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Doping in isoelectronic cuprate superconductors

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Thermoelectric power in the charge-compensated 1:2:3 family $(\mathrm{Ca}_x\mathrm{La}_{1-x})(\mathrm{Ba}_{1.75-x}\mathrm{La}_{0.25+x})\mathrm{Cu}_3\mathrm{O}_y$ shows that doping occurs also under *isoelectronic* (constant electron concentration) conditions obtained by keeping the oxygen content y constant. For all values of x and y there exists a single doping parameter $y-y_{\mathrm{M\text{-}I}}(x)$, where $y_{\mathrm{M\text{-}I}}$ is the value of y at the metal-insulator transition, suggesting that a single mobile band controls transport and superconductor properties. Isoelectronic doping occurs via capture of mobile electrons by lower-lying low-mobility states, requiring either a shift of the band relative to these states or transfer of spectral density near the Fermi energy.

The relationship between the transition temperature T_c in cuprate superconductors and the doping level (i.e., the mobile-hole density per CuO_2 plane p_{plane}) has received much attention in recent years.[1] This relationship was investigated by controlling the electron concentration, as determined from chemical valence, through the change of cation composition or of oxygen content. p_{plane} is assumed to change by these substitutions. The rationale behind using the microscopic hole density p_{plane} was the observation that in many underdoped cuprates T_c increases with conductivity. The BCS formula also suggests use of this parameter due to the close relation between p_{plane} and the density of states (DOS) at the Fermi energy E_F. As an example, in $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_y$ (YBCO), substitution of Ca for Y (Ca_{Y}) changes T_c and is believed to increase hole concentration.[2] Substitution of La for Ba ($\mathrm{La}_{\mathrm{Ba}}$) by the same amount dopes the material with an equal number of electrons.[2] Apparently, substitution of Ca_{Y} or $\mathrm{La}_{\mathrm{Ba}}$, respectively, increases or decreases the hole population by one hole. On the other hand, hole doping by the addition of oxygen is believed to occur via charge transfer from the planes to states added to the so-called charge reservoir.

The effect of substitution on T_c supports the assumption that the electron concentrations determined by chemistry and the doping level are related. However, the role of the energy levels (or bands) that are involved in these charge transfers, in particular the position of the CuO_2 band relative to the levels of the charge reservoir or of the substituted ions, is not entirely clear. For instance, one could assume safely that the energy level of Ca_{Y} lies much below the CuO_2 band since it acts as an efficient acceptor at 0 K. Similarly, the level of $\mathrm{La}_{\mathrm{Ba}}$ lies much above this band. In the case of separate substitution, i.e., either Ca_{Y} or $\mathrm{La}_{\mathrm{Ba}}$, the charge transfer from the substituent atom to the bands in the vicinity of E_F is complete. On the other hand, upon simultaneous cosubstitution of both dopants in equal amounts, one would expect *complete charge compensation between the substituent atoms alone.* In this case the CuO_2 band is not involved in the charge transfer. Hence, no doping effects would be expected since E_F remains fixed, in which case both T_c and the resistivity ρ should remain constant.

In this paper we investigate the effect on p_{plane} of substitution under conditions where the electron concentration remains constant. We show that under these *isoelectronic* conditions, one observes substantial changes in T_c, ρ, and the thermoelectric power (TEP). Hence, doping does occur. We conclude that additional states have to exist near E_F capable of capturing electrons released from the CuO_2 band and at the same time keeping the electron concentration constant.

Recently, we have investigated the tetragonal 1:2:3 family $(\mathrm{Ca}_x\mathrm{La}_{1-x})(\mathrm{Ba}_{1.75-x}\mathrm{La}_{0.25+x})\mathrm{Cu}_3\mathrm{O}_y$, Ca-La-Ba-Cu-O, that exists in the composition range $0 \leq x \leq \sim 0.5$.[3] In this family Q (the total valence of the non-copper cations) remains constant ($Q = 7.25$),[3] *independent of* x. This occurs due to equal amounts of charge-compensating cosubstitutions on the Y and Ba sites (first and second brackets, respectively), provided that Ca, Ba, and La keep their regular valence (+2, +2, and +3, respectively), which is common practice. By careful reduction and accurate determination of oxygen content y we were able to maintain y constant.[3] Under these conditions, the electron concentration remains constant, the system becomes isoelectronic, and no doping effects were expected. Nevertheless, we observed big changes in both T_c and ρ.[3] These unusual results[3,4] provide perhaps an indication that doping might occur even under truly isoelectronic conditions.

