Similar depression of T_c by Zn and Ni impurities in 1:2:3 $(Ca_{0.4}La_{0.6})(Ba_{1.35}La_{0.65})(Cu_{1-z}M_z)_3O_y$

D. Goldschmidt, Y. Direktovitch, A. Knizhnik, and Y. Eckstein

Department of Physics and Crown Center for Superconductivity, Technion, Haifa 32000, Israel

Substitution of $M=$ Zn or Ni impurities in 1:2:3 $(Ca_{0.4}La_{0.6})(Ba_{1.35}La_{0.65})(Cu_{1-z}M_z)_3O_y$ depresses T_c^{max} with almost equal effectiveness, i.e., -9 and -7 K/%, respectively. (In YBCO, Zn is three times more effective in depressing T_c than Ni.) In these impurity-containing materials, the dependence of thermopower on T_c/T_c^{max} departs substantially from the universal behavior observed in other cuprates. There is no definite trend in the resistivity of these ceramic materials with impurity concentration z. Our results suggest pair breaking or weakening of the interaction at constant carrier density when z is increased. [S0163-1829(96)08341-5]

Among the many ions that can be substituted to control T_c of cuprates, Zn and Ni are quite interesting. Substituting primarily for planar copper in YBCO,[1-6] these impurities may introduce carrier scattering or intervene with their pairing. However, Zn—which is a nonmagnetic ion—is three to four times more effective than Ni in depressing T_c,[4,7-9] i.e., $dT_c/dz \cong -(12$ to $13)$ K/% and $-(3$ to $4)$ K/%, respectively, where z is the metal impurity concentration per Cu atom. This is accompanied by a difference in magnetic behavior, observed by NMR and dc moment measurements.[4,6,7] NMR studies suggest that, *unlike* Ni, the Zn ion strongly depresses the spin correlations of Cu ions which are adjacent to an impurity.[4,7] The big difference in T_c depression that both ions induce in 1:2:3 YBCO, as well as the simultaneous depression of T_c and local spin correlations were taken as strong evidence for the spin-fluctuation mechanism in cuprates.[10] In order to examine the generality of these results in other 1:2:3 materials, we substituted Zn and Ni impurities in 1:2:3 Ca-La-Ba-CuO. We found that, compared with YBCO, *the depression of T_c by both substitutions is almost the same*, i.e., $dT_c/dz \cong -9$ and -7 K/%, respectively. By tuning the oxygen content to optimal doping we found for each impurity concentration the maximal T_c attainable by doping, denoted T_c^{max}. We show that these figures (i.e., -9 and -7 K/%) actually correspond to depression of T_c^{max}. We also found that the thermoelectric power (TEP) departs substantially from the universal behavior observed in many cuprates, when taken as function of T_c/T_c^{max}, and that the resistivity does not show a definite increase with impurity concentration.

Recently, we investigated the newly-discovered 1:2:3 family of materials $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ (CaLaBaCuO).[11] Being tetragonal in a wide range of compositions, this system allows one to perform systematic investigations void of structural phase transitions and of long-range oxygen order. Moreover, charge compensation on the Y and Ba sites (first and second brackets, respectively), allows investigation at constant electron concentration by keeping the oxygen content y constant. We observed big changes in T_c, resistivity ρ and TEP S suggesting that doping—i.e., change in mobile carrier density—occurs despite holding the average electron concentration constant.[12] We also found that in the underdoped region there exists a

single parameter $y-y_{MI}(x)$, that determines T_c, transport properties and carrier density (y_{MI} is the oxygen content at the metal-insulator MI transition).[12,13] In particular, all materials with a given T_c also have the same TEP. Our results can readily be interpreted within a single band picture modified to consider the existence of additional low-mobility states near E_F in addition to planar CuO_2 band states.[12,13] $y-y_{MI}$ was thought to be a macroscopic parameter representative of the doping level. We have extended our studies to materials in which the total La concentration has been changed as well as materials in which La has been replaced by Nd and found the same doping parameter as before.[13] Moreover, we investigated the behavior of T_c under pressure P and have shown that the dependence of dT_c/dP on the doping level can be described by the same two parameters, i.e., T_c^{max} and $y-y_{MI}$.[14] To sum up: In the underdoped region changing x changes the doping level through $y_{MI}(x)$ even when holding the amount of oxygen constant, but does not influence the interaction or pair breaking. This follows from the observation that materials with the same TEP also have the same T_c.

