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Differences between Ca-Th and Ca-Pr doped 1:2:3 superconductors: Evidence for disorder-depressed T_c for Ca-Th doping

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Charge-neutral doped 1:2:3 superconductors have been studied in well characterized sintered samples of Y- and Nd-based hosts with Ca-Pr and Ca-Th doping. The superconducting T_c, the electrical resistivity, and the relative change of the upper critical field slope $dH_{c2}(T)/dT$ were investigated. The results show that the depression of T_c in Ca-Th doped 1:2:3 systems is correlated with an increase in the resistivity. Conventional disorder theories were found to qualitatively describe these data as well as published results for irradiated thin films. Significant differences between Ca-Th and Ca-Pr doping were found both in the much stronger depression of T_c as a function of the increase in resistivity for Ca-Pr doped samples and in the different doping dependences of the upper critical field slope. [S0163-1829(98)03822-3]

I. INTRODUCTION

In high-temperature superconductors the strong sensitivity of the superconducting transition temperature T_c to even small amounts of several dopants or to other forms of disorder has been a challenging problem from the outset. The relation to charge density was noted early. In particular, T_c was found to decrease linearly with n_s/m^* over an extended range of doping concentrations and of different materials.[1] n_s is the superfluid charge density and m^* the effective mass. However, in a region of strong doping T_c saturates and varies slowly in spite of substantial variations of n_s/m^* as measured by the muon spin relaxation rate. Alternatively, the decrease of T_c can be studied in a single sample by introducing defects. For instance, from ion irradiation of $YBa_2Cu_3O_{7-\delta}$, T_c was reduced and a metal-insulator transition could be reached.[2] From simultaneous studies of the Hall effect it was concluded that in this case the reduction of T_c did not result from a drop in the carrier density, but was rather due to a reduced mobility.

Charge-neutral dopings provide an interesting alternative to study a controlled deterioration of superconductivity. The usual parabolic dependence of T_c on doping is suppressed by substitution of equal amounts of Ca-Pr or Ca-Th on the Y site in 1:2:3 compounds. Yet the resulting linear depression of T_c can be remarkably strong. In early studies of Ca-Pr doping in Y-1:2:3 compounds, it was found that $-dT_c/dx$ was about 97 K,[3] with x defined from $Y_{1-2x}Ca_xPr_xBa_2Cu_3O_{7-\delta}$, and for Ca-Th doping in Y-1:2:3 compounds, the depression rate was even stronger.[4] In Ca-Th doped Nd-based 1:2:3 compounds it was recently observed that $-dT_c/dx$ is about 230 K.[5] These values are much larger than those found for charge-neutral dopings on the Ba site, such as in $YBa_{2-x}Sr_xCu_3O_{7-d}$ with $-dT_c/dx$ of about 10 K.[6,7] It is a challenge to understand the large effect on T_c for charge-neutral dopings on the Y site. Suggested explanations include pair breaking or pair localization in the CuO_2 planes for Ca-Pr doping,[3,8] a depression with doping of the electron-phonon interaction of the Cu(1)-O(4) mode for Ca-Th doping,[9] or charge transfers due to small changes in bond lengths, as suggested by neutron diffraction results and calculations of bond valence sums (BVS's).[10]

When doping different 1:2:3 compounds with Pr, it has been observed that the decrease of T_c becomes more pronounced for increasing size of the rare earth (RE) ion.[11–13] A similar trend has been found also for the linear depression of T_c in Y-, Sm-, and Nd-based 1:2:3 compounds, when Ca and Pr were substituted for the RE ion in equal amounts.[8] This observation may suggest an interpretation in terms of magnetic interactions, where an increasing overlap between RE and Pr ions for increasing RE radius would account for the stronger depression of T_c. However, this picture accentuates the problem of Ca-Th doping, where the effects on T_c may be even stronger, as exemplified above, and magnetic effects seem unlikely. BVS calculations have indicated some differences between Ca-Pr and Ca-Th doping.[5] For instance, with increasing Ca-Th doping there is an increased tendency for holes on oxygen sites in the CuO_2 planes in contrast to Ca-Pr doped samples where this quantity instead decreased. Furthermore, the hole density in the planes remained almost constant for Ca-Th doping and decreased with increased Ca-Pr doping.[5]

In this paper we study the electrical resistivity and superconducting properties of Ca-Pr and Ca-Th doped 1:2:3 superconductors in order to further understand this problem. It is found that the doping concentration dependence of the electrical resistivity is much larger for Ca-Th doping than for Ca-Pr doping. The results suggest that the depression of T_c in Ca-Th doped 1:2:3 compounds is qualitatively described by conventional disorder theories, associating the decrease of T_c with an increasing electronic scattering rate. Published results for irradiated thin films[2,14] were found to confirm this picture. The small effect on the resistivity by Ca-Pr doping suggests that mainly other mechanisms depress T_c in these systems. Critical magnetic field measurements were also made in view of the interesting possibility to separate different pairing mechanisms by the disorder dependence of the upper critical field H_{c2}.[15,16] The trend of these results did not lead to conclusive results on the nature of the pairing. However, marked differences between Ca-Pr and Ca-Th dopings were again observed.

