

Effect of magnetic and nonmagnetic impurities (Ni, Zn) substitution for Cu in $\text{Bi}_2(\text{SrCa})_{2+n}(\text{Cu}_{1-x}\text{M}_x)_{1+n}\text{O}_y$ whiskers

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We have measured the change in the resistive T_c of $\text{Bi}_2(\text{SrCa})_{2+n}(\text{Cu}_{1-x}\text{M}_x)_{1+n}\text{O}_y$ whiskers due to substitution of $M = \text{Ni}$ (magnetic) or $M = \text{Zn}$ (nonmagnetic) for Cu. These whisker crystals show resistance drops for both the 2212 and 2223 ($n=1,2$) phases, with transition widths (10–90 %) of 1 K. We checked the effect of oxygenation at several values of x , and found that T_c is maximum for the y obtained by growing and annealing in 1 atm of O_2 . We observed a linear depression of T_c for both 2212 and 2223 phases with $D = dT_c/dx \approx -800$ K for both Ni and Zn. This is in contrast with YBCO in which $D_{\text{Zn}} \approx 3D_{\text{Ni}}$. [S0163-1829(97)03933-7]

I. INTRODUCTION

One characteristic of the copper-oxide superconductors is the close relation between magnetism and superconductivity. In particular it has been found that in YBCO, nonmagnetic impurities affect the transition temperature T_c much more than magnetic impurities do.¹ This is contrary to the behavior of conventional low-temperature superconductors, and has been described as definitively linking copper-oxide superconductivity with magnetism.²

This may not be the case in $\text{Bi}_2(\text{SrCa})_{2+n}(\text{Cu}_{1-x}\text{M}_x)_{1+n}\text{O}_y$ (BSCCO), where Zn and Ni impurities have been reported to decrease T_c equally.^{3–11} Since the amount of Zn which can be dissolved in BSCCO is limited, these studies are difficult. We have repeated these studies in “whisker” crystals that have the advantage of narrow transitions, easy growth of alloys, and short oxygen annealing times.

In the conventional Abrikosov-Gorkov theory,¹² $+k\uparrow$ electrons scatter the same as $-k\downarrow$ electrons when they interact with a nonmagnetic impurity, limiting the pair-breaking effects. For magnetic impurities, different scattering of $+k\uparrow$ electrons and $-k\downarrow$ electrons leads to a rapid depairing and depression of T_c . For the $\text{YBaCu}_{1-x}\text{M}_x\text{O}_y$ system (where M is Zn or Ni), dT_c/dx is found to be about -1200 K for Zn, whereas dT_c/dx for Ni is only about -350 K.¹ This puzzling result favors a magnetic mechanism of pairing and an asymmetric order parameter, such as $d_{x^2-y^2}$.²

In the YBCO system, the existence of two kinds of Cu sites (planes and chains) as well as the sensitivity of T_c to the oxidation state complicates the experimental results. The BSCCO compounds have essentially one kind of Cu site (there are two slightly different sites in the 2223 phase, one on the inner and one on the outer two of the three closely spaced CuO planes in the unit cell). Thus BSCCO seems to be a simpler, and therefore better, candidate for studying the effect of substitution on T_c than YBCO. Our whiskers, grown in 1 atm of O_2 are close to the maximum in the shallow inverted- U dependence of T_c on the oxidation state.

Consequently they are less apt to be sensitive to changes in the oxidation state that might occur as a result of substitutions of Zn and Ni for Cu.

Many studies have been reported on transition-metal substitutions in $\text{Bi}_2(\text{SrCa})_{2+n}(\text{Cu}_{1-x}\text{M}_x)_{1+n}\text{O}_y$, mostly in the $n=1$ phase (2212 phase with $T_c \approx 80$ K). But the results so far do not agree from study to study. For example, the magnitude of dT_c/dx for Zn substitution in the 2212 phase has been measured to be as little as -500 K,¹³ and as large as -1800 K.¹⁴ vom Hedt *et al.* reported that the amount of Zn that can be dissolved in the 2212 phase is small ($x < 0.004$),³ making the total shift in T_c less than 2 K, which is difficult to discern in samples whose transition width is often more than 3 K.