Having established the doping behavior of T_c and transport in this system, we now turn to examine effects due to Zn and Ni impurities believed to substitute directly into the CuO_2 planes. We hoped by these substitutions to control T_c (including T_c^{max}) without changing the doping level, and thereby investigate other effects due to pair breaking or the interaction. That Zn does not change the carrier density has been suggested by Alloul *et al.*[15] for YBCO and actually shown through TEP measurement by Williams *et al.*[16] for 1:2:4 materials. To this end, we prepared the $x=0.4$ member of the CaLaBaCuO family, i.e., $(Ca_{0.4}La_{0.6})(Ba_{1.35}La_{0.65})(Cu_{1-z}M_z)_3O_y$ with $M=$ Zn or Ni. The actual impurity site in this material is not known. Regular XRD is unable to distinguish the copper from the impurity. Going along with the observations that in YBCO and 1:2:4 Zn and Ni go both to the planes, we tentatively assume that in CaLaBaCuO both impurities go mostly into the CuO_2 planes as well, or at least, that the fraction which goes into the planes is constant, independent of z.

Preparation of the Zn- and Ni-substituted CaLaBaCuO by the conventional solid reaction route followed the same procedure as in the nonsubstituted material.[11,13] We used ZnO
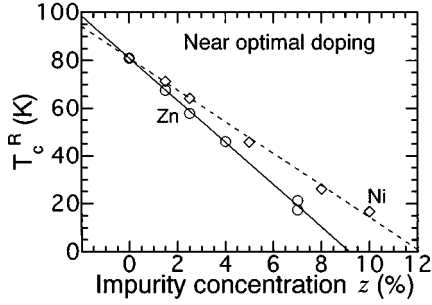
FIG. 1. Dependence of T_c near optimal doping on nominal impurity concentration z in Zn- and Ni-substituted CaLaBaCuO.
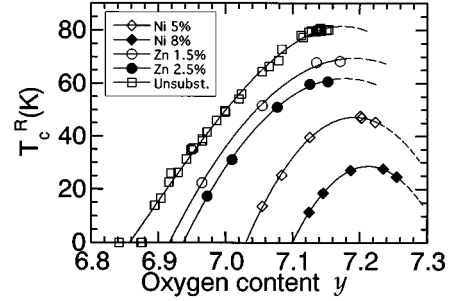

FIG. 2. T_c as function of oxygen content y for various impurity concentrations. Notice strong depression of T_c^{max} for both Zn and Ni. Curves are guides for the eye.

and NiO (both $>99\%$) as starting materials. Our long exposure XRD measurements showed no traces of impurity phase for the highest impurity concentrations used in this work. The results reported here correspond mostly to sintering at $955\,°C$ for 60 h in flowing O_2. We observed slight dependence of T_c^{max} on preparation (e.g., temperature and duration of firing and sintering). This dependence shows up as a systematic vertical shift (a few degrees) of the entire curve of T_c vs oxygen content. This has no effect on the conclusions of this work. In order to minimize scatter in our data, we have presented in each figure results corresponding mostly to a single batch which are reproducible, even though among figures we have used different batches. We estimated z from the nominal impurity concentration. The $10\,°C/h$ cooling rate provides materials close to optimal doping, where $T_c = T_c^{\mathrm{max}}$. Further oxygenation occurred upon annealing under oxygen pressure of 10 atm at $420\,°C$. By regular annealing we changed the oxygen content in the same way as in pure CaLaBaCuO.[11] In particular, we were able to tune the oxygen level near optimal doping. The Zn and Ni ions posed no problem for the accurate determination of oxygen content y by titration,[11] as the final oxidation state in solution is $+2$ in both cases. Our measurements of y near optimal doping (y_{opt}) suggest that a fraction of the Ni ions enter the material in the $+3$ state, since in this case y_{opt} increases slightly with z. The resistivity and particularly susceptibility transitions remain narrow as in the pure material[11,14] and the resistivities remain low implying low resistivity of grain boundaries and good oxygen homogeneity.[11]

The dependence of T_c on impurity concentration z is shown in Fig. 1. Both T_c^{R} (resistive onset) and T_c^{χ} (ac susceptibility, not shown) depend linearly on z up to $z \cong 0.1$. Notably, the difference in dT_c/dz for both substitutions is $\sim 30\%$. In YBCO, the difference in dT_c/dz of Zn and Ni materials exceeds 300%.

