

Superconductivity of $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ single crystals with substitution of Ni and Co on the Cu position

Matthias Brinkmann, Heinrich Bach, and Kurt Westerholt

Institut für Experimentalphysik/Festkörperphysik, Ruhr-Universität Bochum, D-44780 Bochum, Germany

(Received 18 March 1996)

We report magnetic susceptibility, electrical resistivity, and Hall-coefficient measurements on single crystals from the electron-doped high- T_C superconductor $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ with Cu replaced by Ni and Co partly. The impurities on the Cu position lead to a strong increase of the residual resistivity of about $450 \mu\Omega \text{ cm/at. \%}$ substitution, T_C is suppressed at a rate of -20 K/at. \% substitution for both, Ni and Co, in quantitative agreement with previously published results on polycrystalline samples. We find that the Hall coefficient R_H is strongly shifted towards positive values with increasing concentration of Ni and Co, simultaneously the low-temperature upturn in $R_H(T)$ is suppressed. This indicates a different impurity scattering rate for the hole and electron type of charge carriers coexisting on the Fermi surface of the electron doped superconductors.

[S0163-1829(96)04933-8]

INTRODUCTION

The substitution of different elements on the Cu position in the CuO_2 planes of the high- T_C superconductors is an important tool for testing parameters essential for superconductivity.¹⁻¹⁶ For the hole-doped high- T_C superconductors it is found that the superconducting transition temperature T_C is suppressed by any sort of substitutional element on the Cu position in the superconducting CuO_2 layers (see Ref. 1 and references therein). The magnetic moment of the elements from the $3d$ transition metals seems not to be essential in suppressing T_C , in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, e.g., nonmagnetic Zn is most effective,² in the hole-doped high- T_C systems with only one Cu position in the unit cell as, e.g., $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ and $\text{Bi}(2212)$ the rate of T_C suppression is very similar for different substitutional elements namely about -10 K/at. \% in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ (Ref. 3) and about -5 K/at. \% in $\text{Bi}(2212)$.⁴ Thus the conventional pair breaking by spin-flip scattering on magnetic impurities, as described by the Abrikosov-Gor'kov (AG) theory,⁵ is not the dominant mechanism suppressing T_C in the hole-doped systems. However, the observations are consistent with d -wave symmetry of the superconducting order parameter, since in this case any nonmagnetic scattering is pair breaking.⁶

Investigations on the electron-doped high- T_C superconductor $\text{La}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ ($L=\text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$) with substitutional elements as Fe, Co, Ni, or Zn on the Cu position in polycrystalline material revealed a remarkable effect at variance to the hole-doped superconductors: Whereas Ni and Co strongly suppress T_C with a critical concentration for a vanishing superconducting transition below 1 at. %, ⁷⁻¹³ nonmagnetic Zn substitution has a much weaker influence.⁷⁻¹⁶ This has been interpreted in the model of conventional AG-type pair-breaking scattering on magnetic impurities^{8,10} and would imply that the electron-doped high- T_C superconductors have an order parameter with s -wave symmetry. Tunneling data¹⁷ and the temperature dependence of the penetration depth¹⁸ actually strongly suggest that in the electron-doped superconductors the order parameter is of s -wave symmetry.

A delicate problem in substitution experiments on polycrystalline high- T_C superconductors is the determination of the true dopant concentration within the grains, especially if the solubility limit for a specific substitutional element is low. It may happen that impurity phases rich in the substitutional elements segregate in the grain boundaries or form coherent precipitations within the grains. This has been observed, for example, by Mössbauer spectroscopy in polycrystalline $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4+\delta}$ samples with substitutions of Fe.¹³ In order to avoid these difficulties working with single crystals is advantageous and gives more reliable quantitative results on the concentration dependence of T_C .

In addition, the study of single crystals in many cases allows a more quantitative analysis of the physical properties. For example, it is a well-known problem with the electron-doped high- T_C superconductors that the intrinsic in-plane electrical resistivity $\varrho_a(T)$ with its nearly quadratic temperature dependence cannot be resolved in superconducting polycrystalline material. Polycrystalline samples usually even exhibit the wrong sign in $d\varrho_a/dT$ with $\varrho_a(T)$ increasing with decreasing temperature over the whole temperature range up to room temperature.^{8,10,12,14-16}

To our best knowledge work on single crystals of the electron-doped compounds with substitutional elements on the Cu position have not been published until now in the literature. It is the main aim of the present work to fill this gap and investigate systematically crystals of the system $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ with substitutions of $3d$ elements for Cu in order to verify the data obtained on polycrystalline samples and to gain additional insight into the change of the superconducting parameters and transport properties with substitutions.