However, variations in T_c and ρ are in themselves insufficient to prove that doping actually occurs. For instance, variation with composition of the strength of the pairing interaction due to chemical disorder could be another reason for changes in T_c. Similarly, variation in scattering lifetime could contribute to changes in ρ with composition. Thus an independent measurement such as TEP is required if doping under isoelectronic conditions should become unequivocal.

Recently, a remarkable universal relationship between the room-temperature TEP S and $T_c/T_{c,\max}$, has been found by Obertelli *et al.*[5] ($T_{c,\max}$ denotes the maximum

T_c attainable by doping within a given family). It was shown that many cuprate superconductor systems fall on a single and therefore universal curve on this plot (Fig. 1), suggesting similarities in the band structure of p-type cuprates. Moreover, for large positive values of S the cuprate is in its underdoped region, while for negative S it is overdoped.[5] This approach is powerful in determining qualitatively the doping level of a given material within a family, since it utilizes easily determined empirical parameters. In particular, it is possible to measure small changes in the doping level.

In the present work we show that our TEP results on isoelectronic (constant y) Ca-La-Ba-Cu-O fall on the universal plot of S vs $T_c/T_{c,\mathrm{max}}$, with S varying as function of x. Since S can be taken to represent the doping level,[5,6] this provides unequivocal evidence that doping does occur even under isoelectronic conditions. We also show that in this family the doping level is related to $y - y_{\mathrm{M\text{-}I}}(x)$, the departure of oxygen content from its value at the metal insulator (M-I) transition. (The latter was identified with the full suppression of superconductivity, i.e., when $T_c \to 0$ K.) Besides, in samples in which both the chemical composition x and oxygen content y are varied in such a way as to keep T_c constant (i.e., nonisoelectronic conditions), S remains constant as well (example given later). This justifies the scaling of T_c to a *single* $T_{c,\mathrm{max}}$ *in this family.* It also strongly supports the assumption of a simple relationship between T_c, S, and p_{plane}, as all remain constant when $y - y_{\mathrm{M\text{-}I}}(x)$ is constant.

TEP measurements, relative to copper,[7] have been made near room temperature by the dynamic technique[8] in which a small ($\sim$ 0.5 K) temperature difference is spanned continuously across the sample and the thermal voltage is measured in steps of $\sim$ 0.005 K at a rate of $\sim$ 1 step/sec. Both positive and negative temperature differences were employed yielding the same emf. Thermal contact between the sample and the small copper blocks was maintained via a thin layer of In-Ga amalgam. The temperature difference was measured by means of Chromel-Constantan thermocouples, embedded inside the amalgam within a hole in the copper blocks and electrically insulated by a thin coating of heat conducting varnish. We have calibrated the apparatus against Constantan and against Chromel; our results agreed with standard tables to within 1%. The room-temperature TEP $S_{290\,\mathrm{K}}$ was obtained by interpolating between S measurements in a 20 K range around 290 K.

We used bar-shaped ceramic samples of length between 9 and 13 mm, reduced under flowing O_2 gas, and quenched into liquid nitrogen, as was described elsewhere.[3] No aging effects on S or on T_c were observed following this quench. The small transition width[3] indicates oxygen homogeneity of the samples. Oxygen content was determined by iodometric microtitration[3,9] to within an accuracy better than 0.005.[3] TEP, resistivity, susceptibility, and oxygen content were all measured on the same sample, thereby minimizing scatter in the data.[3] For the resistivity measurements we used gold wires as implanted electrodes. Through comparison with samples having external electrodes we have verified that the wires had no effect on the value of the TEP to within the stated accuracy (see both points at $x = 0.4$, $y = 6.966$, and $S = 29\mu V/K$ in Fig. 1).

Our TEP results for various x and y values are shown in Fig. 1 superimposed on the universal curve of S vs $T_c/T_{c,\mathrm{max}}$ which has been reproduced from Obertelli *et al.*[5] Clearly, these data fall in the region of strong underdoping (S on the order of tens of μV/K) for most y values of the $x = 0.1$ and 0.2 members, and for the low-y values of the $x = 0.4$ member. For higher values of oxygen content in the $x = 0.4$ samples, the TEP goes down and the doping level comes close to optimal.[5] This establishes the obvious effect of doping under conditions of varying electron concentrations.

