specimens were heated to 800°C for 76 hrs, reground, pressed and heated again to 800°C for another 46 hrs. To prevent the reabsorption of oxygen (Tallon[9] has pointed out that the Bi superconductors which are slowly cooled are over doped), the heated pellets were immediately quenched in liquid nitrogen.

The pellets of all the $Bi_2(Sr_{1-x}A_x)_2CaCu_2O_{8+y}$ series swelled during their fabrication. The resistivities of all the superconductors were measured at temperatures between 68 K and room temperature using the standard four probe method. Temperatures below 77 K were achieved by pumping on the liquid nitrogen. The temperatures were monitored with a carbon glass resistor. The X-ray diffraction patterns were obtained using the Cu K_α line. The AC susceptibilities of some of the superconductors were measured using the mutual induction method.

RESULTS

The X-ray diffraction patterns of the $Bi_2(Sr_{0.8}A_{0.2})_2CaCu_2O_{8+y}$ (A = Li, K, Rb and Cs) specimen of each series of the substituted "2212" superconductors are shown in Figs. 1 and 2. The XRD patterns of all of the Li and Rb substituted ceramics exhibited a strong [002] peak at approximately 2O = 6°, indicating the two layer phase of the bismuth superconductor was the dominant phase in these two series. The lack of this peak in the XRD patterns of the other alkali substituted series specimens indicate that the dominant phase in these specimens was not the two layer phase.

Most of the peaks observed belong to the two layer ("2212") bismuth superconductor and were indexed to the tetragonal structure. Refinement of the XRD patterns of the Li and Rb substituted specimens yield the values of the **a** and **c** axis lattice parameters listed in Table I. No refinement of the XRD patterns of the other alkali substituted series was

TABLE 1. Lattice Parameters of the Substituted Bismuth Superconductor $Bi_2(Sr_{1-x}A_x)_2$ $CaCu_2O_{8+y}$ Refined in the Tetragonal Structure.

Composition	Lattice Parameters		Unit Cell Volume
(x)	$a(\overset{\circ}{A})$	$c(\overset{\circ}{A})$	A^3
Undoped			
	5.431(6)	30.978(4)	913.712
Lithium Substitution			
0.1	5.429(15)	30.811(44)	908.125
0.2	5.408(8)	30.795(23)	900.645
0.3	5.398(28)	30.806(119)	897.638
Rubidium Substitution			
0.1	5.417(6)	30.903(4)	906.814
0.2	5.426(5)	30.933(4)	910.713
0.3	5.403(4)	30.644(3)	894.572

attempted since the XRD patterns of the $Bi_2(Sr_{1-x}A_x)_2CaCu_2O_{8+y}$ (A = K and Cs) specimens exhibit a strong diffuse background pattern. As is seen from Table I, increasing substitution of the alkali dopants in general leads to a decrease in the **c** axis lattice parameters. This occurred regardless of whether the ionic radius of the dopant is larger or smaller than that of the Sr ion. To understand why increasing the level of doping always leads to a shrinking unit cell in our fabrication process, we first note that most ceramics undergo increased densification as they are cooked at higher temperatures. Maintaining the same processing temperature as the amount of dopant is increased would be equivalent to raising the temperature since the increased doping would lower the melting temperatures.

The dependences of the resistivities of the different series of alkali doped bismuth superconductors on the temperature are shown in Figs. 3 to 6. The resistivity curves for the Li and Rb doped superconductors, Figs. 3 and 4, have already being reported in refs. 3 and 4. The temperatures at which the resistivities of $Bi_2(Sr_{1-x}Li_x)_2CaCu_2O_{8+y}$ (x = 0.0, 0.1, 0.2 and 0.3) goes to zero, T_{c0}, are 69 K, 77 K, 86 K and 94 K, respectively, while the T_{c0} of $Bi_2(Sr_{1-x}Rb_x)_2CaCu_2O_{8+y}$ (x = 0.05, 0.1, 0.2 and 0.3) are 72 K, 78 K, 70 K and < 68 K, respectively. In Fig. 5, we see the resistivity curves of the K doped superconductors, $Bi_2(Sr_{1-x}K_x)_2CaCu_2O_{8+y}$. The T_{c0}'s are 83 K, 83 K and < 75 K for x = 0.0, 0.1 and 0.2, respectively. All the resistivity curves for the Cs doped superconductor Bi_2 $(Sr_{1-x}Cs_x)_2CaCu_2O_{8+y}$ (x = 0.1, 0.2 and 0.3), which are shown in Fig. 6., show a very broad transition. The T_{c0}'s for these superconductors are 77.2 K or lower.