The T_c data in Fig. 1 correspond approximately to T_c^{max}. The value of T_c^{max} was obtained by measuring T_c vs oxygen content y for various samples with a given composition z (Fig. 2). In this way, the dependence of T_c^{max} on impurity concentration is determined unambiguously. [Even in Zn samples, where T_c^{max} is only nearly attained due to insufficient oxygen, it is determined quite accurately as the $T_c(y)$ curve saturates.] This is important from an experimental viewpoint because, as we show below, in the presence of impurities T_c^{max} cannot be determined from measurements of T_c and TEP. The depression of T_c^{max} is clearly seen in Fig. 2.

As the TEP does not change much at optimal doping (next paragraph), we conclude that this depression of T_c^{max} with impurity concentration is due to pair breaking or interaction weakening in accordance with previous observations in other materials.[16–18] Notice that dT_c/dz in reduced samples (at constant y) is larger than dT_c^{max}/dz. Recall that a large dT_c/dz is observed also in reduced YBCO.[7] This seems to suggest that impurity effects (i.e., pair breaking or interaction weakening) also depend on the amount of oxygen or state of doping.

The results of room-temperature TEP $S_{290\,\mathrm{K}}$ as function of oxygen content y are presented in Fig. 3, mostly for underdoped materials. Notice that at a given y the TEP is constant independent of impurity concentration z for both Ni and Zn impurities. (In the case of Ni, this impurity independence of TEP holds also for slight overdoping.) This strongly suggests that the carrier concentration remains essentially constant when these impurities are added. In other words the decrease in T_c that accompanies the addition of these impurities is not related to carrier density effects. This has been already shown in 1:2:4 materials[16] and was also suggested in YBCO.[15] Thus the decrease in T_c is associated either with pair breaking or interaction weakening[17] or both. Both kinds of effects have been observed in underdoped 1:2:4 materials.[18]

There exists a universal TEP curve that describes $S_{290\,\mathrm{K}}$ as a function of T_c/T_c^{max} and makes the determination of the state of doping of a given material quite easy.[19] In particular, based solely on the measurement of T_c and room temperature TEP, one can determine T_c^{max} of a given material even if T_c^{max} is experimentally inaccessible. Many cuprates including the pure $x = 0.4$ CaLaBaCuO follow this universal curve.[12] However, when Ni and Zn are introduced, one observes strong departure from the universal TEP curve as is shown in the inset of Fig. 3. In other words, a given value of T_c/T_c^{max} does not correspond any more to a specific value of the room-temperature TEP. Therefore, measurement of T_c and $S_{290\,\mathrm{K}}$ is insufficient to determine T_c^{max}. Apparently, T_c/T_c^{max} is no more a good measure of the state of doping in impurity-substituted materials. This can be seen also by inspection of Fig. 2, where both T_c^{max} and T_c are shown to decrease with z, but not in the same proportions. For instance, in the Ni 8% material, T_c goes to 0 K at $y = 7.1$. Thus $T_c/T_c^{\mathrm{max}} = 0$ while the doping level is close to the optimal value.
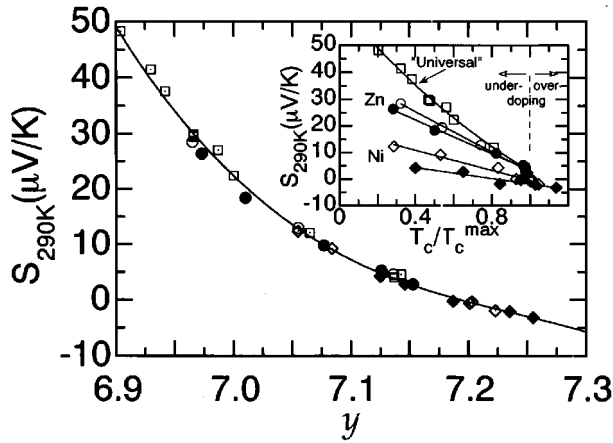
FIG. 3. Dependence of thermopower on amount of oxygen. Notice that carrier density is independent of impurity concentration. Inset: The universal plot of TEP vs T_c/T_c^{max} (open squares denote the unsubstituted $x = 0.4$ material). Zn- and Ni-substituted materials depart substantially from this plot. Symbols as in Fig. 2.