PREPARATION AND EXPERIMENT

Our single-crystal growth procedure in the system $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ using the slow cooling CuO self-flux method¹⁹ is described in detail in Ref. 20. The platelet-shaped crystals have a typical size of $2 \times 2 \times 0.02 \text{ mm}^3$ with the c axis perpendicular to the plate surface. For the growth

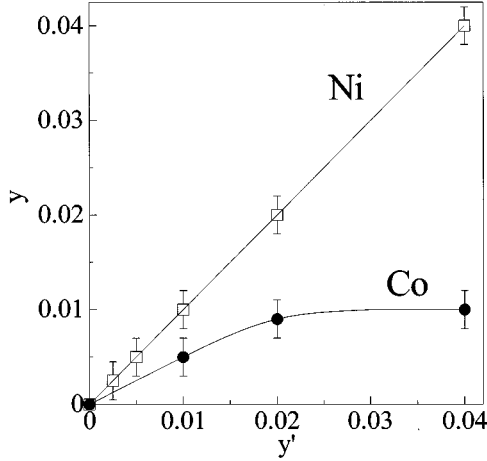


FIG. 1. The Ni and Co concentration y in the single crystals vs the concentration in the melt y' for the growth experiments of the present study.

of samples with different substitutional elements on the Cu position we replaced up to 4% of the complete CuO in the melt by MnO_2 , $(1/2) \text{Fe}_2\text{O}_3$, $(1/2) \text{Co}_2\text{O}_3$, NiO , and ZnO . Quantitative analysis of the sample stoichiometry using wavelength disperse x-ray electron microprobe analysis (WDX) revealed that only Ni and Co entered the $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ single crystals.²⁰

In Fig. 1 the average Ni and Co concentration y of the crystals is plotted as a function of the Ni and Co concentration in the melt y' . The two concentrations y and y' are identical for the case of Ni up to the maximum concentration $y'=4\%$ applied in this work. For the case of Co approximately one-half of the concentration in the melt is found in the crystals up to the solubility limit of about 1 at. %. For both substitutional elements no lateral concentration gradient in the a - b plane could be detected in the crystals within the experimental resolution of ± 0.2 at. % of the WDX analysis. Within the same error bars we also could not detect any Ni or Co concentration gradient along the c axis when comparing the WDX spectra taken at the top and the bottom side of the crystals.

For the case of Mn, Fe, and Zn substitution we found no traces of these elements in the crystals even when starting with a high Mn, Fe, or Zn concentration $y'=4\%$ in the melt. The solubility is below the detection limit of our microprobe analysis of about 0.5 at. % (referring to Cu). Instead, we found Fe- or Zn-rich impurity phases on the crystal surfaces separated from the interior during the growth process.²⁰ Since for the problem of magnetic versus nonmagnetic T_C suppression mentioned in the Introduction it would be highly desirable to have single crystals with nonmagnetic substitutional elements for Cu we have tried to substitute Ga, Al, and Sn, however, with the same negative result. So our present investigation is limited to $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ single crystals with Ni and Co substitution.

In Table I we summarize the composition, c -axis lattice parameter, and the superconducting transition temperature for the crystals of the present study. The Ce and the Ni or Co concentrations vary slightly even for crystals from the same batch and have to be determined individually for each crystal. The Ce concentration x of each crystal was measured

TABLE I. Composition, c -axis lattice parameter, and superconducting transition temperatures for the crystals of the present study. The first column gives the capital letters used to identify the crystals in the figures.

No.	Composition	$c/\text{\AA}$	T_c/K
A	$\text{Pr}_{1.85(1)}\text{Ce}_{0.15(1)}\text{CuO}_{4+\delta}$	12.132(1)	22.9
B	$\text{Pr}_{1.87(1)}\text{Ce}_{0.13(1)}(\text{Cu}_{0.997(2)}\text{Ni}_{0.003(2)})\text{O}_{4+\delta}$	12.147(1)	18.0
C	$\text{Pr}_{1.84(1)}\text{Ce}_{0.16(1)}(\text{Cu}_{0.993(2)}\text{Ni}_{0.007(2)})\text{O}_{4+\delta}$	12.125(1)	12.2
D	$\text{Pr}_{1.83(1)}\text{Ce}_{0.17(1)}(\text{Cu}_{0.980(2)}\text{Ni}_{0.020(2)})\text{O}_{4+\delta}$	12.115(1)	-
E	$\text{Pr}_{1.89(1)}\text{Ce}_{0.11(1)}(\text{Cu}_{0.960(2)}\text{Ni}_{0.040(2)})\text{O}_{4+\delta}$	12.158(1)	-
F	$\text{Pr}_{1.85(1)}\text{Ce}_{0.15(1)}(\text{Cu}_{0.995(2)}\text{Co}_{0.005(2)})\text{O}_{4+\delta}$	12.130(1)	14.1
G	$\text{Pr}_{1.87(1)}\text{Ce}_{0.13(1)}(\text{Cu}_{0.990(2)}\text{Co}_{0.010(2)})\text{O}_{4+\delta}$	12.145(1)	8.2

directly by WDX. Because of the negligible influence of the Ni and Co substitution on the lattice parameters the c -axis unit-cell length can also be used to determine the Ce concentration x .⁹ One sees that the Ce concentration x in the crystals of Table I deviates from the ideal composition $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4+\delta}$ which we tried to meet in all growth experiments of the present study. The influence of these deviations in the Ce concentration for the results on different crystals must be carefully considered.