Na substitution was also attempted. These compounds were calcinated at 730° C for 12 hrs and then sintered for 48 hrs at 800° C. All the resistivity curves exhibited a tail which never dropped to zero. The determination of the T_{c0}'s in these situation would then have to be by extrapolation of the resistivity drop down to zero. Since we have defined
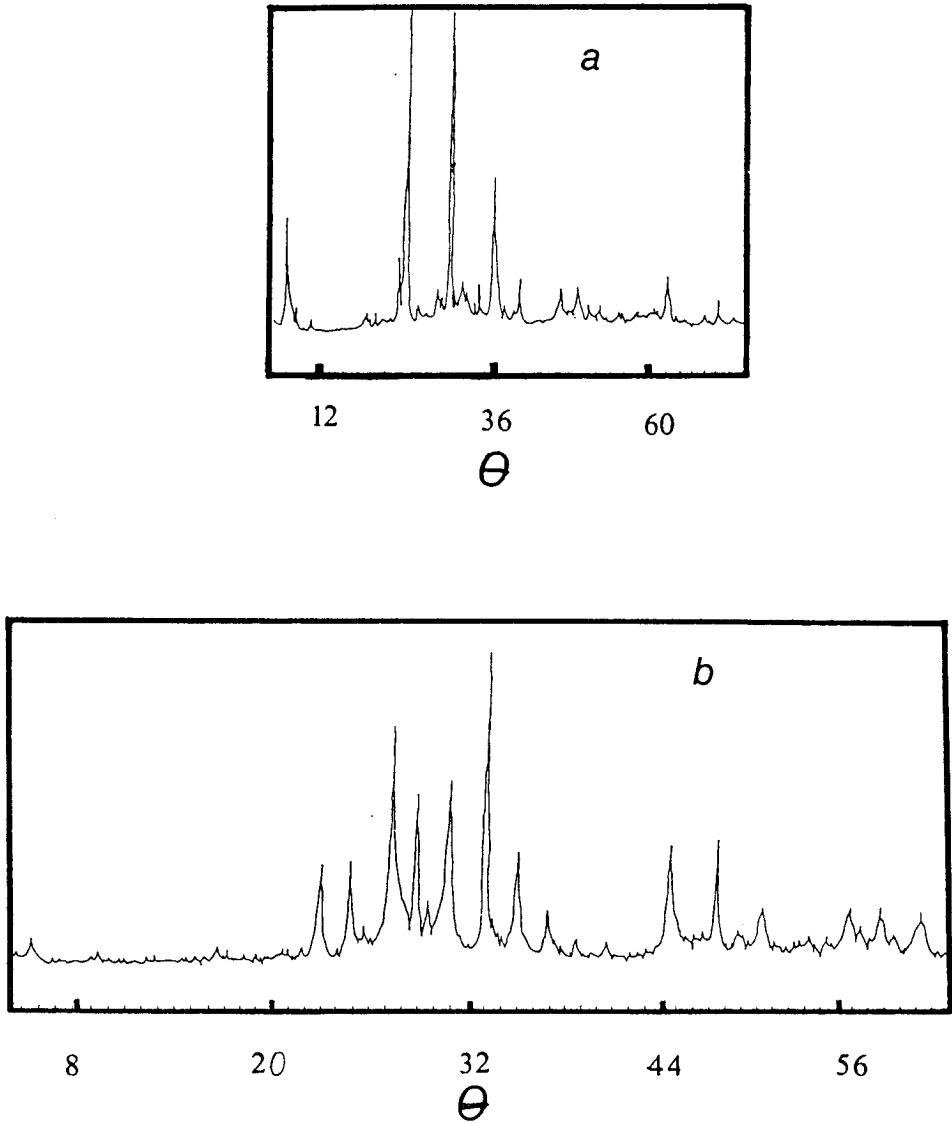
Fig. 1. a. XRD Pattern of $Bi_2(Sr_{0.8}Li_{0.2})_2CaCu_{8+y}$. b. XRD Patterns of $Bi_2(Sr_{0.8}Rb_{0.2})_2CaCu_{8+y}$.

