Influence of Ni, Fe, and Zn substitution on the superconducting and antiferromagnetic state of $YBa_2Cu_3O_{7-\delta}$

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We report magnetic and electric measurements on $YBa_2Cu_3O_{7-\delta}$ with up to 15 at.% substitution of Ni, Fe, and Zn for Cu in the insulating state ($\delta \simeq 1$) and the metallic state ($\delta \simeq 0.1$). The concentration dependence of the Pauli susceptibility and the electrical conductivity indicates that the shift of the Fermi energy towards the mobility edge with increasing degree of substitution is one important mechanism for the suppression of the superconducting transition temperature. In the insulating antiferromagnetic state the Fe and Ni spins are very weakly coupled to the Cu spins. The Ni spins remain paramagnetic down to the lowest measuring temperature of 3 K, the Fe spins order at 5 K, independent of the Fe concentration. The Néel temperature depends weakly on the Fe and Zn concentration but decreases strongly with the Ni concentration. This different behavior reflects the different site preference for the substitution in the insulating state, namely Cu(2) for Ni and Cu(1) for Fe and Zn.

INTRODUCTION

The substitution of different atoms in the high-temperature superconductor $YBa_2Cu_3O_{6.9}$ is an important method for probing the parameters essential for the superconductivity. In $YBa_2Cu_3O_{6.9}$ any substitution for Cu, which can be done by other $3d$ elements[1-8] or by elements with a similar ionic radius such as Al, Mo, and Ge,[9,10] shifts the superconducting transition temperature T_c towards lower values. The rate of the T_c suppression is found to be highest for the substitution of the nonmagnetic elements Zn, Al, and Mo and reaches values of $dT_c/dc \simeq 15$ K/(at.% replacement of Cu). It is remarkable that a substitution of less than 10 at.% of, e.g., Zn suppresses the superconductivity completely.

Concerning the mechanism causing the suppression of T_c no consistent picture evolved until now. The mechanisms proposed in the literature are disorder in the oxygen sublattice, change of the local symmetry, magnetic pair-breaking scattering, and purely electronic mechanisms such as band filling and electron localization.

For a comparison of the influence of the different elements on T_c it is a prerequisite to know the site in the lattice where the substitutional elements reside. For the substitutional elements Ni, Fe, and Zn there exists recent experimental information about the site preference from neutron scattering. The Ni atoms substitute for Cu in the plane position Cu(2), Zn has a definite site preference for the chain position Cu(1),[7] contrary to the conclusions of many authors from indirect arguments that Zn resides on Cu(2).

Especially for the substitution of Fe, the situation is controversial. The neutron scattering work of Ref. 11 gives an occupancy of nearly 100% of Fe in Cu(1); in Ref. 12 a reasonable fit of the neutron scattering data could only be obtained with the assumption of Fe residing in the Ba and Cu(2) positions.

There exists much work in the literature on Mössbauer spectroscopy of Fe-substituted samples with an indirect assignment of the quadrupole doublets to positions in the lattice.[12-15] Most authors assume that in the superconducting state Fe substitutes for both Cu(1) and Cu(2). The change of the Mössbauer spectra when transforming the samples to the semiconducting state indicates one single, well-defined position for Fe in the semiconducting state,[13] which is usually assigned to the Cu(1) position with one type of O coordination. Especially for the substitution of Fe in $YBa_2Cu_3O_{7-\delta}$, problems concerning the homogeneity of the Fe distribution exist. The Fe ions seem to form clusters[15] or coherent two-dimensional precipitations[16] in the $YBa_2Cu_3O_{7-\delta}$ lattice.

In the first part of the present paper we study the superconducting properties of Fe-, Ni-, and Zn-substituted $YBa_2Cu_3O_{7-\delta}$ and provide experimental evidence that a shift of the Fermi energy towards the mobility edge is one important mechanism suppressing T_c.

In the second and major part of this paper we study the magnetic properties of the same samples in the insulating, antiferromagnetic state. This analysis gives direct information about the magnetic moments of Fe and Ni ions in the $YBa_2Cu_3O_{7-\delta}$ matrix and the interactions of the Fe and Ni spins with the Cu spins. From paramagnetic susceptibility measurements on superconducting, oxygen-rich $YBa_2Cu_3O_{7-\delta}$ with Fe and Ni substitution rather low effective magnetic moments have been derived,[1,5] e.g., an effective moment of Fe decreasing with increasing Fe concentration with $\mu_{\text{eff}} \simeq 3.9\mu_B$ at 10 at.% of substitution, which is neither consistent with a low spin state nor a high spin state of Fe^{3+}.