For the reduction process, which is essential for establishing superconductivity in the electron-doped superconductors, we used an atmosphere of 1 bar Ar with 0.05 mbar O_2 at 1080 °C for 3 days with special precautions for avoiding the decomposition of the surfaces as described in Refs. 20 and 21. With this technique we can establish superconductivity over a broad range of Ce concentrations and not only close to $x=0.15$ as obtained for the standard reduction procedure at lower temperatures. In Ref. 21 we have shown that the superconducting phase of $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ extends down to a Ce concentrations $x \approx 0.04$, i.e., to much lower values than previously reported in the literature. For the $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ single crystals the T_C values change only slightly by about 2 K in the Ce concentration range for the crystals of Table I. This can be neglected compared to the much larger T_C suppression caused by the substitution of Ni and Co.

The a - b plane resistivity ρ_a of the crystals has been measured by a low-frequency ac method with four silver painted contacts. The current contacts covered the whole a - c area of the crystal in order to ensure a good current homogeneity. The dc magnetization with the magnetic field applied perpendicular to the a - b plane was determined by a noncommercial SQUID magnetometer. The a - b plane Hall coefficient R_H was measured using a five-point dc method and a 180° rotation of the crystals in a perpendicular magnetic field of 4 T. The same equipment is used to measure the magnetoresistivity with the magnetic field parallel to the c direction.

RESULTS AND DISCUSSION

In Fig. 2 we show the results of our resistivity measurements for the crystals of Table I. One sees that the transition temperature is strongly suppressed by the Ni and Co substitution. For both substitutional elements the resistivity curves shift upwards preserving the approximately quadratic temperature dependence. This indicates that the Ni and Co atoms

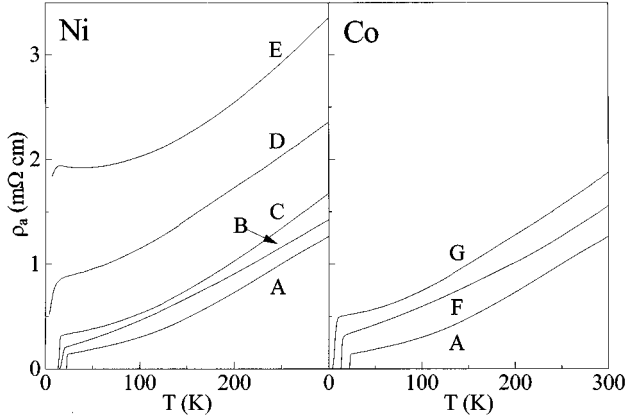


FIG. 2. Electrical resistivity vs temperature for the crystals from Table I. The diagram on the left side displays the Ni series with concentrations: 0 at. % (A), 0.3 at. % (B), 0.7 at. % (C), 2 at. % (D), and 4 at. % (E). On the right side the corresponding series for Co is plotted with concentrations: 0 at. % (A), 0.5 at. % (F), and 1 at. % (G).

on the Cu position mainly contribute a temperature-independent scattering process, i.e., a residual resistivity. The resistivity curves in Fig. 2 can be reasonably well fitted by the empirical formula²¹

$$\varrho_a(T) = \varrho_R + AT^\alpha \quad (1)$$

(α , A : fit parameters). The residual resistivity ϱ_R thus defined is plotted versus the true Ni and Co concentration in Fig. 3. One derives an increase of the residual resistivity $d\varrho_R/dy \approx 450 \mu\Omega \text{ cm/at. \%}$ substitution for both Ni and Co. Because of the strong influence of the Ni and Co impurities on $\varrho_a(T)$ one can neglect the relatively small changes due to the variation of the Ce concentration.²¹

In Fig. 4 we show two examples of magnetic dc-susceptibility curves below the superconducting transition temperature. The good screening capability of the crystals indicates the bulk character of the superconductivity. There is, however, a clear tendency of a broadening of the superconducting transition with increasing concentration of Ni and

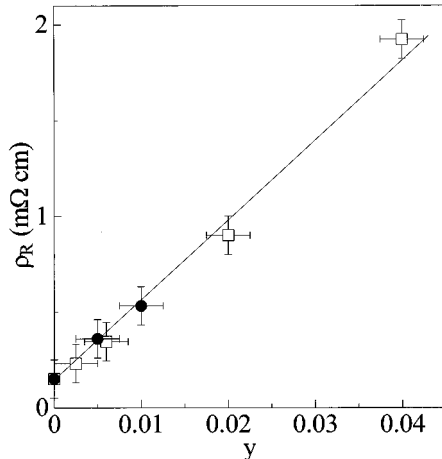


FIG. 3. Residual resistivity ϱ_R for the crystals of Table I as fitted by Eq. (1) for the crystals of the present study; empty squares: Ni series; full circles: Co series.