FIG. 4. Dependence of room-temperature and residual resistivities at optimal doping on impurity concentration in ceramic CaLaBaCuO.

We believe that the departure from the universal TEP curve (plotted against T_c/T_c^{max}) will occur whenever there exist pair breaking or interaction weakening. In fact, such departure could serve as an indication of these effects. Notice, however, that it is still possible to determine the state of doping because it does not change upon substitution of impurities.

In Fig. 4 we have plotted the room-temperature resistivity $\rho_{290\,K}$ and residual resistivity ρ_0 of ceramic CaLaBaCuO, both measured at optimal doping where the $\rho(T)$ behavior is linear. The resistivities are slightly higher than in the pure CaLaBaCuO. Within the scatter of available ρ_0 data ($\pm 5\%$ for Ni substitution, $\pm 20\%$ for Zn) we observe no definite trend in the dependence of resistivity on z which was unexpected. Measurements on single crystals or thin films might illuminate this point. Away from optimal doping the $\rho(T)$ curve becomes slightly concave ($d^2\rho/dT^2 < 0$) or convex ($d^2\rho/dT^2 > 0$) for underdoping ($y < y_{opt}$) or overdoping ($y > y_{opt}$), respectively. Still further away on the underdoped side (i.e., when T_c approaches zero), a semiconductorlike behavior (large negative $d\rho/dT$ above the onset of superconductivity) was observed in the Zn-substituted materials but is almost absent in the Ni-substituted ones.

The major result of this work concerns the difference in depression of T_c by Zn and Ni in 1:2:3 CaLaBaCuO which, for T_c^{max} is an order of magnitude smaller than the corresponding difference in YBCO. This difference in YBCO, which stands against expectation of classical superconductor theory, was taken as strong evidence for a magnetic interaction with its d-wave pairing assuming that Zn is nonmagnetic and Ni is a strong magnetic ion.[10] [In fact, it turns out that Zn induces a sizable local moment in YBCO (Ref. 1) and other cuprates[18]]. Our observation in CaLaBaCuO shows that such a difference is not generic to 1:2:3 materials, but rather that the response to impurities is sensitive to the specifics of the material (e.g., amount of oxygen, existence of ordered chains, doping level, number of chains, and so on). In fact, in 1:2:4 materials containing two ordered chains the situation changes again. There the difference in T_c depression between Zn and Ni is also small but Ni makes a 20%
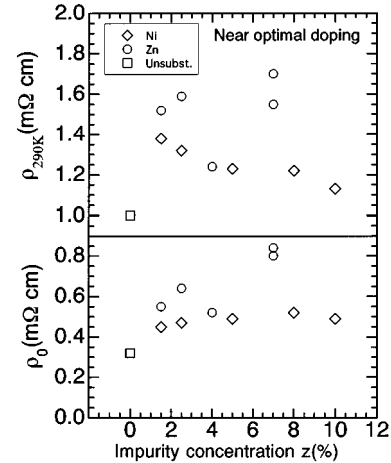
stronger depression than Zn.[17] However, even though it is plausible that these impurities occupy the same site in all cuprates (in YBCO it is the planar Cu site), the possibility that Zn and Ni occupy other sites cannot be ruled out at this point. It would therefore be important to identify the exact site location and occupancy of these ions in 1:2:3 CaLaBaCuO and 1:2:4 materials.

Another observation (Fig. 2) is that the onset of superconductivity (where $T_c \to 0$ K) on the underdoped side requires an increasing number of carriers when impurities are added. This observation can be interpreted assuming interaction weakening (i.e., decrease of V) upon impurity substitution. Since V decreases with z, the DOS N_0 at the superconductivity onset must increase provided that at the onset the product $N_0 V$ remains constant, i.e., that there exists a minimal interaction parameter required for superconductivity to show up.