PREPARATION AND EXPERIMENT

The samples were prepared following the standard procedure starting with thoroughly mixed powders of high-purity Y_2O_3, $BaCO_3$, CuO and NiO, ZnO, or Fe_2O_3. The first sintering process was done in air at a temperature of 960 °C for 24 h; after regrinding and pressing into pellets

the samples were annealed in oxygen atmosphere for 20 h at 860 °C and then oven-cooled to room temperature. For the samples with higher concentration of Ni, Fe, or Zn we had to reduce the temperature of the second annealing process towards 830 °C in order to get single-phase samples.

For the Fe- and Ni-substituted $YBa_2Cu_3O_{7-\delta}$ samples the x-ray analysis revealed the formation of one single phase for Fe and Ni concentrations up to 10 at.%. With more than 5 at.% Zn substitution weak Bragg peaks at high scattering angles, which could not be indexed, indicated the formation of impurity phases.

The lattice parameters of all samples prepared for the present work are summarized in Fig. 1. Consistent with the results of other authors,[1-8] the unit cell is orthorhombic for up to 10 at.% Ni or Zn substitution, and the samples with Fe substitution are tetragonal for a concentration higher than 3 at.%.

The total oxygen content of the as-prepared samples was determined for some samples by measuring the weight loss after reducing in H_2 atmosphere at 900 °C. In agreement with the published results we found that the oxygen content is unchanged and close to $O_{6.9}$ in the Ni and Zn-substituted samples. With Fe substitution the total oxygen content increases slightly. For our sample with 10 at.% Fe substitution we determined a concentration $O_{7.2\pm0.1}$; this corresponds approximately to one additional oxygen atom for two Fe atoms.

In the second part of this paper we will present susceptibility data on all samples from Fig. 1 in the insulating, antiferromagnetic state, obtained after degassing the samples in vacuum at 600 °C. The oxygen concentration of the samples given in the subscripts of the figures and Table I has been determined thermogravimetrically. Consistent with the results known from the literature, we found that the lowest oxygen concentration one can achieve corresponds to $O_{6.0}$ for the Ni- and Zn-substituted samples, but is definitely higher for the Fe-substituted samples, e.g., $O_{6.3}$ for the 10 at.% Fe sample.

The electrical resistivity was measured on bars cut from the pellets by a standard four-point ac technique. The electrical contacts were made by sputtering gold contacts and attaching the leads by silver epoxy.

The low-field magnetization measurements in the superconducting state were done by a homemade superconducting quantum interference device magnetometer, and the magnetic field was 5 Oe unless otherwise noted.

The susceptibility measurements at high temperatures were done in a Faraday balance covering a temperature range from 3 to 1000 K. The Faraday technique offers the advantage of changing and controlling the oxygen content of the sample *in situ* by using the balance as a sensitive thermogravimetric apparatus. The measurements reported below for samples at different oxygen concentration have been done on one single sample by varying the oxygen content *in situ* in the Faraday balance. The magnetic field applied for the high-temperature susceptibility measurements was 1 T.

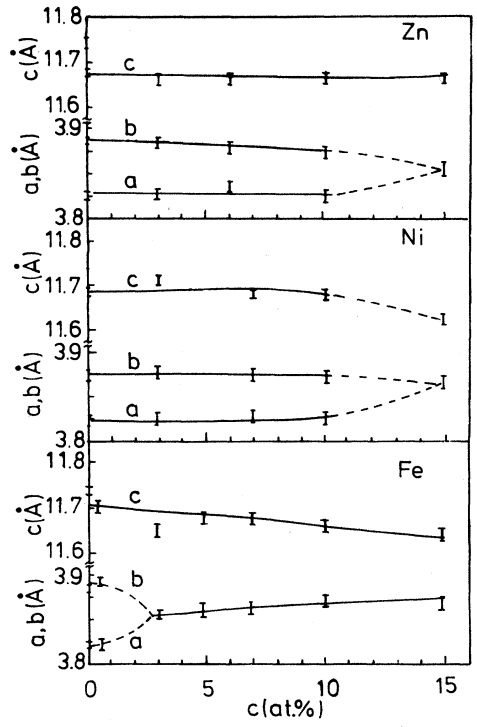

FIG. 1. Lattice parameters of superconducting $YBa_2(Cu_{1-x}(Zn,Ni,Fe)_x)_3O_{7-\delta}$ ($\delta=6.9$ for the Ni and Zn systems; $\delta\geq 7$ for the Fe system).