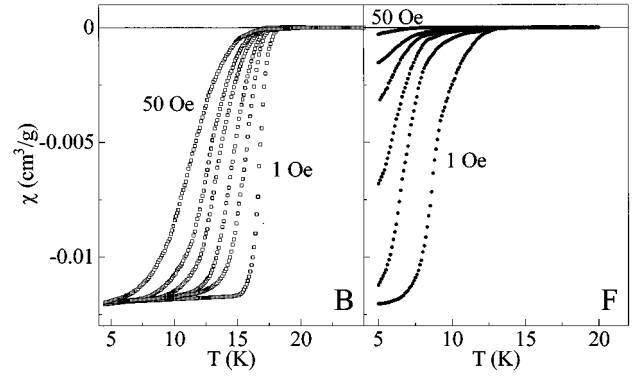


FIG. 4. dc zero-field-cooled susceptibility vs temperature for crystal B (0.3 at. % Ni) and F (0.5 at. % Co). The applied field was 50, 30, 20, 10, 5, and 1 Oe (from the left to the right).

Co, indicative of a slight inhomogeneity or a presence of weak links (see crystal F in Fig. 4). However, the shielding fraction at low fields remains constant for Ni and Co concentrations up to the solubility limit.

In Fig. 5 we have plotted the transition temperatures of the crystals as a function of the Ni and Co concentration. For the definition of T_C we take the 50% value of the resistivity, this is in good agreement with the onset temperature taken from the magnetic susceptibility. One finds that T_C is suppressed rapidly with an initial slope of about -20 K/at. \% for both systems. This is in good quantitative agreement with previously published data on polycrystalline $\text{Nd}_{1.85}\text{Ce}_{0.15}(\text{Cu}_{1-y}\text{M}_y)\text{O}_{4+\delta}$.^{8,10,12} The functional form of $T_C(y)$ is consistent with the AG formula for pair-breaking scattering on paramagnetic impurities with T_C given by the implicit formula:⁵

$$\ln\left(\frac{T_{C0}}{T_C}\right) = \psi\left(\frac{1}{2} + \frac{2J^2S(S+1)N(\epsilon_F)y}{2k_B T_C}\right) - \psi\left(\frac{1}{2}\right) \quad (2)$$

[$\psi(z) = d\Gamma(z)/dz$, where $\Gamma(z)$ is the γ function, T_{C0} the superconducting transition temperature for $y=0$, J the ex-

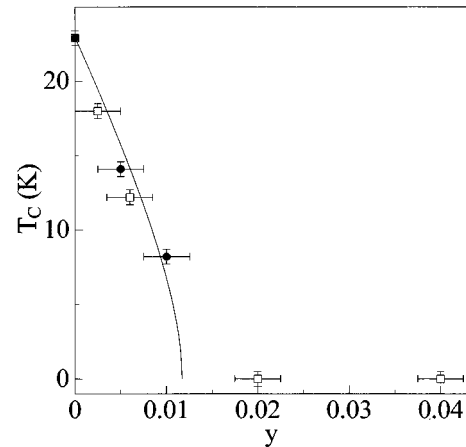


FIG. 5. Superconducting transition temperature vs the Ni concentration (open squares) and Co concentration (full circles) substitutional for the crystals of the present study, the drawn line is a fit using Eq. (3) with an AG pair-breaking parameter: $\alpha=1.5 \text{ meV/at. \%}$.

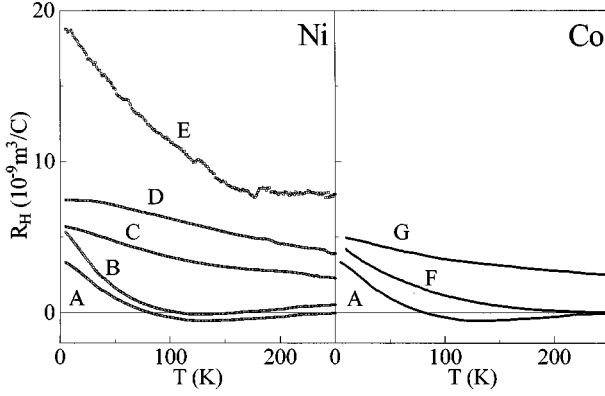


FIG. 6. Hall-coefficient vs temperature for the crystals from Table I, diagram on the left side: Ni-doped samples with $y=0$ at. % (A), 0.3 at. % (B), 0.7 at. % (C), 2 at. % (D), and 4 at. % (E); right side: Co-doped crystals with $y=0$ at. % (A), 0.5 at. % (F), and 1 at. % (G).

change interaction energy between an electron and the impurity spin S , and $N(\epsilon_F)$ the density of states at the Fermi energy ϵ_F]. The slope $dT_C(y)/dy$ for $y \rightarrow 0$ is determined by the pair-breaking parameter: $\alpha = 2\pi N(\epsilon_F)J^2S(S+1)$.