We have measured the decrease in T_c due to substitution of Zn and Ni in BSCCO whiskers. The dependence of T_c (and the resistance vs temperature curves) was also examined as a function of oxygen content at several levels of substitution. The very narrow resistive transitions in our whisker samples (0.5–1 K from 10% to 90% of R_{normal} for the 2223 phase, 1–2 K for the 2212 phase, even in the samples with the highest concentrations of substituents), reflects the high quality of our samples and permits us to examine the T_c shift in very fine detail. All the oxygen doping measurements showed T_c to be a maximum when the annealing oxygen pressure was 1 atm.

Our results show that dT_c/dx for Zn and Ni substitution in 2212 as well as in 2223 is essentially the same, approximately -800 K. Thus the difference between Zn and Ni substitution in YBCO is not representative of all CuO superconductors, but rather is peculiar to YBCO.

II. EXPERIMENTS AND RESULTS

A. Crystal growth

The growth method we used was pioneered by Matsubara *et al.*¹⁵ The proper ratio of Bi_2O_3 , SrCO_3 , CaCO_3 , and

CuO and differing amounts of NiO or ZnO powders were mixed thoroughly and melted in an Al_2O_3 crucible at 1200°C for half an hour. Hereafter, the nominal concentrations derived from the powder mix will be referred to as the starting material concentrations. Then splat-cooling the melt in about 1 s produced glass shards. The whiskers were produced by annealing the glass shards in flowing oxygen at 1 atm for at least 120 h. The growth temperature for each substituent level x is slightly different. Therefore a three-zone furnace with a 30°C temperature difference along the growth region was used to increase the probability that some of the shards were at the proper growth temperature. For other growth details see Ref. 16.

B. Characterization of samples

These Bi-based whisker samples are believed to be nearly perfect single crystals, with few or even zero dislocations. Particularly good ones have been used to show Josephson tunneling between layers that could not be seen in less perfect crystals.¹⁷ Typical dimensions of the whiskers we used are $2\text{--}10\text{ mm}$ (a axis) $\times 10\text{--}100\text{ }\mu\text{m}$ (b axis) $\times 2\text{--}10\text{ }\mu\text{m}$ (c axis). A standard four-probe dc technique with a typical excitation current $I = 100\text{ }\mu\text{A}$ was used for the a -axis electric resistance measurements from which we deduced the transition temperature T_c . Making electrical contacts to these samples is not trivial. A direct silver paint contact normally yields $\text{k}\Omega$ contact resistances or even no contact at all. We find that evaporating four silver pads on the sample and then annealing at 570°C for 1 min in oxygen flow at 1 atm gives typical contact resistances of $1\text{ }\Omega$ when silver paint is applied afterwards. The depth to which the silver diffuses is not known.

Since we must differentiate between the changes we make in $\text{Bi}_2(\text{SrCa})_{2+n}(\text{Cu}_{1-x}\text{M}_x)_{1+n}\text{O}_y$, where M stands for Zn or Ni, we will call making changes in x “substituting,” and changes in y “doping.” Based on crystal chemistry principles, but not experimentally validated, we make the assumption that Ni and Zn ions substitute for Cu ions on the BSCCO lattices. Figure 1 shows the temperature dependence of the normalized resistance along the a axis of as-grown (1 atm O_2), unsubstituted samples in the range $4\text{ K} < T < 300\text{ K}$. The resistance is linear in T in the normal state. The sharp drop in R at 108 K corresponds to the T_c of the 2223 phase and the second small drop at about 80 K corresponds to the 2212 phase. In some samples, an excitation current as large as 2 mA was applied for the resistance measurements in order to pick up the second transition signal at the microvolt level. Even though the drop in the resistance due to the transition of the 2223 phase is larger than the drop at the 2212 transition, bulk probes, such as x-ray, flux shielding, microprobe analysis, and heat capacity measurements, fail to show more than 5% 2223 phase in our samples.¹⁸ Thus they can be viewed as a 2212 matrix in which a small volume of 2223 phase, no more than 5%, percolates to form an almost complete filamentary path from one potential contact to the other. Below 110 K , the 2223 phase nearly shorts-out the dominant 2212 phase; however, the transition signature of the 2212 matrix phase is evident at 80 K . The presence of 2212 and 2223 conductive paths in the whisker provides an advantageous material venue for the study of doping effects. In a