RESULTS AND DISCUSSION

The results of our electrical resistivity measurements are shown in Figs. 2(a)-2(c). Our pure sample $YBa_2Cu_3O_{6.9}$ has a residual resistivity of 500 $\mu\Omega$ cm and a transition width of 0.5 K. One finds that in all three substitution systems the residual resistivity is strongly increasing with the degree of substitution and the temperature coefficient of the resistivity at low temperatures and high concentrations of the substitutional elements changes from positive to negative, indicating a transition from metallic to semiconducting electron transport. A flat, nearly temperature-independent resistivity is observed at $\rho=10$ mΩ cm, thus this value marks the lowest metallic conductivity in compounds derived from $YBa_2Cu_3O_{7-\delta}$. It should be stressed that if this value holds for our polycrystalline and partly granular material, the corresponding value for single crystals might be different. The change of the resistivity as given in Fig. 2 is a characteristic feature of all $YBa_2Cu_3O_{7-\delta}$ samples with a substitution of Cu (Refs. 1-10) and indicates that the substitution of any element for Cu drives the Fermi energy towards the mobility edge.

The strongly increasing residual resistivity in $YBa_2Cu_3O_{6.9}$ with substitution for Cu will definitely change some important parameters of the superconductors. From standard dirty limit theory for superconductors of the second type one has for the Ginsburg-Landau correlation length at $T=0$, $\xi\propto(\rho_n\gamma T_c)^{-1/2}$ and for the magnetic field penetration depth $\lambda\propto(\rho_n T_c)^{1/2}$ (linear specific-heat coefficient γ, residual resistivity ρ_n, and transition temper-

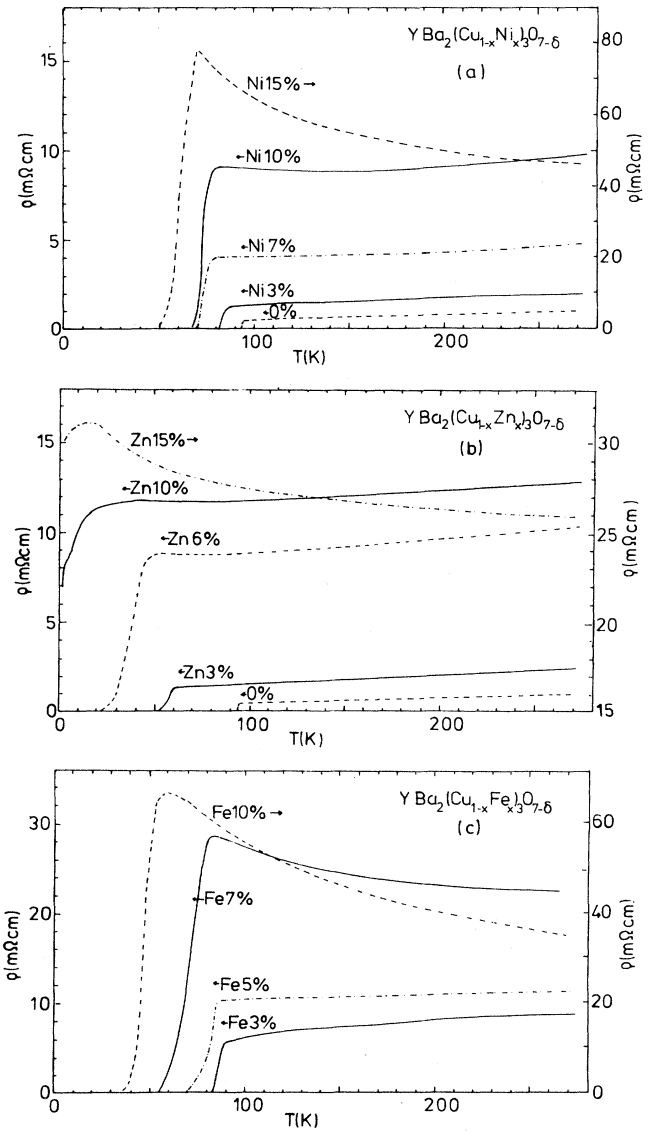

FIG. 2. (a)–(c) Electrical resistivity vs temperature for superconducting $YBa_2(Cu_{1-x}(Zn,Ni,Fe)_x)_3O_{7-\delta}$.