Due to the small Ni and Co concentration in the crystals and the strong contribution from the Van Vleck magnetism of the Pr spins we could not resolve the effective moments of the Ni and Co spins in the crystals by susceptibility measurements. The determination of the effective moments of Fe and Ni substitutions in polycrystalline $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ gave values of $\mu_{\text{eff}} \approx 2.2\mu_B$ for Fe and $\mu_{\text{eff}} \approx 2.0\mu_B$ for Ni,^{7,10} consistent with cluster calculations for low spin Fe^{3+} ($\mu_{\text{theor}} = 2.82\mu_B$) and low spin Ni^{3+} ($\mu_{\text{theor}} = 2.00\mu_B$) in planar oxygen coordination.⁷ Similar calculations and measurements for the case of Co substitution do not exist. It might be assumed that Co is in the low-spin Co^{3+} state, but this is improbable, since this state would be nonmagnetic. So Co probably is either in the Co^{2+} low-spin state with a moment identical to that of Fe^{3+} or it is in the Co^{3+} high-spin state with $\mu_{\text{eff}} \approx 5\mu_B$.

In Fig. 6 we present the results of our Hall-coefficient measurements on the crystals from Table I. We observe a strong shift of the Hall coefficient to positive values with increasing concentration of Ni and Co. A similar shift of the Hall coefficient towards higher values has also been reported for polycrystalline $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4+\delta}$ substituted with Co, Ni, and Zn.^{8,14} In the electron-doped superconductors a crossover of the Hall coefficient from negative towards positive values with decreasing temperature (as shown for crystal A in Fig. 6) or a positive $R_H(T)$ with an anomalous upturn at low temperatures is usually observed.^{21,22} The Hall coefficient at room temperature shifts towards more positive values with increasing Ce concentration.^{21,23} This is regarded as one indication that electron-type and hole-type orbits coexist on the Fermi surface of the electron-doped high- T_C superconductors.²² A second and more unambiguous proof of the coexistence of electrons and holes at the Fermi surface comes from a comparison of the Hall voltage and Nernst voltage for superconducting thin films of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4+\delta}$.²⁴

The relevance of the hole-type charge carriers for the oc-

currence of superconductivity is a controversial issue in the literature.²⁴ The gross change of the Hall coefficient with the Ce concentration has been explained theoretically in Ref. 25 by a weakening of the correlation energy between the charge carriers with increasing Ce concentration. The character of the charge carriers should change from electron type in the strongly correlated system to hole type when the Hubbard gap closes at high Ce concentrations.^{25,26} The coexistence of electrons and holes has been attributed in another model calculation to a combined delocalization process of electrons and holes when doping $\text{Pr}_2\text{CuO}_{4+\delta}$ by Ce^{4+} in the presence of oxygen defects.²⁷ Alternatively, it has been suggested that occupied bands with oxygen 2p character, which appear in local-density-approximation (LDA) band-structure calculations slightly below the Fermi energy ϵ_F ,²³ might shift across ϵ_F by a buckling of the CuO_2 planes and might give rise to a second charge carrier of oxygen p type.²⁸ In recent photoemission studies of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ a hole-type Fermi surface has been detected²⁹ in the superconducting and overdoped concentration range. No direct evidence for the coexistence of electrons and holes is seen in the photoemission spectra and the band-structure calculations.

Keeping this partially controversial situation concerning the problem of charge carriers in the electron-doped superconductors in mind, it is interesting to interpret our results on the Hall coefficient of the Ni and Co-doped samples in Fig. 6. At the first glance the shift with increasing Ni and Co concentration is similar to the shift observed with increasing charge carrier concentration,^{21,23} i.e., with increasing Ce concentration or increasing oxygen-defect concentration,²⁴ thus it could be due to an additional doping by replacing Cu^{2+} by Ni^{3+} or Co^{3+} or by creating additional oxygen defects on the oxygen position O2. Quantitatively, however, the shift of R_H towards positive values in Fig. 6 is much too strong to be explained by this effect. Actually the absolute values of R_H of the superconducting crystals C and G are definitely higher than those observed in the overdoped concentration range of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$.^{21,23,30} So we cannot attribute the shift of R_H to an additional charge carrier doping by the substitution of Ni^{3+} and Co^{3+} for Cu^{2+} , as it is found, e.g., in polycrystalline $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ with substitutions of Ga^{3+} ions.³¹