In summary, we have shown that Zn and Ni impurities, which are believed to substitute into the CuO_2 planes of CaLaBaCuO, depress T_c^{max} almost with equal effectiveness. This behavior differs markedly from both classical superconductors and from YBCO. It suggests that the magnetic nature of the impurity is not the only factor that determines the pairing even if the magnetic moment resides in the CuO_2 planes. Other factors such as the chains or amount of oxygen may also control the pairing or pair breaking. Another effect of impurities in the CuO_2 planes is substantial departure from the universal TEP curve ($S_{290\,K}$ vs T_c/T_c^{max}). CaLaBaCuO appears to be a rather interesting system allowing one to completely separate effects due to carrier density and the interaction or pair breaking. This is achieved by a variety of chemical substitutions. For instance, under isoelectronic conditions (that is, keeping the oxygen content constant), changing the Ca concentration changes the doping level[12,13] leaving at the same time the interaction essentially unchanged. On the other hand, changing the impurity concentration changes the pair breaking or interaction without affecting carrier density.

[1] A.V. Mahajan, H. Alloul, G. Collin, and J.F. Marucco, Phys. Rev. Lett. **72**, 3100 (1994).

[2] H. Maeda *et al.*, Physica C **157**, 483 (1989).

[3] R. Villeneuve, I. Mirebeau, G. Collin, and F. Bouree, Physica C **235-240**, 1597 (1994).

[4] K. Ishida, Y. Kitaoka, N. Ogata, T. Kamino, K. Asayama, J.R. Cooper, and N. Athanassopoulou, J. Phys. Soc. Jpn. **62**, 2803 (1993).

[5] Y. Kitaoka, K. Ishida, G.-q. Zheng, S. Ohsugi, and K. Asayama, J. Phys. Chem. Solids **54**, 1385 (1993).

[6] T.M. Riseman, H. Alloul, A.V. Mahajan, P. Mendels, N. Blanchard, G. Collin, and J.F. Marucco, Physica C **235-240**, 1593 (1994).

[7] P. Mendels, H. Alloul, G. Collin, N. Blanchard, J.F. Marucco, and H. Bobroff, Physica C **235-240**, 1595 (1994).

[8] J.A. Hodges, P. Bonville, P. Imbert, D. Colson, N. Genand-Riondet, and A. Pinatel-Philippot, Physica C **218**, 272 (1993).

[9] S.S. Ata-Allah, Y. Xu, and Ch. Heiden, Physica C **221**, 39 (1994).

[10] P. Monthoux and D. Pines, Phys. Rev. B **49**, 4261 (1994); D. Pines, Physica B **199&200**, 300 (1994).

[11] D. Goldschmidt, A. Knizhnik, Y. Direktovitch, G.M. Reisner, and Y. Eckstein, Phys. Rev. B **49**, 15 928 (1994); **48**, 532 (1993).

[12] D. Goldschmidt, Y. Direktovitch, A. Knizhnik, and Y. Eckstein, Phys. Rev. B **51**, 6739 (1995).

[13] D. Goldschmidt, A. Knizhnik, Y. Direktovitch, G.M. Reisner, and Y. Eckstein, Phys. Rev. B **52**, 12 982 (1995).

[14] D. Goldschmidt, A.-K. Klehe, J.S. Schilling, and Y. Eckstein, Phys. Rev. B **53**, 14 631 (1996).

[15] H. Alloul, P. Mendels, H. Casalta, J.F. Marucco, and J. Arabski, Phys. Rev. Lett. **67**, 3140 (1991).

[16] G.V.M. Williams, J.L. Tallon, and R. Meinhold, Phys. Rev. B **51**, 16 503 (1995).

[17] Ratan Lal, S.P. Pandey, and A.V. Narlikar, Phys. Rev. B **49**, 6382 (1994).

[18] G.V.M. Williams, J.L. Tallon, and R. Meinhold, Phys. Rev. B **52**, R7034 (1995).

[19] S.D. Obertelli, J.R. Cooper, and J.L. Tallon, Phys. Rev. B **46**, 14 928 (1992).