The XRD patterns of the other Li and Rb doped superconductors are similar to this. Most of the lines could be indexed to the tetragonal structure of the "2212" bismuth superconductor. The [002] peak at $2\theta = 6°$ clearly show the presence of the two layer phase.

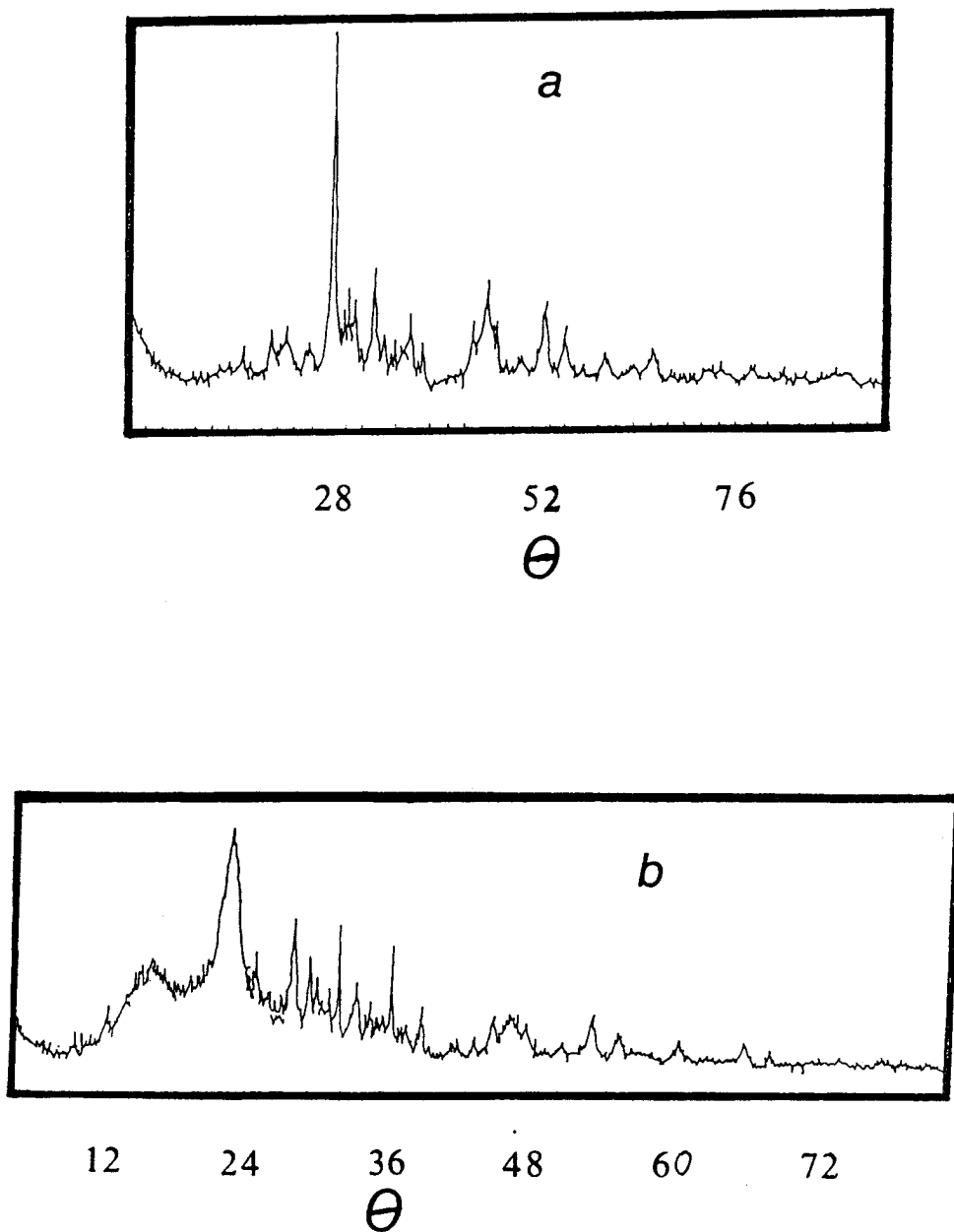**Fig. 2.** a. XRD Pattern of $Bi_2(Sr_{0.8}K_{0.2})_2CaCu_{8+y}$. b. XRD Pattern of $Bi_2(Sr_{0.8}Cs_{0.2})_2CaCu_{8+y}$.