One could think of two possible mechanisms for the explanation of the shift in R_H in Fig. 6. First, in a two-band model with two charge carriers with concentrations n_h and n_e and mobilities μ_h and μ_e for the hole- and the electron-type charge carrier the Hall-coefficient is given by

$$R_H = \frac{1}{e} \frac{n_h \mu_h^2 - n_e \mu_e^2}{(n_h \mu_h + n_e \mu_e)^2}. \quad (3)$$

Assuming a different temperature dependence of the mobilities $\mu_h(T)$ and $\mu_e(T)$ one can qualitatively explain the low-temperature upturn in $R_H(T)$ observed for crystal A in Fig. 6 by assuming a strongly increasing mobility of the holes compared to the mobility of the electrons at low temperatures.²² An overall shift of R_H towards positive values observed for crystal C or G in Fig. 6 can be attributed to a stronger scattering of the electrons than of the holes by the Ni or Co impurities. Second, it seems possible in a rigid band type of model that the change of the effective mean potential of the cation lattice with the substitution of Co^{3+} and Ni^{3+} for

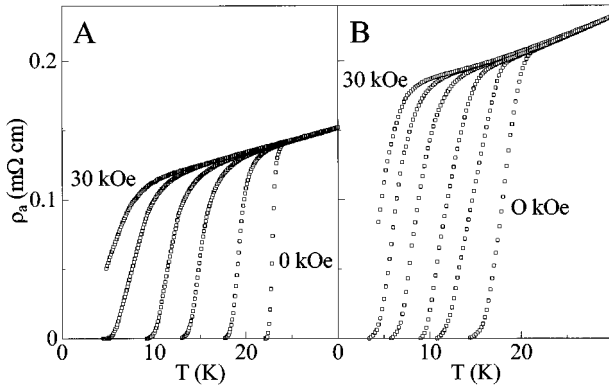


FIG. 7. Resistivity vs temperature in a perpendicular magnetic field 30, 22, 13, 6, 2, and 0 kOe (from the left to the right) for crystal A (0 at. % Ni) and B (0.3 at. % Ni).

Cu^{2+} shifts the relative position of the electron bands and modifies the Fermi surface in a manner that the hole-type orbits get a higher density of states. However, since the concentration of the impurities is low and the unit-cell lattice parameters do not change with the substitution of Ni and Co we regard this explanation as rather improbable and would prefer the first explanation above.

In Fig. 7 we show representative examples of the shift of the resistive superconducting transition in a superimposed perpendicular magnetic field. In the electron-doped high- T_C superconductors the lower transition temperatures and the larger superconducting coherence length³² weaken the influence of thermal fluctuations on the resistive transition. Contrary to the strong broadening in the hole-doped high- T_C superconductors³³ there is only a weak broadening of the transition curves with increasing field³⁴ (see Fig. 7). The shift of the transition can be interpreted similar to classical BCS superconductors as given by the shift of the upper critical field H_{c2} .

One finds that $H_{c2}(T)$ determined by the 50% criterion of the resistivity in Fig. 8 is strongly suppressed with increasing concentration of Ni and Co. The $H_{c2}(T)$ curves exhibit a negative curvature, contrary to the usual BCS superconductors. This curvature seems to be an intrinsic phenomenon of

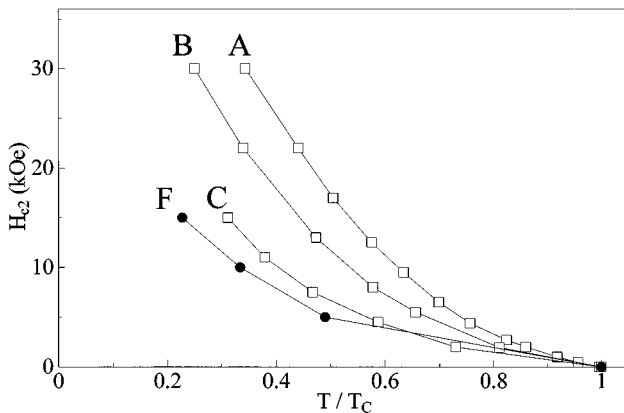


FIG. 8. Upper critical field vs the reduced temperature for the superconducting crystals A (0 at. %), B (0.3 at. % Ni), F (0.5 at. % Co), and C (0.7 at. % Ni). The transition temperature T_c is given in Table I.