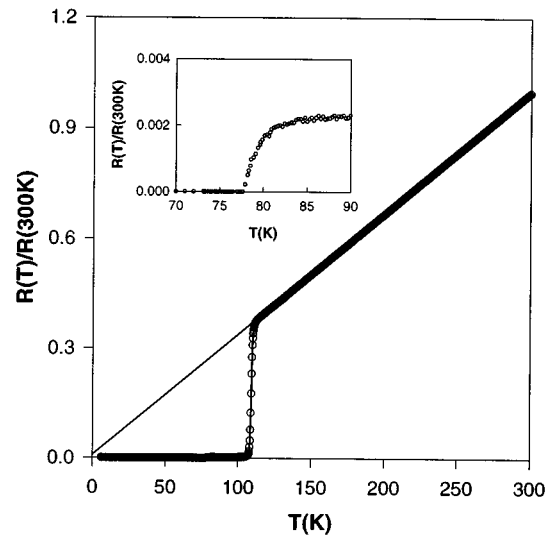


FIG. 1. R vs T curve over a wide temperature range for an undoped whisker. Excellent linearity of the normal-state resistance, a small residual resistance and a sharp transition all reflect the high quality of the whisker samples. The inset shows a blowup plot near the 2212 phase transition.

single-filamentary-crystal sample, given a well-controlled thermal treatment, the responses of the two superconducting phases to changes in x and y can be determined in a single set of measurements.

On the other hand, it is true that the resistance measurements only sample a small fraction of the sample once the 2223 begins to superconduct. That portion consists of the 2223 filaments and the regions of 2212 that exist between the filaments. Suppose the substituents reside preferentially in these regions. In this case, we would be measuring the resistivity of a different region than our compositional analysis measures. We do not believe this is the case for the following reasons: (1) The dT_c/dx that we measure for Ni substitution agrees with the literature on single-crystal samples. There are not enough points available from other studies to check our Zn data. (2) We find that dT_c/dx is the same for 2223 and 2212. If substituents preferentially reside in the 2223 or grain boundaries, this would be an unlikely coincidence. Of course, bulk measures such as heat capacity or magnetization would be the most reliable way to resolve this issue. Unfortunately, the sample size and yield decrease with substituent level, leaving us with sample masses on the order of $10\text{ }\mu\text{g}$. This is not enough material to accurately determine the transition temperature of the 2212 phase by a bulk measurement, much less the 2223 phase which constitutes less than 5% of the sample.

C. Compositional analysis of substituted samples

The samples were mounted with silver paint on 1-in.-diam aluminum stubs for analysis by nondestructive quantitative electron probe microanalysis techniques using a Cameca SX50 four-wavelength-spectrometer automated electron microprobe. The samples were mounted flat on the sample holders and were examined optically and by secondary elec-

TABLE I. A representative microprobe run on two whiskers grown from $x=0.015$ Ni starting material. Different spots correspond to different positions probed along the samples.

Spot	Sample 1 Ni/Cu ratio	Sample 2 Ni/Cu ratio
1	1.03%	0.94%
2	0.77%	0.72%
3	0.67%	0.95%
Average	$(0.87 \pm 0.08)\%$	$(0.87 \pm 0.07)\%$

tron imagery using the electron microprobe; the location of the analysis points was thus precisely located with a 1- μm -precision sample stage.

The whiskers were analyzed with the electron microprobe using operating conditions designed to provide precise quantitative compositional data at 100–200 ppm concentration levels. Analyses were obtained during several analytical sessions at either 15 kV accelerating voltage and 20 nA probe current, or 20 kV accelerating voltage and 30 nA probe current; the latter conditions were employed to verify the very low-level Zn contents. The standards used for the measurements were pure metals for Bi, Cu, and Ni; CaMgSiO_3 (diopside) for Ca; SrCO_3 for Sr; and ZnAl_2O_4 (gahnite) for Zn. These are all homogeneous, well-characterized standards. Counting times varied from 20 s for the major elements to 300 s for the minor elements; Ni was measured for 100 s and Zn was measured for 300 s. Minimum limits of detection, based on the standard peak and background counts and the stated counting times, are 0.025% (250 ppm) for Ni and 0.013% (130 ppm) for Zn. As oxide components the stated detection limits are 0.034% for NiO and CoO and 0.016% for ZnO. Analyses were corrected for instrumental drift and dead time, and electron-beam–matrix effects using the PAP $\Phi(\rho z)$ correction procedures provided with the Cameca microprobe automation system; these correction procedures are based on the model of Pouchou and Pichoir.¹⁹