The XRD patterns of the other K and Cs doped superconductors exhibit a more diffuse background indicated some amorphous structure in the ceramics. The [002] peak is missing in all the patterns.
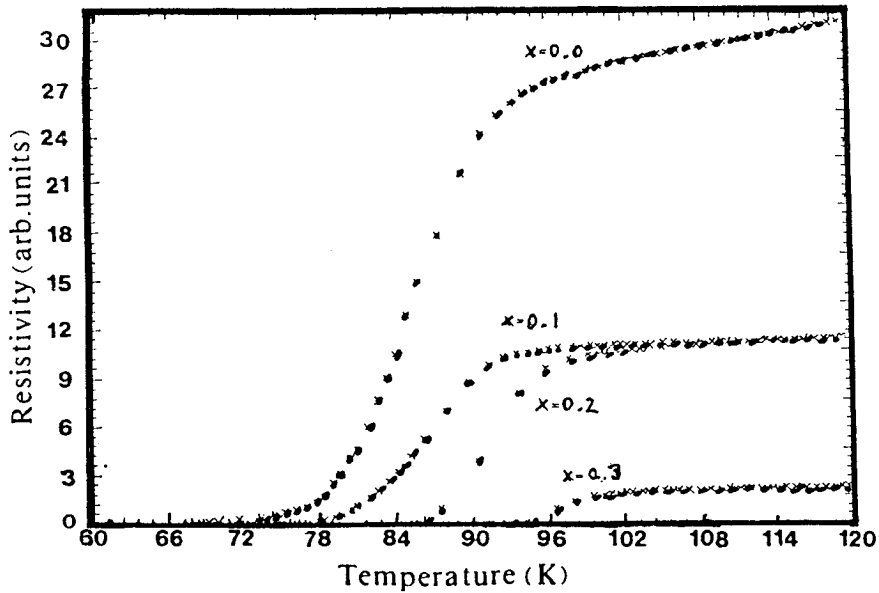
Fig. 3. Resistivity Curves for the Li-doped "2212" bismuth superconductors, $Bi_2(Sr_{1-x}Li_x)_2CaCu_2O_{8+y}$. The transition temperature T_{co} is defined as the temperature at which the resistance goes to zero. In this figure, one finds that the T_{co}'s are 69 K, 77 K, 86 K and 94 K for x = 0.0, 0.1, 0.2 and 0.3, respectively.
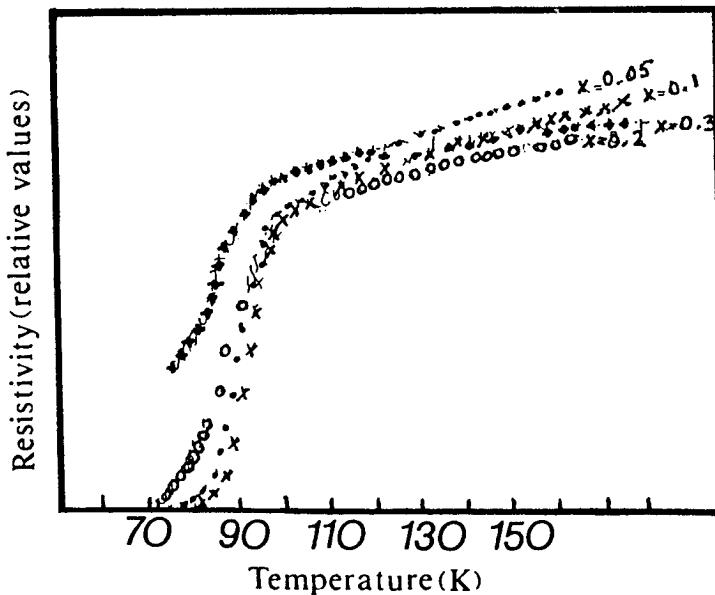
Fig. 4. Resistivity Curves for the Rb-doped "2212" bismuth superconductors, $Bi_2(Sr_{1-x}Rb_x)_2CaCu_2O_{8+y}$ The T_{co}'s for the Rb-doped superconductors are 72 K, 78 K, 72 K and less than 68 K for x = 0.05, 0.1, 0.2 and 0.3, respectively.
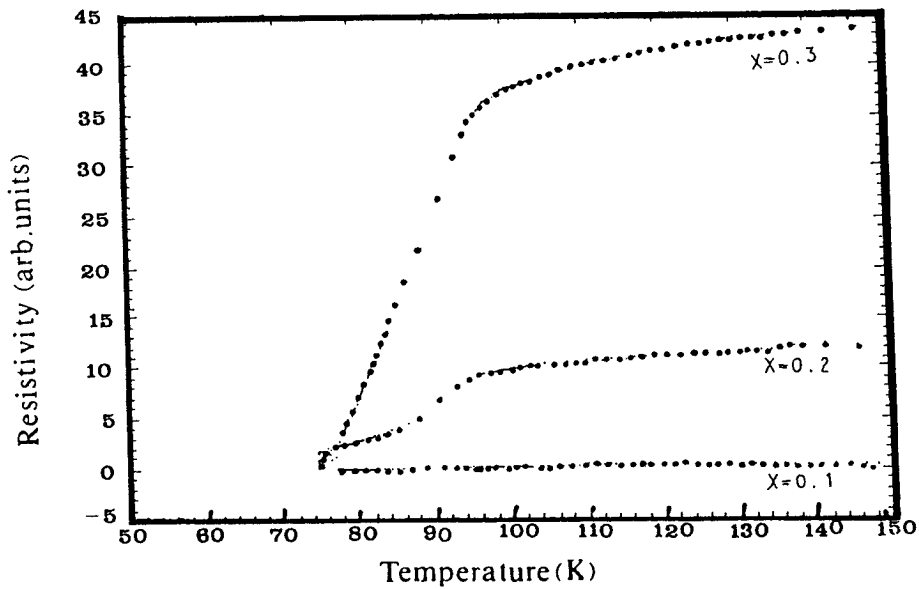
Fig. 5. Resistivity Curves for the K-doped "2212" bismuth superconductors, $Bi_2(Sr_{1-x}K_x)_2CaCu_2O_{8+y}$ The T_{co}'s for the K doped superconductors are 83 K, 83 K and less than 75 K for x = 0.0, 0.1 and 0.2, respectively.