More interesting are the results under isoelectronic conditions. For increasing x but constant y, all TEP results still fall on the universal TEP curve with decreasing values of S (see points marked with × for $y = 7.00$ and with + for $y = 7.07$ in Fig. 1). This proves unambiguously that *doping takes place under isoelectronic conditions.*

The second point we want to emphasize is that there exists a single parameter controlling the doping level, namely, $y - y_{\mathrm{M\text{-}I}}(x)$. This is shown in Fig. 2 in which $\rho(T)$ curves have been displayed as function of this parameter for $x = 0.4$ and $x = 0.1$ [Figs. 2(a) and 2(b), respectively]. For clarity we have assigned to each curve the corresponding value of $y - y_{\mathrm{M\text{-}I}}$, taking for $y_{\mathrm{M\text{-}I}}$ the value 6.895, 6.96, and 6.975 for $x = 0.4$, 0.2, and 0.1,

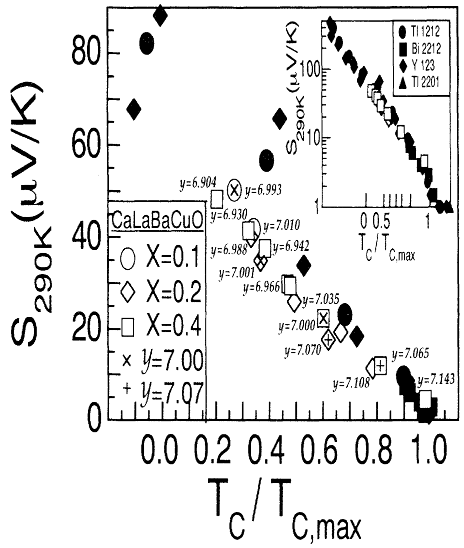

FIG. 1. Room-temperature thermoelectric power (TEP) vs normalized transition temperature $T_c/T_{c,\mathrm{max}}$. Solid symbols represent the universal doping common to many cuprate systems (reproduced from Ref. 5). Open symbols correspond to $(\mathrm{Ca}_x\mathrm{La}_{1-x})(\mathrm{Ba}_{1.75-x}\mathrm{La}_{0.25+x})\mathrm{Cu}_3\mathrm{O}_y$. Notice that open symbols marked with + and with × represent doping under isoelectronic conditions with $y = 7.07$ and $y = 7.00$, respectively. Equal TEP and T_c for different x and y (e.g., at $S = 41$ or 12 μV/K) yield a single $T_{c,\mathrm{max}}$ in this family. Inset: logarithmic plot as in Ref. 5. Notice that our data fall smoothly on the universal plot.

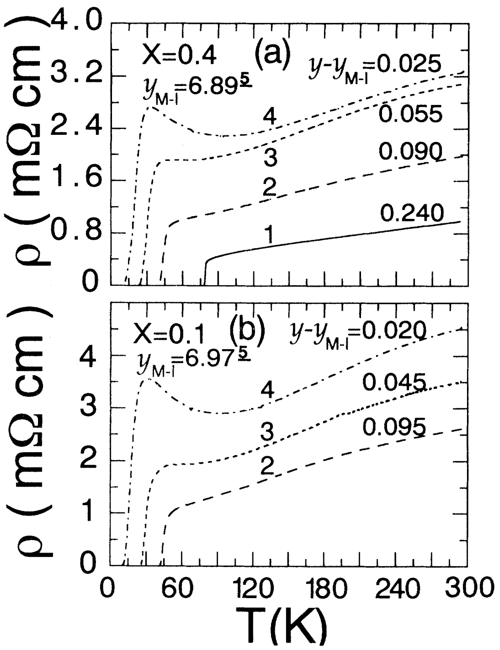

FIG. 2. Temperature dependence of the resistivity of (a) $x = 0.4$ and (b) $x = 0.1$ for various values of oxygen content. Notice that the shape of the curves depends on $y - y_{\mathrm{M\text{-}I}}(x)$, the departure of oxygen content y from its value at the metal-insulator transition, $y_{\mathrm{M\text{-}I}}$.

respectively, as obtained from Ref. 3. Notice the similarities in the shape of these curves at both compositions. In Fig. 3 we show that when the curves of T_c, ρ, and S for a variety of x and y values are plotted as a function of the parameter $y - y_{\mathrm{M\text{-}I}}(x)$, they coalesce each into a single curve, suggesting that p_{plane} is related to $y - y_{\mathrm{M\text{-}I}}(x)$.