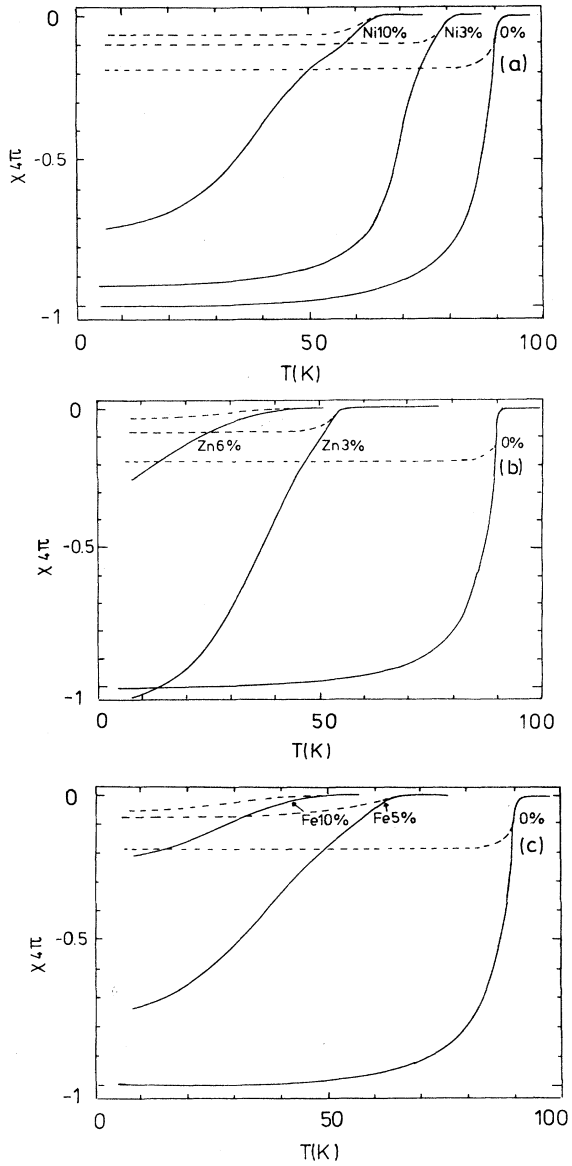

FIG. 3. (a)–(c) Low-field magnetic susceptibility vs temperature for superconducting $YBa_2(Cu_{1-x}(Zn,Ni,Fe)_x)_3O_{7-\delta}$. Solid line: zero-field-cooled curve; dashed line: field-cooled curve.

ature T_c). The increase of the residual resistivity of up to a factor of 20 in the superconducting range will probably overcompensate the decreasing γ and T_c and thus we expect the correlation length to decrease and the penetration depth to increase with increasing concentration of the substitutional atoms. This will make the superconductivity more sensitive to any sort of inhomogeneity and grain-boundary effects.

The low-field magnetization curves of the superconducting samples from Fig. 2 are given in Figs. 3(a)–3(c). For the calculation of the susceptibility, the demagnetizing field has been estimated from the geometrical shape of sample.

Compared to pure $YBa_2Cu_3O_{6.9}$ the transition width broadens with increasing concentration of the substitutional elements and the superconducting total volume estimated from the amplitude of the zero-field-cooled magnetization curve decreases. This behavior is characteristic for most $YBa_2Cu_3O_{7-\delta}$ systems with substitution for Cu. It can either be interpreted as a distribution of transition temperatures due to an inhomogeneous distribution of the substitutional elements, or as an increasing influence of Josephson-type weak couplings between superconducting grains. The fact that the observed broadening of the transition is much weaker in the field-cooled magnetization than in the zero-field-cooled magnetization points towards the latter explanation.

As described in more detail in the second part of this paper, one can separate the total paramagnetic susceptibility measured at high temperatures into an intrinsic Pauli-type of susceptibility and a paramagnetic part due

to impurity phases with paramagnetic Cu^{2+} ions or, in the case of Ni- and Fe-substituted samples, due to the paramagnetic Fe and Ni moments.

The Pauli type of susceptibility thus determined is given in Figs. 4 and 5 for $YBa_2Cu_3O_{6.9}$ substituted with Zn and Ni. The corresponding curves for the samples containing Fe cannot be given, since the complex behavior of the Fe moments makes a precise determination of the Pauli susceptibility impossible. One finds that the Pauli susceptibility decreases with the concentration of Zn and Ni very similar to the decrease observed with decreasing oxygen content in $YBa_2Cu_3O_{7-\delta}$ (see Fig. 7). This indicates that the number of charge carriers in $YBa_2Cu_3O_{6.9}$ with substitution of Ni and Zn decreases in a similar manner as observed in $YBa_2Cu_3O_{7-\delta}$ with increasing δ.[17,18]

The results of this section are summarized in Fig. 6, where we give the concentration dependence of the superconducting transition temperatures of the three systems. Zn induces by far the strongest suppression of T_c.

We want to close this section with some remarks about the possible origin of the T_c suppression with substitution of Cu.

The concentration dependence of the resistivity shows that with increasing degree of substitution the residual resistivity increases and eventually a hopping type of mobility at higher concentrations of the substitutional atoms dominates the transport process. This either means that the mobility strongly decreases with the concentration of the substitutional atoms, or the number of charge carriers decreases so that the Fermi energy shifts towards the mobility edge. The observed decrease of the Pauli susceptibility suggests that the change of the charge carrier number is the main effect. The decreasing charge carrier number can certainly explain the shift of the superconducting transition temperature partly. But this explanation is not sufficient, as is evident from a comparison of the Zn and Ni system in Fig. 6. In both systems the resistivity and the Pauli susceptibility changes with the Zn or Ni concentration in a similar manner; nevertheless, the substitution of Zn is a factor of about 10 more effective in suppressing T_c.