The analytical precision is approximately 1% of the amount present for oxide concentrations greater than 10 wt %, 1–2 % for oxide concentrations between 1 and 10 wt %, and 5–10 % for oxide concentrations between 0.01 and 1 wt %. The relative accuracy of the analyses, based upon comparison of measured with published compositions of the standards, is 1–2 % for oxide concentrations greater than 1 wt % and 10% for oxide concentrations less than 1 wt %.

We found the composition to be uniform along the sample length within this precision (the narrow transition widths are a better measure of this) and the values of x to be consistent within 5% for samples grown from the same starting materials. A representative microprobe analysis for two whiskers grown from a starting materials with a Ni content $x=0.015$ is shown in Table I. In Fig. 2 we plot x in the whiskers versus x in the starting materials, where the error bars represent the standard deviation within microprobe measurements of the same sample. For all M and x reported here, we found that the value of x in the whiskers differed from the value of x in the starting materials, x being lower in the whiskers. Hereafter, concentrations determined quantitatively by microprobe analysis will be referred to as measured

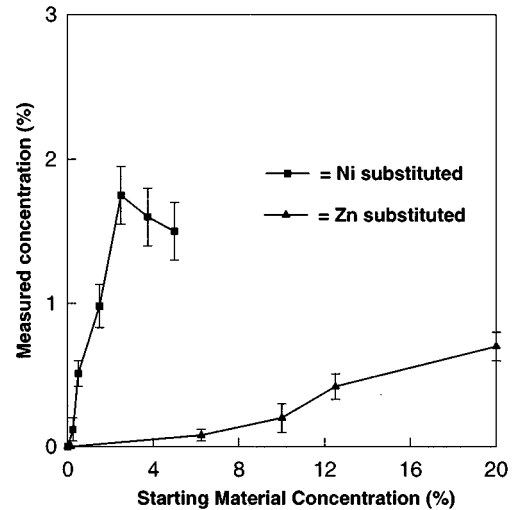


FIG. 2. Substituent concentration measured by microprobe analysis vs the substituent concentration in the starting materials (at. % x) of BSCCO whiskers. Lines are guides for the eye.

concentrations. For Ni, x in the whiskers is about $2/3 x$ in the starting material. For Zn, there is no detectable Zn in the whiskers for $x < 0.06$ in the starting material, while for $x = 0.2$ in the starting material, $x = 0.007$ in the whisker. As observed by vom Hedt *et al.*, it is difficult to get Zn to substitute in a single crystal of BSCCO. Saturation is reached at about $x = 0.018$ for Ni and $x = 0.007$ for Zn. We have been able to substitute Ni, Co, Fe, and Pd more readily. It is likely that Zn substitution on the Cu-O layers of the BSCCO lattices is inhibited by the high thermodynamic stability of ZnO.

D. Depression of T_c and the normalized residual resistance as a function of Ni and Zn substitution and oxygen doping

First we discuss Ni substitution. Because of the difficulty of accurately determining the dimensions of our whisker samples, in Fig. 3(a) we show the temperature dependence of the normalized resistance $R(T)/R(120 \text{ K})$ of Ni-substituted samples near the transitions, rather than the resistivity $\rho(T)$ itself. All samples exhibit a linear decrease in resistance from 300 K to T_c (not completely shown in the figure), and a dual transition with both 2212 and 2223 phases. The T_c 's of both phases decrease monotonically as the amount of Ni in the whiskers is increased, until the amount of Ni in the whiskers saturates at $x = 0.018$. From Fig. 3(b), we find $dT_c/dx = -950 \pm 50 \text{ K}$ for $M = \text{Ni}$ in the 2223 phase and $dT_c/dx = -820 \pm 50 \text{ K}$ in the 2212 phase. Another feature is that, as shown in Fig. 4(a), the normalized residual resistance $\text{NRR}(x) = R(T \rightarrow 0)/R(120 \text{ K})$, obtained by extrapolating the normalized resistance to $T = 0$, increases with increasing x . The perfection of these whisker samples leads to a value of NRR which is nearly zero for the nominally pure samples. The NRR increases with increasing x : $\text{NRR}(x) = 0.02 + 15x$ for Ni, as plotted in Fig. 4(b). To our knowledge, this is the first detailed study on the impurity dependence of the NRR for BSCCO. The similar linear dependences of T_c and NRR in Figs. 3 and 4 is expected in standard models,²⁰ since