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II. SAMPLE CHARACTERIZATION AND EXPERIMENTS

We studied alloy systems of the type $R_{1-2x}Ca_xA_xBa_2Cu_3O_{7-\delta}$, where R is Y, Nd, or Sm and A is Pr or Th. The maximum x in the orthorhombic phase is about 0.1, except for Ca-Pr in Y-1:2:3 compounds where this phase can be preserved up to $x \approx 0.25$. Three alloy systems of sintered samples were prepared for the present investigations. Data from recent publications of similar samples[5,10,17,18] were also included. Standard techniques were used with powders from oxides and carbonates of the respective elements to prepare $Nd_{1-2x}Ca_xPr_xBa_2Cu_3O_{7-\delta}$ with $x=0$, 0.025, 0.05, and 0.10 and two Ca-Th doped series with $x=0$, 0.03, 0.05, and 0.10 for $Nd_{1-2x}Ca_xTh_xBa_2Cu_3O_{7-\delta}$ and $Y_{1-2x}Ca_xTh_xBa_2Cu_3O_{7-\delta}$. After careful mixing, the powders were compacted to cylindrical pellets, subjected to a heat treatment, crushed, reground, and sintered a second time. After a third regrinding and sintering, the samples were annealed in flowing oxygen at 460 °C for three days. The Y-based samples were quenched to room temperature while the Nd-based ones were slowly cooled at a rate of 12 °C/h. This procedure has previously been found to be necessary for good oxygenation.[10]

X-ray powder diffraction patterns were obtained at room temperature in a Guinier-Hägg focusing camera using Cu $K\alpha$ radiation and Si as an internal standard. This is a sensitive technique for detecting small amounts of impurities. All samples were found to be of single phase orthorhombic structure, except for the two Ca-Th samples with $x=0.1$, where a few weak additional lines could be observed. Further sample characterizing investigations have been carried out on several samples including energy dispersive spectrometry in an electron microscope, selected area electron diffraction, high resolution electron microscopy,[17] and neutron diffraction.[5] These investigations confirm that the samples were of well-ordered orthorhombic structure, with the desired chemical composition, and with the doping elements substituting the rare earth site in the 1:2:3 compounds.

The pellets were cut into bars for the electrical measurements. Current and voltage contacts were attached by silver paint and annealed at 300 °C for 30 min followed by quenching to room temperature. Electrical measurements were made by a standard four-probe dc technique. The error of the room temperature resistivity was estimated to be $\leqslant 20\%$. This fairly large error is due to the small dimensions of the samples and the comparatively large widths of the silver strips. Low-temperature measurements were made in a cryostat equipped with a 12-T magnet and a variable temperature inset. The samples were cooled in field through the superconducting transitions and data were recorded during slowly upward drifting temperature.

III. RESULTS

A. Resistivity and T_c

The superconducting transition temperatures in zero field were generally quite sharp, with a width below 1 K for $x=0$ samples (10–90 % of the resistance drop), and with some disorder induced broadening for increasing doping concentration. With the exception of the $x=0.1$ Ca-Th samples in Nd- and Y-1:2:3 compounds, all transition widths were below 3 K. These are small values for sintered samples, confirming the high sample quality inferred from the structural investigations.

TABLE I. Depression of T_c in charge-neutral doped 1:2:3 compounds of the form $R_{1-2x}A_xCa_xBa_2Cu_3O_{7-\delta}$, with $R=$Y, Sm, or Nd and $A=$Pr or Th.

RE ion	A	$-dT_c/dx$ (K)
Nd	Pr	180,[a] 206[b]
Sm	Pr	173[c]
Y	Th	150,[a] 180[d]
Nd	Th	226,[a] 232[e]
Sm	Th	218[c]

[a] Present work.
[b] Reference 10.
[c] Reference 17.
[d] Reference 18.
[e] Reference 5.