One essential difference between the Ni and Zn system is the different site preference for the substitution namely,

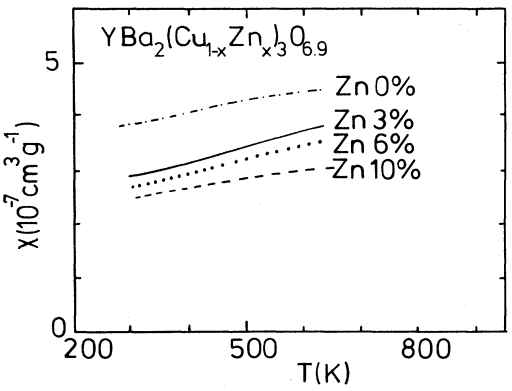

FIG. 4. Pauli susceptibility of superconducting $YBa_2(Cu_{1-x}Zn_x)_3O_{6.9}$ vs temperature.

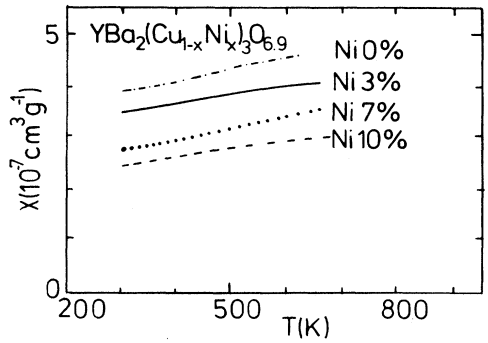

FIG. 5. Pauli susceptibility of superconducting $YBa_2(Cu_{1-x}Ni_x)_3O_{6.9}$ vs temperature.

Cu(1) for Zn and Cu(2) for Ni.[7] Since it seems now generally accepted that the Cu(2) planes are more important for the superconductivity than the Cu(1) chains, the strong influence of a substitution in the chains is puzzling. One important indirect influence a substitution in the chains can have for the superconductivity in the Cu(2) planes is a modification of the charge transfer between the Cu(1) and the Cu(2) plane, which determines the number of mobile p holes in the superconducting Cu(2) plane. A change of this charge transfer has been inferred indirectly from the change of the bond lengths with the substitution of Co for Cu in Ref. 3. This change of charge transfer could explain the decreasing number of charge carriers with the substitution of Zn.

With the substitution of Ni directly in the Cu(2) plane a second mechanism is important for the mobility of the charge carriers, namely scattering by the Ni ions and two-dimensional localization. It will be shown in the next section that the superexchange interaction between the local Ni moments and the Cu moments is very weak in $YBa_2Cu_3O_{7-\delta}$ with Ni substitution. This shows that covalent bonding of the Ni $3d$ and the O $2p$ orbitals is weak and thus the probability of the p hole to be at the Ni ion is low. Thus Ni ions will act as very effective scattering centers and at higher concentrations will cause a two-dimensional localization of the charge carriers.

Thus, although phenomenologically the Pauli susceptibility and the electrical resistivity change in a similar

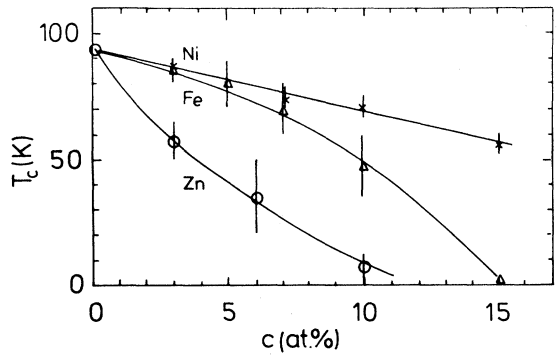

FIG. 6. Superconducting transition temperatures of $YBa_2(Cu_{1-x}(Zn,Ni,Fe)_x)_3O_{7-\delta}$ vs the Zn, Ni, or Fe concentration.

manner in the Zn- and Ni-doped $YBa_2Cu_3O_{6.9}$, the microscopic process might be different and this might give rise to the different concentration dependence of T_c in Fig. 6.

Before coming to the discussion of the paramagnetic susceptibility of the Ni-, Fe-, and Zn-doped samples in the insulating, antiferromagnetic state, we summarize the results of the susceptibility of pure $YBa_2Cu_3O_{7-\delta}$ in the paramagnetic state at high temperatures (Fig. 7).