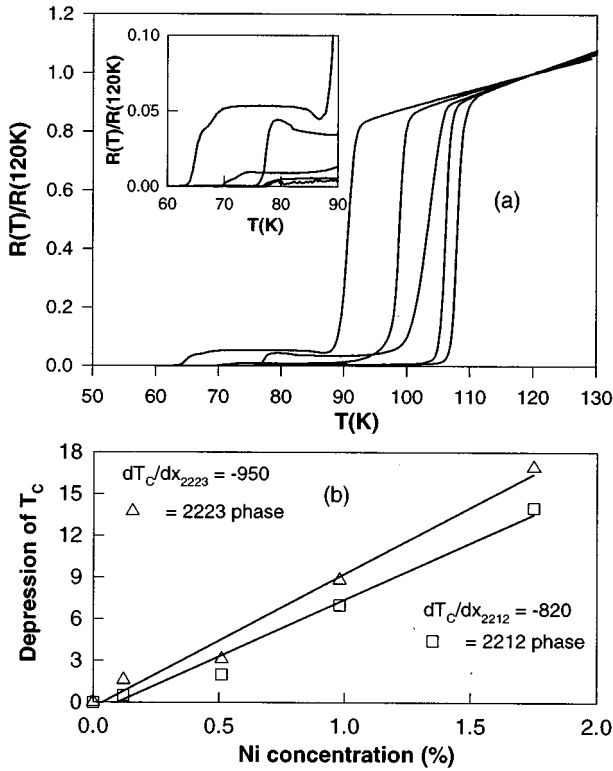


FIG. 3. (a) Normalized resistance $[R/R(120\text{ K})]$ vs T for Ni-substituted whiskers with measured concentrations 0, 0.12, 0.51, 0.98, and 1.75 in at. % x (from right to left). The inset shows a closeup of the 2212 transition. (b) T_c vs Ni concentration for the 2223 phase and the 2212 phase. The depression rate dT_c/dx is determined from a linear least-squares fit.

dT_c/dx and $d(NRR)/dx$ are determined by the same parameter, the normal state scattering rate, for both magnetic and nonmagnetic impurities.

For Zn substitution, we observe no discernible effect on T_c for whiskers grown from starting materials with $x < 0.06$. This is due to the very large ratio of Zn in the starting materials to Zn in the whiskers. For higher Zn concentrations in the starting materials, we can resolve a small decrease in T_c , as shown in Fig. 5(a). For example, with $x = 0.20$ in the starting materials, yielding $x = 0.007 \pm 0.001$ in the whiskers as measured by microprobe, we observe a 5 K depression of T_c for both the 2223 and 2212 phases. A least squares fit to a linear relation between T_c and x for Zn substitution, as shown in Fig. 5(b), yields $dT_c/dx = -600 \pm 100$ K for the 2223 phase and $dT_c/dx = -840 \pm 100$ K for 2212 phase. The uncertainties in the derivatives for Zn are higher than those for Ni due to the low solubility of Zn. As in Ni, the NRR also changes with increasing x ; see Fig. 4(b) for details.

In order to avoid mixing the effect of x and y on T_c , all the results shown in Figs. 3 and 5 were measured on as-grown whiskers or whiskers that were annealed under 1 atm of O_2 at 570°C . We found that this annealing temperature and pressure gave the maximum T_c for all our samples, no matter what the values of x or whether M was Ni or Zn. Figure 6(a) shows representative plots of T_c vs oxygen pressure for a 1 h annealing at 570°C . Notice that (1) the transi-