Table I summarizes results for the depression rate of T_c in the charge-neutral doped compounds studied here. In all cases the decrease of T_c is linear for these co-dopings, in contrast to the parabolic behavior observed for doping with Ca or Pr only. Several examples of T_c vs x have been shown previously.[5,17,18] The results in Table I were calculated from data up to $x=0.05$, since the depression of T_c at $x=0.1$ often was somewhat smaller than expected from data at lower dopings. This is likely due to beginning precipitation of a second phase close to the phase boundary of the orthorhombic phase. This observation could also explain the lower depression rates often reported in earlier publications, where data were evaluated over a larger concentration range.

Results for the electrical resistivity at room temperature are shown in Fig. 1. The filled symbols are for Ca-Pr doped samples and the open symbols for Ca-Th doped samples. The errors in resistivity measurements are shown for some data points. With the exception of Ca-Th doped Y-1:2:3 compounds from Ref. 18, the resistivity increases more strongly with doping in Ca-Th doped systems than in the Ca-Pr ones.

In Fig. 2 the relative depression of T_c is shown as a func-

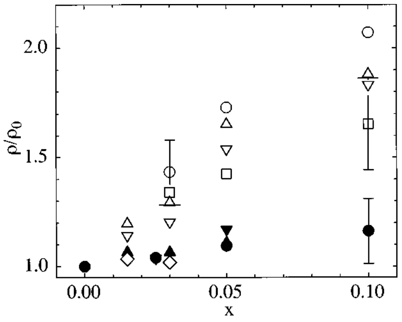

FIG. 1. Normalized increase of room temperature resistivity versus doping concentration x for Ca-Th (open symbols) and Ca-Pr (filled symbols) doped samples for two series of NdCaPr [filled circles (present work) and filled down triangles (Ref. 10)], SmCaPr [filled up triangles (Ref. 17)], two series of YCaTh [open squares (present work) and diamonds (Ref. 18)], two series of NdCaTh [open circles (present work) and down triangles (Ref. 5)], and SmCaTh [up triangles (Ref. 17)].

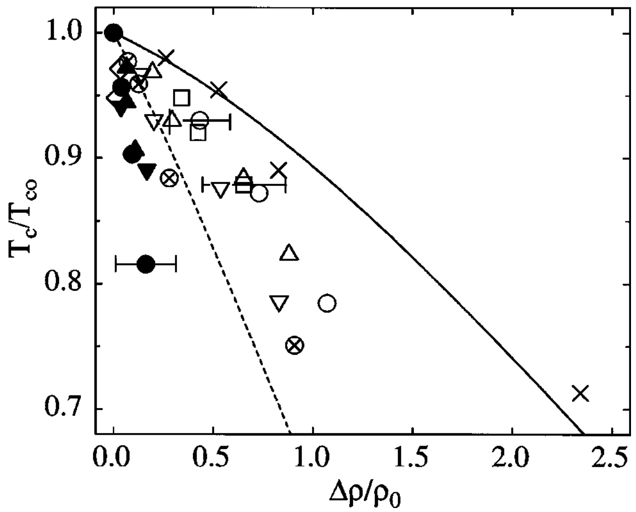

FIG. 2. Normalized depression of T_c vs normalized resistivity increase for two series of NdCaPr [filled circles (present work) and filled down triangles (Ref. 10)], SmCaPr [filled up triangles (Ref. 17)], two series of YCaTh [open squares (present work) and diamonds (Ref. 18)], two series of NdCaTh [open circles (present work) and down triangles (Ref. 5)], and SmCaTh [up triangles (Ref. 17)]. Data for ion irradiated thin films of Y-1:2:3 from Ref. 2 are shown by the crosses and from Ref. 14 by the crosses in circles. The curves were calculated from the FEM theory, as described in the text, as a function of the change in $\hbar/\varepsilon_F\tau$, approximated by $\Delta\rho/\rho_0$, and starting from two values for ε_F of 0.1 eV (dashed curve) and 0.2 eV (full curve).

tion of the relative increase of the resistivity. For Ca-Pr doping, shown by the filled symbols, T_c is depressed without any remarkable effect on the resistivity, while for Ca-Th doped samples the depression of T_c is accompanied by a strong resistivity increase. At small depressions of T_c, below about 10%, the two Ca-Th samples from Ref. 18 are again an exception. This difference is not understood.[19]

Data from the literature[2,14] on irradiated thin films of $YBa_2Cu_3O_{7-\delta}$ have also been included in Fig. 2. The quality of the samples was rather different in these papers, with about twice as large resistivity at room temperature for one unirradiated sample of Ref. 2 as compared to the sample of Ref. 14. Nevertheless, these samples follow the same trend as the Ca-Th doped samples within the scatter of the results.