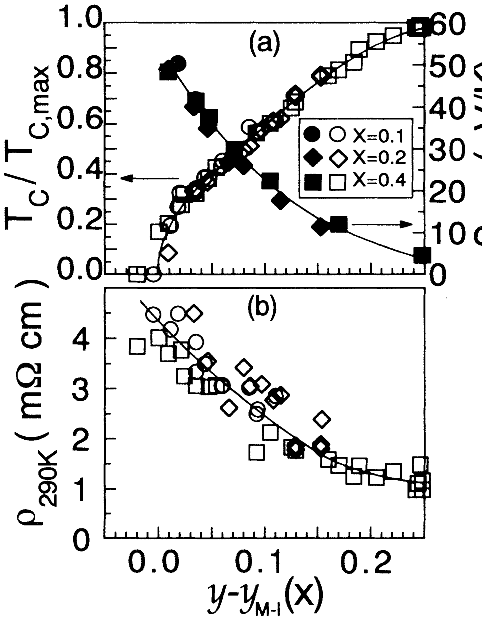

FIG. 3. (a) Normalized T_c (open symbols) and TEP (solid symbols), and (b) resistivity vs $y - y_{\mathrm{M\text{-}I}}(x)$. Since for all x and y values our data fall on the same curve, $y - y_{\mathrm{M\text{-}I}}(x)$ is the single parameter controlling the doping level.

Another conclusion of our TEP results is that $(\mathrm{Ca}_x\mathrm{La}_{1-x})(\mathrm{Ba}_{1.75-x}\mathrm{La}_{0.25+x})\mathrm{Cu}_3\mathrm{O}_y$ constitutes really a single doping family, in the sense that the same $T_{c,\max}$ can be assumed for all compositions x. This was concluded from our observation that samples having the same T_c also have the same TEP, irrespective of the values of x and y (Fig. 1). For instance, at $T_c/T_{c,\max} \cong 0.33$ or 0.80, $S \cong 41$ or 12 μV/K, respectively, independent of x or y. Had there been different values of $T_{c,\max}$ for various values of x, the results of samples with the same T_c would not coincide. $T_{c,\max}$ ($\cong$ 81.5 K in the present family) has been obtained by measuring T_c in the most oxydized high-x samples.

The existence of a single $T_{c,\max}$ and a single doping parameter $y - y_{\mathrm{M\text{-}I}}(x)$, strongly supports the view that a single band (i.e., the CuO_2 band) controls superconductor and transport properties for all values of x and y. In what follows this band is termed the mobile band (MB). Within the independent particle band picture $T_{c,\max}$ is associated with $N_{0,\max}$, the maximum in the DOS of this band (in the sense of the BCS formula). $T_c = T_{c,\max}$ when E_F lies at this maximum. Since $T_{c,\max}$ does not vary with x, the magnitude of $N_{0,\max}$ does not change either. $y - y_{\mathrm{M\text{-}I}}$ might represent in this scheme the change in doping obtained from the integrated spectral density. This is the amount of charge added when going from the M-I transition, where the band is full, to some point on the DOS. Interestingly, the dependence on $y - y_{\mathrm{M\text{-}I}}$ shows that it is possible to cast into a single parameter the doping effects of oxygen addition and of cation substitution which have different energetic origins as was explained above. Independent of whether one changes x or y, these chemical changes introduce the same change in the energetics of the system, i.e., a shift in the position of E_F relative to the band edge. In this sense there is no difference between isoelectronic and regular doping. In the simple band picture the decrease of $y_{\mathrm{M\text{-}I}}$ with increasing x, which controls isoelectronic doping, reflects an upward shift in the position of the MB relative to other bands; in other words, the energy distance between E_F and the top of the band increases. This requires the existence of low-mobility states which are degenerate in energy with the MB, i.e., located in the neighborhood of E_F. We use the term localized band (LB) to describe these states. When empty states of the LB are shifted below E_F, they capture the electrons that were released from mobile states, thereby keeping the electron concentration constant. This is the meaning of "internal charge transfer" from the CuO_2 plane band to states related with the charge reservoir, a term that we used in Ref. 10. The states of the LB must be nearly localized; i.e., they do not contribute to transport or to superconductivity, thereby preserving the single-band nature as noted above. We note that doping under isoelectronic conditions provides clear evidence for the existence of a LB which is degenerate in energy with the MB, as well as for the important role of opposite band shifts and electron trapping in 1:2:3 cuprates. Also notice that within the band picture and under isoelectronic conditions the total number of states in the vicinity of E_F (i.e., in both the MB and