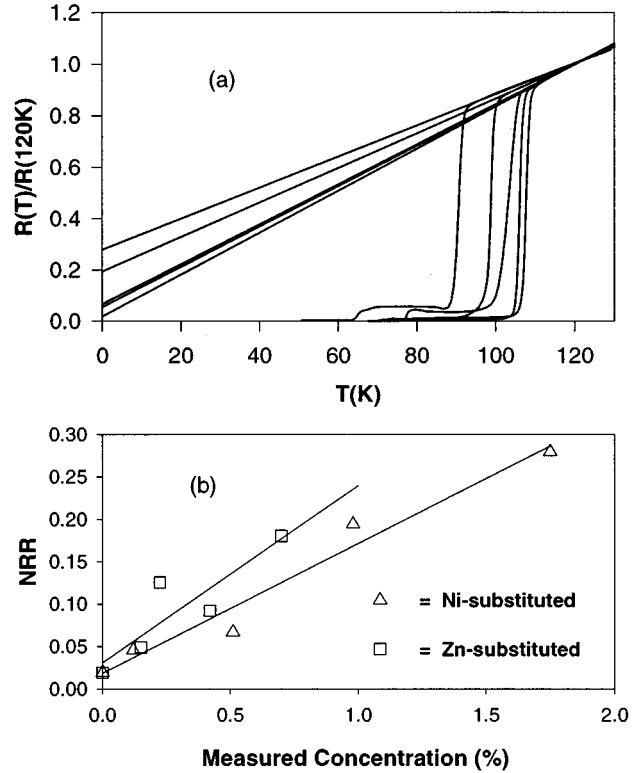


FIG. 4. (a) Same plot as Fig. 3(a) with extended temperature range. The normalized residual resistance NRR is defined from a linear fit, shown as straight lines, above the 2223 transition extrapolated to $T=0$. (b) $NRR(x)$ is approximately a linear function with $NRR(x) = 0.02 + 15x$ for Ni and $NRR(x) = 0.03 + 20x$ for Zn.

sition temperature of the 2223 phase is noticeably affected by the annealing; (2) the annealing procedure is reversible; that is, annealing the whisker under 1 atm of O_2 returns it to its as-grown state; (3) the transition width remains narrow, indicating that the oxygen content is uniform; and (4) annealing under 1 atm of O_2 leads to the highest T_c , as detailed in Fig. 6(a). However, the transition temperature for the 2212 phase remains unchanged within 1–2 K under different annealing conditions, even with higher annealing temperature and longer annealing time. We have no straightforward explanation for this result other than the possible scenario of much stronger CuO bonds in the 2212 phase than in the 2223 phase or that the 2223 phase is further from optimal oxygen doping, or the 2212 phase is less sensitive to oxygen doping for our whisker samples. Although we have not measured the oxygen content directly, these results are in agreement with the results of others on the oxidation state of cuprate superconductors.²¹

III. DISCUSSION AND CONCLUSIONS

We have extended and clarified the results of others on the effect of Zn and Ni substitutions in BSCCO. We have used single crystals with very narrow transitions, carefully measured the substitution levels in the crystals, and shown that oxygen annealing does not interact strongly with substitution. Within the uncertainty of our results, dT_c/dx in $\text{Bi}_2(\text{SrCa})_{2+n}(\text{Cu}_{1-x}\text{M}_x)_{1+n}\text{O}_y$ is essentially the same for