the layered high- T_C superconductors and has also been observed in the hole-doped superconductors.³⁵ A linear extrapolation of $H_{c2}(T)$ for $T \rightarrow 0$ gives a $H_{c2}(T=0) \approx 2.5$ T for the sample F (0.5 at. % Co) in Fig. 8. Using the relation $H_{c2}(0) = \Phi_0 / 2\pi [\xi_a(0)]^2$ (flux quantum Φ_0) we derive a correlation length $\xi_a(0) \approx 120$ Å. An increase of the correlation length with decreasing transition temperature in a system with magnetic pair-breaking scattering can be expected qualitatively from the relation $\xi \sim \hbar v_F / \Delta$ (Fermi velocity v_F , gap parameter Δ), since Δ decreases rapidly with increasing magnetic impurity concentration.³⁶

SUMMARY AND CONCLUSIONS

In this paper we report about results on single crystals of the $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ high- T_C superconductors doped with Ni and Co on the Cu position. We could verify the results obtained previously on polycrystalline material that these substitutional atoms very effectively suppress T_C at a rate of $dT_C/dy \approx -20$ K/at. %, which is much larger than any value observed in the hole-doped superconductors. The interpretation of this strong suppression within the model of conventional AG pair-breaking scattering theory⁵ is consistent with our observation that the superconducting correlation length strongly increases with the concentration of Co and Ni. Unfortunately it turned out to be impossible to substitute non-magnetic Zn, Ga, or Sn atoms for Cu in the crystals. Thus the weak suppression of T_C by the substitution of Zn observed in polycrystalline material could not be verified.

The analysis of the electrical resistivity revealed that the Co and Ni impurities contribute a temperature-independent scattering process, the residual resistivity increases with a slope of about $450 \mu\Omega \text{ cm/at. \%}$ substitution. This increase is much stronger than the increase in the residual resistivity of about $100 \mu\Omega \text{ cm/at. \%}$ substitution observed in Ni- and Zn-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ (Ref. 3) of about $40 \mu\Omega \text{ cm/at. \%}$ reported for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ doped by Zn.² This indicates that the scattering cross section of the Ni and Co ions for the charge carriers in the electron-doped high- T_C superconductors is definitely larger than for the charge carriers in the hole-doped superconductors. It can, however, not be excluded that the substitution of Ni and Co in $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ causes a local rearrangement of the oxygen atoms from planar to octahedral or pyramidal.^{12,15} Disorder in the oxygen sublattice is known to increase the residual resistivity in the electron-doped superconductors^{24,28} and can be contained in the observed increase of the residual resistivity with substitution of Ni and Co.

A new result of our present study is the strong shift of the Hall coefficient towards positive values with increasing degree of substitution of Ni and Co. This is an interesting phenomenon in context with the interpretation of the Hall coefficient in the electron-doped high- T_C superconductors. Since the concentration of the impurities is low and the lattice parameter of the unit cell remains unchanged, we do not expect an essential change of the Fermi surface. The assumption of a coexistence of two charge carriers combined with a stronger scattering of the electron-type charge carriers compared to the hole-type charge carriers provides a more plausible explanation for the shift in $R_H(T)$.