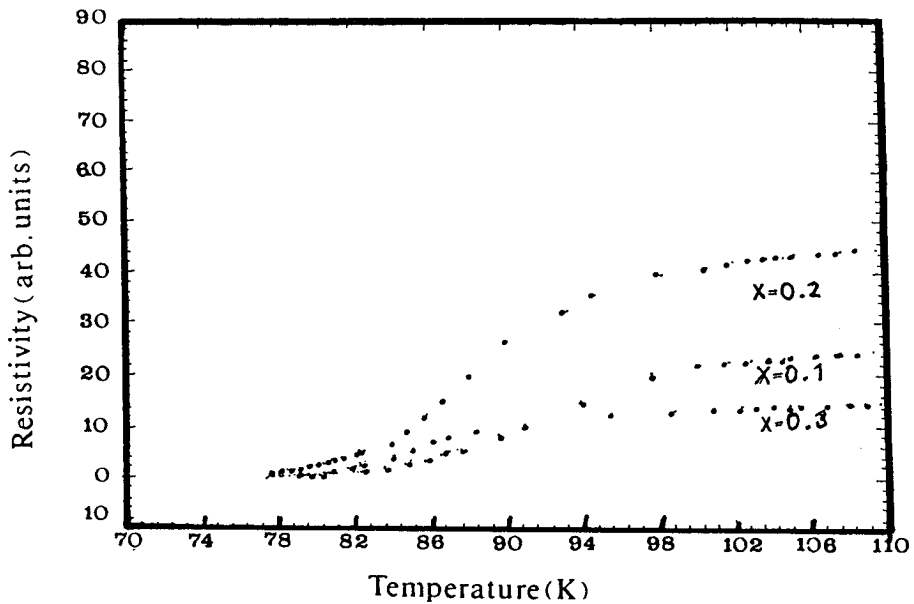**Fig. 6.** Resistivity Curves for the Cs-doped "2212" bismuth superconductors, $Bi_2(Sr_{1-x}Cs_x)_2CaCu_2O_{8+y}$ The T_{co}'s for the Cs-doped superconductors are equal to or less than 77.2 K