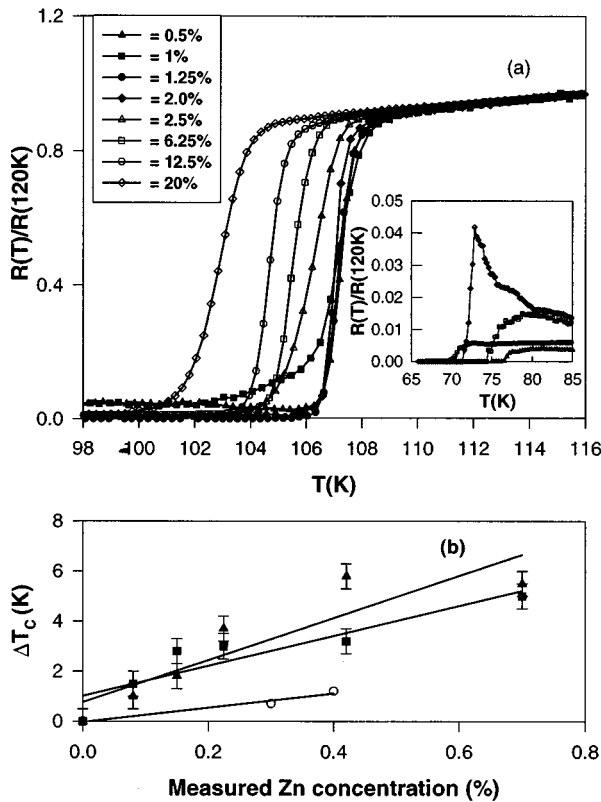


FIG. 5. (a) Normalized R vs T curves for Zn-substituted whiskers with various starting material concentrations from 0.5% to 20%. No significant depression on T_c is observed for either phase with starting material concentrations lower than 6%. With higher concentration, a noticeable shift in T_c is observed for both phases. (b) T_c vs Zn concentration for the 2223 phase and the 2212 phase. The depression rates dT_c/dx are determined from the slopes of linear fits. Triangles and squares represent 2212 and 2223, respectively. The open circles are taken from vom Hedt *et al.* for comparison.

$M=\text{Ni}$ and $M=\text{Zn}$ for $n=1$ and $n=2$. This is contrary to the results of such substitutions in YBCO. Suggestions have been made that the magnetic structure of the CuO planes and/or the scattering of carriers is affected differently by magnetic and nonmagnetic substitutions for Cu. These need to be revised to take into account that the effect does not occur in BSCCO. Large differences in the effects of Zn and Ni substitutions are not generic to CuO superconductors, but may be peculiar to YBCO.

Fehrenbacher makes the point that the difference between the effects that Zn and Ni have on T_c in YBCO could be due

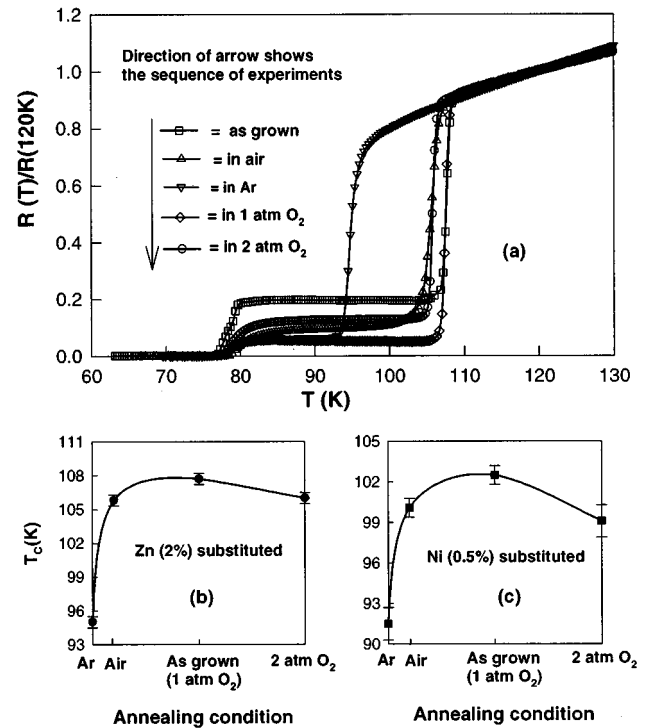


FIG. 6. (a) R vs T curves for a whisker grown from 2% Zn starting material under various annealing conditions. T_c for the 2223 phase is strongly affected by annealing conditions but much less change occurs in the 2212 phase. Notice that the oxygen annealing is completely reversible. T_c vs annealing condition for whiskers grown from 2% Zn and 0.5% Ni starting materials are plotted in (b) and (c), respectively. All annealing was done at 570 °C for 1 h. Lines are guides for the eye.

to the presence of a van Hove singularity (VHS) close to the Fermi surface.²² He quotes $\epsilon_{\text{VHS}} \approx -16$ meV for YBCO and -31 meV for BSCCO 2212. Thus it could be that the difference in the closeness of the VHS to the Fermi surface leads to the difference in the behavior of dT_c/dx in YBCO and BSCCO. Note, however, that the parameters that Fehrenbacher used are an amalgam of YBCO and BSCCO values, so that the different ϵ_{VHS} values are only suggestive.

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