The intrinsic susceptibility of $YBa_2Cu_3O_{7-\delta}$ at different oxygen content has been determined from the measured values by subtracting a Curie-Weiss term corresponding to 2 at.% of paramagnetic Cu^{2+} in impurity phases (see Ref. 19 for details).

In the semiconducting concentration range with $\delta > 0.5$ the susceptibility exhibits the typical behavior of a two-dimensional Heisenberg antiferromagnet[20] with the Néel temperature as given by the arrows in Fig. 7. The quantitative analysis of the susceptibility gives an exchange interaction of about 1000 K for the superexchange interaction Cu(2)-Cu(2) and an even larger value of 3000 K for the interaction Cu(1)-Cu(1). The continuous behavior of the susceptibility at the metal-semiconductor phase boundary with $\delta = 0.5$ indicates the existence of magnetic fluctuations in the superconducting state.

In Fig. 8 we show the paramagnetic susceptibility of Zn-doped $YBa_2Cu_3O_6$ for temperatures up to 900 K. With a substitution of 3 at.% Zn the absolute value of the susceptibility at high temperatures is slightly below the value for the pure sample. The minimum in χ, which correlates with the magnetic order (cf. Fig. 7), is flatter and shifted towards lower temperatures. At higher Zn concentrations one finds a strong increase of the paramagnetic Curie-Weiss contribution, which has also been observed by other authors.[21] The Curie-Weiss term is sometimes interpreted as being due to frustrated Cu spins in the $YBa_2Cu_3O_6$ lattice, but we conclude that it is caused by paramagnetic impurity phases for two reasons. First, we find that the Curie-Weiss term is independent of the oxygen concentration (Fig. 9 gives one example) and the existence of frustrated spins in the metallic state with all Cu ions in the Cu^{2+} state is improbable. Second, the occurrence of the Curie-Weiss term correlates with the intensity of weak Bragg peaks of impurity phases, as mentioned above. One calculates that the concentration of the Cu^{2+} ions in paramagnetic impurity phases increases up to 12 at.% for the sample with 15 at.% Zn.

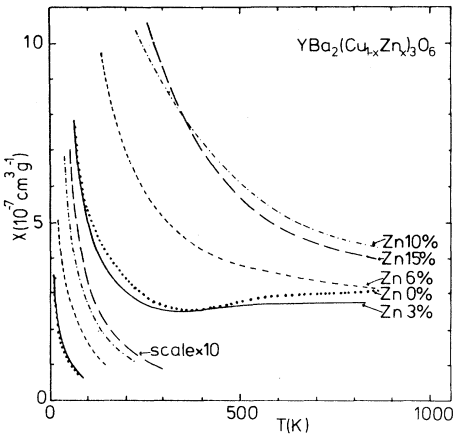

FIG. 8. Magnetic susceptibility of antiferromagnetic $YBa_2(Cu_{1-x}Zn_x)_3O_6$ vs temperature.

In the presence of a large Curie-Weiss term and with some additional smearing of the phase transition, T_N can no longer be resolved in the $\chi(T)$ curves directly for the samples with more than 6 at.% Zn in Fig. 8. By taking the thermal derivative $d\chi/dT$ numerically one can clearly resolve an anomaly caused by the drop of the intrinsic susceptibility just above T_N (Fig. 10). This anomaly defines the magnetic ordering temperature and allows a derivation of the relative shift of the Néel temperature with the concentration of Zn (Fig. 11). One finds that T_N first drops slightly for 3 and 6 at.% substitution of Zn but at higher concentration is again at about 400 K, as in the pure sample $YBa_2Cu_3O_6$.

From the shift of the Néel temperature with the Zn concentration it is possible to draw some conclusions about the site preference of the Zn ion in $YBa_2Cu_3O_6$. As is known from detailed neutron scattering experiments[22–25] the Cu(2) spins in the insulting compound

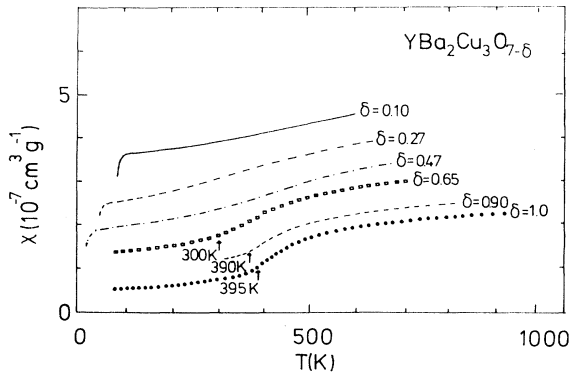

FIG. 7. Magnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$ vs temperature for different oxygen content. The arrows denote the Néel temperatures.