LB) remains constant because y does not change. It is essential to have these opposite band shifts that uncover states in order to capture the uppermost electrons. The existence of degenerate bands and of band shifts under regular (nonisoelectronic) conditions implies that, in contrast to the assumption in Ref. 2, substitution of Ca_Y or La_{Ba} in YBCO contributes less than one mobile hole or electron to p_{plane}, respectively, since the chemical charge is split between the MB and LB. Band shifts under isoelectronic conditions might be associated with oxygen reordering in the basal plane,[3] or with change in internal electric field with composition.[11]

These changes in band structure can be demonstrated qualitatively by comparing the $x = 0.1$ and $x = 0.4$ members under isoelectronic conditions. For $x = 0.1$, $E_{\max}$ ($x = 0.1$), the energy at which the DOS of the MB equals $N_{0,\max}$, lies considerably below E_F even for the more oxidized samples ($y = 7.07$). Therefore, E_F is close to the M-I boundary, the mobile hole density is relatively low, and the material is underdoped. A decrease in y by as little as ~ 0.1 (to $y = 6.975$) is sufficient to drive the material into the insulator state. For $x = 0.4$, $E_{\max}(x = 0.4)$ has shifted upwards compared with $E_{\max}(x = 0.1)$, E_F lies now further away from the top of the MB, and the mobile-hole density increases. Therefore, it takes now a bigger change in y (i.e., ~ 0.2, from $y = 7.07$ to $y = 6.895$) to drive the $x = 0.4$ material into the insulator state. Thus, the $x = 0.4$, $y = 7.07$ sample is more doped than its isoelectronic counterpart $x = 0.1$, $y = 7.07$ sample. Further increase in y (beyond 7.07) in the $x = 0.4$ samples induces a downward shift in $E_F(y)$ until at $y = 7.15$, $E_F(y) \cong E_{\max}(x = 0.4)$. This then corresponds to $T_c \cong T_{c,\max}$.

It is more difficult to interpret our results within the interacting particle picture. Recently a doping theory for strongly correlated particles has been developed.[12] In the charge transfer scheme of this theory, spectral density is transferred from the upper Hubbard band to the CuO_2 band. This could provide, in principle, the empty states required for electron capture in isoelectronic doping. However, according to the theory these spectral changes require change in electron (or hole) concentration. As this seems to remain constant under isoelectronic conditions, our isoelectronic doping results remain unexplained. Besides, the dependence on $y - y_{\text{M-I}}$ would restrict the shape that the changing DOS is allowed to take. It seems that a theory in which electron concentration is not the direct microscopic parameter might explain our results more easily. To this end, another many particle theory based on electron polarizability has been developed recently.[13] The screening, or the closely related effective electron-electron distance, is the microscopic parameter that determines the shape of the DOS and the strength of the pairing interaction which, respectively, determine transport properties and T_c as function of chemical substitution. It still remains to be shown how the polarizability is related to the doping parameter $y - y_{\text{M-I}}$.

In summary, we have shown that a single parameter $y - y_{\text{M-I}}(x)$ controls the doping level in Ca-La-Ba-Cu-O and that a single $T_{c,\max}$ exists for all compositions. This strongly suggests the existence of a single band (the MB corresponding to the CuO_2 planes) in which doping occurs. $T_{c,\max}$ has been associated with the existence of a maximum $N_{0,\max}$ in the DOS of the MB. Besides and based on our TEP results, we have shown that doping occurs also under isoelectronic conditions where the electron concentration remains constant. In the band picture this requires the existence of low-mobility states (the LB, corresponding to the charge reservoir) which are *degenerate in energy* with states of the MB in the vicinity of E_F. Isoelectronic conditions also require that the total number of states of both the MB and LB in the neighborhood of E_F remains constant, since no extra atoms are added. Hence, with increasing x, the LB has to shift downwards relative to the MB so as to make room for mobile electrons, thereby allowing for doping to occur while keeping the electron concentration constant.

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