These observations suggest that T_c of Ca-Th doped 1:2:3 samples is depressed due to disorder, while for Ca-Pr doped samples other mechanisms would seem to dominate. To further investigate this idea we now compare the results in Fig. 2 with conventional disorder theories.

Quantum corrections to T_c due to disorder have been calculated for BCS-like superconductors by Fukuyama, Ebisawa, and Maekawa as a function of a disorder parameter $\hbar/\varepsilon_F\tau$.[20] ε_F is the Fermi energy and τ the elastic relaxation time. $\hbar/\varepsilon_F\tau$ is closely related to the resistivity ρ and is usually replaced by ρ in work where experiments are compared with this theory. For example, it has been shown that Fukuyama-Ebisawa-Maekawa (FEM) theory can account well for the depression of T_c in a large number of three-dimensional amorphous superconductors where disorder had been varied by different means.[21]

It can first be noted that the shape of the T_c vs $\Delta\rho$ curve is consistent with FEM theory. The following assumptions were made: ρ of a pure single crystal of the Y-1:2:3 compound was taken to be 60 $\mu\Omega$ cm at 100 K and the mean free path $l\approx 100$ Å. Scaling l down by about the same factor by which the measured resistivity of the pure sintered sample was larger than that of a single crystal, we took $l\approx 20$ Å for our pure Y-1:2:3 compound at 100 K. With[22] $v_F=2\times 10^5$ m/s, the initial value of τ in Fig. 2 would be about 10 fs. For ε_F we took 0.1 and 0.2 eV, covering a range of values often used in estimates for Y-1:2:3 compounds.[23,24] The results are shown by the dashed and full curves in Fig. 2.

This calculation is crude since we have (i) assumed that FEM theory is applicable, (ii) chosen values of the electron-phonon interaction λ, the Coulomb pseudopotential μ^*, and the Debye temperature from Ref. 25 (4, 0.13, and 375 K, respectively) to reproduce the observed T_c of the undoped materials, and (iii) chosen values of ε_F and τ that are reasonable but nevertheless rather uncertain. However, variations of the parameters chosen to give T_c at $x=0$ are the least crucial. For large values of λ the relation between T_c and λ approaches[26] $T_c\approx\lambda^{1/2}$ and in fact a range of different choices for λ and μ^* gives similar results. As for $\varepsilon_F\tau$, the varying estimates shown in Fig. 2 comprise reasonable variations of $\varepsilon_F\tau$ and give a significant variation of T_c values including most of the observations for thin films and Ca-Th doped samples. It can therefore be concluded that estimates of the parameters in FEM theory, and no adjustable parameter, can give a fair qualitative description of the depression of T_c for these samples. Additional contributions to the change of T_c can of course be present. The strong decrease of T_c for Ca-Pr doping would suggest such contributions.

B. Upper critical field

It is well known that in resistive measurements on high T_c superconductors, full information on the upper critical field H_{c2} is generally obscured by the inaccessibility of $H_{c2}(T)$ at low T and by the significant broadening of the transition in the magnetic field associated with flux flow. However, when relative changes of properties are studied, useful information can nevertheless be obtained from resistive measurements. One recent example is the determination of the irreversibility line from such measurements and a somewhat arbitrary definition of this line from the lower end of the resistive transition curve in the magnetic field.[27] Another example is the study of the concentration dependence of $dH_{c2}(T)/dT$ in certain doped Y-1:2:3 systems from a similarly arbitrary definition of H_{c2} in the upper range of the resistive transition.[8]

We employed this approach and studied the relation between doping concentration, H_{c2} and T_c from resistivity. Two definitions of H_{c2} were generally used to confirm the trends obtained, $H_{c2}^{50\%}$ and $H_{c2}^{90\%}$, corresponding to the magnetic fields at 50% and 90%, respectively, of the normal state resistance. The resistive transitions in magnetic fields were measured up to 12 T and dH_{c2}/dT was evaluated from straight lines fitted to these data in the region $\geqslant 4$ T, with the same procedures used consistently for all data.