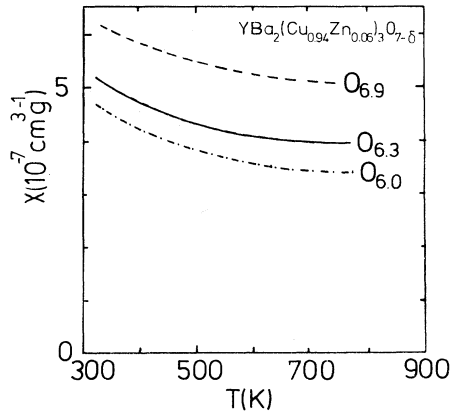

FIG. 9. Magnetic susceptibility vs temperature for $YBa_2(Cu_{0.94}Zn_{0.06})_3O_{7-\delta}$ at different oxygen content.

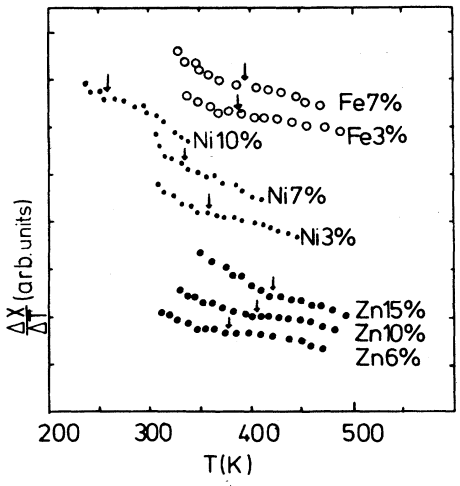

FIG. 10. Thermal derivative of the magnetic susceptibility vs temperature for the antiferromagnetic samples $YBa_2(Cu_{1-x}(Zn,Ni,Fe)_x)_3O_{7-\delta}$ ($\delta \simeq 1$ for the Zn and Ni systems, $\delta \simeq 0.8$ for the Fe system).

$YBa_2Cu_3O_6$ form an antiferromagnetic lattice with antiferromagnetic orientation of the moments within each Cu(2) plane and between two subsequent Cu(2) planes. The Cu(1) ions are in the valence state 1+ with a closed d^{10} shell and thus are nonmagnetic.

Since the two Cu positions in $YBa_2Cu_3O_6$ are thus very different, namely, magnetic and nonmagnetic, the influence of a nonmagnetic substitution on Cu(1) and Cu(2) is expected to be very different.

The Néel temperature of a two-dimensional Heisenberg magnet is given by $T_N \propto J' \xi_{2d}^2$ with the weak interaction between the Cu(2) planes J' and the two-dimensional correlation length within the Cu(2) plane ξ_{2d}. A substitution of nonmagnetic Zn on the nonmagnetic Cu(1) positions will only modify J' slightly, e.g., by changing the higher-order superexchange between two Cu(2) layers. This can slightly increase or decrease T_N. A substitution of nonmagnetic Zn on the magnetic Cu(2) position, however, will very effectively reduce ξ_{2d} and thus strongly reduce T_N. As an example we mention that the substitution of 10 at.% of Zn for Cu in the two-dimensional antiferromagnet K_2CuF_4 reduces T_N by about 40%.[26,27]

Applying this reasoning to the shift of T_N with the Zn concentration given in Fig. 11, it is straightforward to conclude that at higher concentrations Zn has a site preference for the nonmagnetic position Cu(1). From the slight decrease of T_N at low Zn concentrations one can suppose that some Zn resides in Cu(2). These conclusions are very consistent with the site preference of Zn in the superconducting state $YBa_2Cu_3O_{6.75}$, where for a 10 at.% Zn sample a site preference of 8 at.% on Cu(1) and 2 at.% for Cu(2) has been determined by neutron scattering.[7]

The separation of the measured susceptibility into a Pauli susceptibility and contribution from paramagnetic moments in impurity phases has been done by fitting a Curie-Weiss law below 50 K, where the paramagnetic term dominates for the samples in the antiferromagnetic state with $\delta > 0.5$. This Curie-Weiss term has been subtracted from the measured susceptibility in the superconducting state in order to derive the Pauli susceptibility given in Fig. 4. We thus assumed that the paramagnetic term from impurity phases does not change in the metallic concentration range $\delta < 0.5$, as is apparent from the δ dependence of the total susceptibility shown in Fig. 9.

The susceptibility measured for our Ni-doped samples in the insulating state with the oxygen concentration O_6 is given in Fig. 12. One observes a Curie-Weiss contribution to the susceptibility increasing linearly with the Ni concentration, which is caused by the paramagnetic Ni spins in the $YBa_2Cu_2O_6$ lattice. The Ni spins do not show any indication of magnetic order down to the lowest measuring temperature of 3 K (Fig. 13), thus the exchange interactions between the antiferromagnetically ordered Cu spins and the Ni spins are very weak.