T_{c0} for the other alkali-doped superconductor as being the temperature at which the resistance goes to zero, comparison of the T_{c0}'s of the Na-doped "2212" superconductors with those of the other alkali-doped "2212" superconductors would not be a valid one and so we have not attempted it.

To compare the superconductivity among the other alkali doped superconductors, we note that the optimal T_c's for each of the doped superconductors are 94 K (Li doping), 83 K (K doping), 78 K (Rb doping) and 77.2 K (Cs doping). The relative ordering of these T_c's are in the same order as $T_{c,mid}$ (the temperature at which the resistivity falls to 50% of its value) as that found by Kawai *et al.*[2], i.e.,

$$T_{c,mid}{}^{Li} > \quad T_{c,mid}{}^{Na} > \quad T_{c,mid}{}^{K} > T_{c,mid}{}^{Rb}, \; T_{c,mid}{}^{Cs} \qquad (1)$$

DISCUSSION

Recently, Anderson and coworkers[10] have introduced a new version of his theory which has been labelled "...one of two leading candidates" for the theory of high T_c superconductivity. An essential feature of this "new theory" is the tunneling of Cooper pairs between adjacent layers. In this theory, the interlayer mechanism plays the dominant role in determining the T_c's of the higher T_c materials, while in the lower T_c' materials, their T_c's are increasing determined by the intralayer mechanism. Tesanovic[11] has pointed out previously that interlayer interaction should be through the particle-particle channel. One of the present authors (IMT) has taken this idea and has applied the strong coupling approach to superconductivity, the Eliashberg formalism, to obtain the following expression for the transition temperature[12]

$$T_c = \quad T^* (1 + \Gamma) \qquad (2)$$

where T^* is the transition temperature due to the coupling within the CuO layer and Γ is proportional to the modules square of the interlayer coupling (Josephson tunneling) strength . Similar expressions were obtained by others[13] based on a Ginzburg Landau theory of superconductivity.

Assuming that T^* is the same for all of the alkali doped bismuth superconductors, the differences in the optimal T_c's of the four types of the alkali doped superconductors would be due to the differences in the values of Γ. To account for the inequalities given in eqn. (1), the values of the interlayer coupling strength would have to satisfy a similar inequality, i.e.,

$$\Gamma_{Li} > \quad \Gamma_K > \quad \Gamma_{Rb} > \quad \Gamma_{Cs} \; . \qquad (3)$$

One can only conjecture on why the interlayer coupling strengths change as different ions are substituted into the I-type layer. The correlation between the decrease in the

coupling strength and the increase in the ion size may only be a coincidence. The replacement of Sr ions by larger Ba ions in the two copper layer thallium superconductors, $TlBa_2CaCu_2O_8$ and $TlSr_2CaCu_2O_8$, raises the T_c from 75 K to 91 K, while the replacement of some of the Sr ions by smaller Ca ions in the single copper layer Bi superconductors, $Bi_2Sr_2CuO_6$ and $Bi_2SrCaCuO_6$ raises the T_c's from less than 22 K to over 50 K. Of course, these isovalent substitutions do not lead to any changes in the hole concentration as the alkali metal substitution does. The order of the decrease in the interlayer coupling strength indicated by eqn. (3) may instead be due to the increase in the polarizabilities of the alkali metal ions, which leads inturn to an increase in the dielectric constant of the insulating layer.

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