The depression of T_c and the change of dH_{c2}/dT were both calculated[15] as a function of the parameter γ/T_{c0}, with $\gamma=\pi V_0^2 cN(0)$, where T_{c0} is taken to be $T_c(x=0)$, V_0 is a potential for electron scattering from randomly distributed

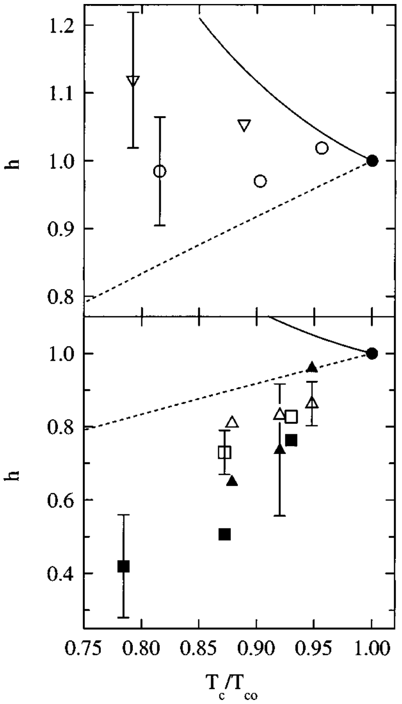

FIG. 3. Normalized slope $h=[dH_{c2}/dT]_x/[dH_{c2}/dT]_{x=0}$ vs $T_c(x)/T_c(0)$. Top: circles, NdCaPr (50% data); down triangles, YCaPr (50%, data from Ref. 8). Bottom: squares, NdCaTh; triangles, YCaTh; open symbols, 50% data; filled symbols, 90% data. The curves in both panels are calculations from Ref. 15: full curve, s-wave pairing; dashed curve, d-wave pairing.

impurities of concentration c, and $N(0)$ is the density of states. To allow for a direct comparison with this theory, avoiding assumptions about the parameters in γ, we display our results in the form of normalized change of the critical field slope versus the normalized transition temperature: $h=[dH_{c2}/dT]_x/[dH_{c2}/dT]_{x=0}$ vs $T_c(x)/T(x=0)$. The results are shown in Fig. 3. Estimated errors in evaluating $h(x)$ are shown for some data points. In particular, there are large errors in data obtained from $H_{c2}^{90\%}$. Data points with errors in h exceeding 25% were omitted.

Striking differences between Ca-Pr and Ca-Th doping are again observed. For Ca-Th doping $h(x)$ decreases strongly with x for both hosts and both the 50% and 90% estimates of H_{c2}, while for Ca-Pr doping h is constant or increases slightly with doping. Data for Ca-Pr doping in Y-1:2:3 compounds[8] have also been included in this figure.

However, the results in Fig. 3 cannot be described by the results of Ref. 15, either for s-wave pairing or for d-wave pairing, as shown by the full and dashed lines calculated by us from Ref. 15. Further work by these authors[16] shows, in addition, that when different values of the normalized anisotropic scattering rate are taken into account, the predictions for the development of $h(x)$ in the case of d-wave pairing may change sign for certain values of anisotropy, which further complicates comparisons with this theory. It is concluded that disorder effects alone are not likely to account for the relation between dH_{c2}/dT and T_c in these charge-neutral doped samples.

IV. BRIEF SUMMARY AND DISCUSSION

Although the depression rates of T_c for Ca-Pr and Ca-Th doping in 1:2:3 hosts are both strong and of comparable magnitudes, there are striking differences between these dopings regarding both the sensitivity of the resistivity and the change of the critical field slope with doping. Disorder theories for conventional superconductors were found to account qualitatively for the depression of T_c in Ca-Th doped samples. Data from the literature on irradiated thin films also qualitatively confirm this picture. In particular, the results of Ref. 2 support an interpretation in terms of an increased elastic scattering rate. For Ca-Pr doping, on the other hand, alternative mechanisms dominate, e.g., pair-breaking or pair-weakening effects.

On the other hand, the critical field data do not lead to conclusive results. In spite of the success of the FEM theory to describe the disorder depression of T_c in three-dimensional amorphous superconductors, it fails completely to account for the critical magnetic field and predicts a reduction of the zero temperature critical field when, in contrast, experiments show an enhancement.[21] We cannot directly apply the FEM analysis of the critical field to the present results since only a small range of the H_{c2}-T plane is probed. However, the greatly different results for dH_{c2}/dT in Fig. 3 indicate that such a FEM description is not feasible. Furthermore, since there is no reason to believe that the pairing symmetry would be different for Ca-Pr and Ca-Th doping, the model of Ref. 15 also fails to account for the data in Fig. 3. Apparently, a description of the influence of disorder on H_{c2} remains a too difficult problem experimentally and/or theoretically for amorphous as well as high-T_c superconductors.

The differences observed between the two charge-neutral Ca-Pr and Ca-Th dopings are striking. Strong differences are apparent also in the different solubilities of these elements, where Pr is fully soluble in the orthorhombic 1:2:3 phase and Th is insoluble when standard methods are used.[4] These large differences between Th and Pr substituting elements in 1:2:3 compounds both in atomic and in scattering potentials are interesting and merit further investigations.

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