- ¹K. Westerholt and B. vom Hedt, J. Low Temp. Phys. **95**, 123 (1994).
- ²J. Clayhold, N. P. Ong, P. H. Hor, and C. W. Chu, Phys. Rev. B **38**, 7016 (1988); K. Westerholt, H. J. Wüller, H. Bach, and P. Stauche, *ibid.* **39**, 11 680 (1989).
- ³J. M. Tarascon, L. H. Greene, P. Barboux, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner, and E. J. McNiff, Phys. Rev. B **36**, 8393 (1987); G. Xiao, A. Bakhshai, M. Z. Cieplak, Z. Tesanovic, and L. Z. Chien, *ibid.* **39**, 315 (1989).
- ⁴B. vom Hedt, W. Lisseck, K. Westerholt, and H. Bach, Phys. Rev. B **49**, 9898 (1994).
- ⁵A. A. Abrikosov and L. P. Gor'kov, Sov. Phys. JETP **12**, 1243 (1961).
- ⁶J. P. Foulkes and B. L. Gyorffy, Phys. Rev. B **15**, 1395 (1977).
- ⁷B. Jayaram, H. Chen, and J. Callaway, Phys. Rev. B **52**, 3742 (1995).
- ⁸J. Sugiyama, S. Tokuono, S. Koriyama, H. Yamauchi, and S. Tanaka, Phys. Rev. B **43**, 10 489 (1991).
- ⁹G. Hilscher, M. Forsthuber, S. Pollinger, A. Hanninger, and P. Rogl, Supercond. Sci. Technol. **4**, S79 (1991).
- ¹⁰J. Sugiyama, H. Yoshikawa, H. Hidaka, T. Sakurai, H. Yamauchi, and S. Tanaka, Phys. Rev. B **42**, 803 (1990).
- ¹¹S. Yamagata, K. Adachi, M. Onoda, H. Fujishita, M. Sera, Y. Ando, and M. Sato, Solid State Commun. **74**, 177 (1990).
- ¹²J. M. Tarascon, E. Wang, S. Kivelson, B. G. Bagley, G. W. Hull, and R. Ramesh, Phys. Rev. B **42**, 218 (1990).
- ¹³I. Felner, D. Hechel, and U. Yaron, Physica C **165**, 247 (1990).
- ¹⁴S. Ikegawa, T. Yamashita, T. Sakurai, R. Itti, H. Yamauchi, and S. Tanaka, Phys. Rev. B **43**, 2885 (1991).
- ¹⁵C. Barlingay, V. Garcia-Vazquez, C. M. Falco, S. Mazumdar, and S. H. Risbud, Phys. Rev. B **41**, 4797 (1990).
- ¹⁶G. Hilscher, S. Pollinger, M. Forsthuber, N. Pillmayr, K. Remschnig, P. Rogl, M. Reissner, W. Steiner, and P. Knoll, Physica C **167**, 472 (1990).
- ¹⁷Q. Huang, J. F. Zasadzinski, N. Tralshawala, K. E. Gray, D. G. Hinks, J. L. Peng, and R. L. Greene, Nature **347**, 369 (1990).
- ¹⁸D. H. Wu, J. Mao, S. N. Mao, J. L. Peng, X. X. Xi, T. Venkatesan, R. L. Greene, and S. M. Anlage, Phys. Rev. Lett. **70**, 85 (1993).
- ¹⁹Y. Hidaka and M. Suzuki, Nature **338**, 635 (1989).
- ²⁰M. Brinkmann, T. Rex, H. Bach, and K. Westerholt, J. Cryst. Growth (to be published).
- ²¹M. Brinkmann, T. Rex, H. Bach, and K. Westerholt, Phys. Rev. Lett. **74**, 4927 (1995).
- ²²Z. Z. Wang, T. R. Chien, N. P. Ong, J. M. Tarascon, and E. Wang, Phys. Rev. B **43**, 3020 (1991).
- ²³S. J. Hagen, J. L. Peng, Z. Y. Li, and R. L. Greene, Phys. Rev. B **43**, 13 606 (1991).
- ²⁴Jiang Wu, S. N. Mao, X. X. Xi, Jiang Xiuguang, J. L. Peng, T. Venkatesan, C. J. Lobb, and R. L. Greene, Phys. Rev. Lett. **73**, 1291 (1994).
- ²⁵H. Fehske and M. Deeg, Solid State Commun. **93**, 41 (1995); J. Low Temp. Phys. **99**, 425 (1995).
- ²⁶S. Massidda, N. Hamada, Yu Jaejun, and A. J. Freeman, Physica C **157**, 571 (1989); N. Hamada, S. Massidda, Yu Jaejun, and A. J. Freeman, Phys. Rev. B **42**, 6238 (1990).
- ²⁷J. E. Hirsch, Physica C **243**, (1995).
- ²⁸S. J. L. Billinge and T. Egami, Phys. Rev. B **47**, 14 386 (1993).
- ²⁹D. M. King, Z.-X. Shen, D. S. Dessau, B. O. Wells, W. E. Spicer, A. J. Arko, D. S. Marshall, J. DiCarlo, A. G. Loeser, C. H. Park, E. R. Ratner, J. L. Peng, Z. Y. Li, and R. L. Greene, Phys. Rev. Lett. **70**, 3159 (1993).
- ³⁰X. Q. Xu, S. N. Mao, W. Jiang, J. L. Peng, and R. L. Greene, Phys. Rev. B **53**, 871 (1996).
- ³¹I. Felner, U. Yaron, Y. Yeshurun, E. R. Yacoby, and Y. Wolfus, Phys. Rev. B **40**, 11 366 (1989); I. Felner, D. Hechel, and U. Yaron, Physica C **165**, 247 (1990).
- ³²Y. Dalichaouch, B. W. Lee, C. L. Seaman, J. T. Markert, and M. B. Maple, Phys. Rev. Lett. **64**, 599 (1990).
- ³³T. T. M. Palstra, B. Batlogg, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **61**, 1662 (1988).
- ³⁴L. Fabrega, B. Martinez, J. Fontcuberta, X. Obradors, and S. Píñol, Phys. Rev. B **46**, 5581 (1992).
- ³⁵M. S. Osofsky, R. J. Soulen, S. A. Wolf, J. M. Broto, H. Rakoto, J. C. Ousset, G. Coffe, S. Askenazy, P. Pari, I. Bozovic, J. N. Eckstein, and G. F. Virshup, Phys. Rev. Lett. **71**, 2315 (1993).
- ³⁶S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, Phys. Rev. **136**, A1500 (1964).