The Néel temperatures can be resolved on the $d\chi/dT$ curves in Fig. 10; one finds that T_N decreases linearly with the Ni concentration (Fig. 11). Since the Ni spins and the

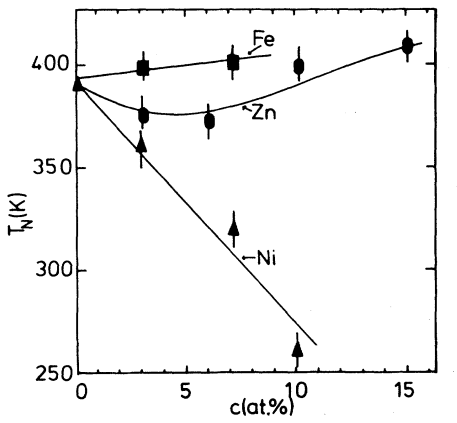

FIG. 11. Néel temperature vs the concentration of Fe, Ni, and Zn in $YBa_2(Cu_{1-x}(Fe,Ni,Zn)_x)_3O_{7-\delta}$.

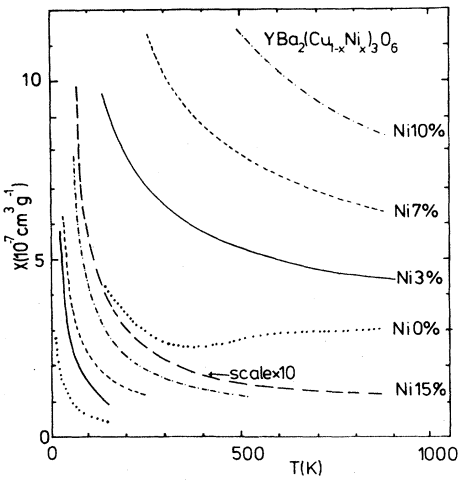

FIG. 12. Magnetic susceptibility of antiferromagnetic $YBa_2(Cu_{1-x}Ni_x)_3O_6$ vs temperature.

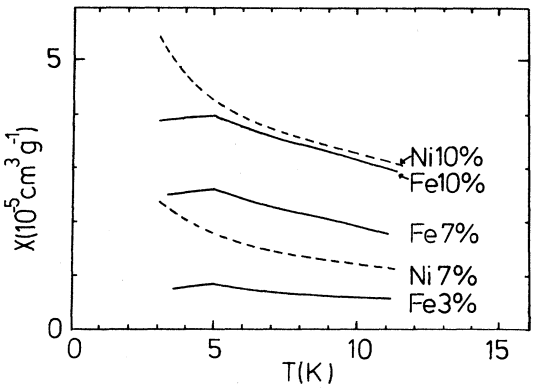

FIG. 13. Magnetic susceptibility vs temperature of antiferromagnetic $YBa_2(Cu_{1-x}(Fe,Ni)_x)_3O_{7-\delta}$ at low temperatures.

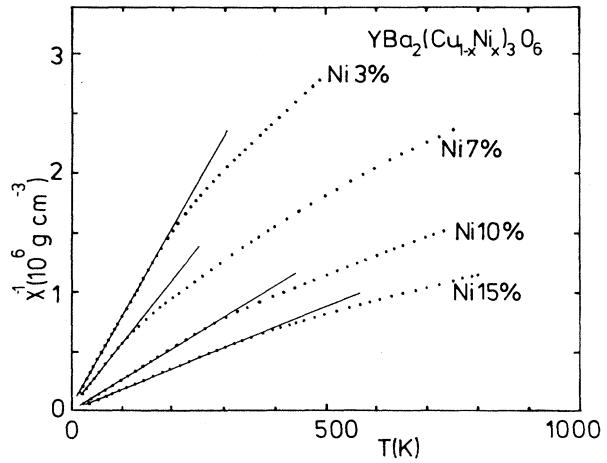

FIG. 14. Reciprocal magnetic susceptibility vs temperature for antiferromagnetic $YBa_2(Cu_{1-x}Ni_x)_3O_6$. The parameters of the fit by the Curie-Weiss law are given in Table I.

Cu spins are only weakly coupled (we will show below that the superexchange interaction Ni-Cu is at least two orders of magnitudes lower than the Cu-Cu superexchange), the Ni ions on the Cu positions act effectively as a nonmagnetic dilution of the Cu lattice, similar to Zn. Then it is straightforward to conclude from the observed strong decrease of T_N in Fig. 11 that at least a part of the Ni ions reside on the magnetic Cu(2) position.

One finds in Fig. 11 that T_N decreases by about 35% for a substitution of 10 at.% Ni; this value is comparable to the 40% decrease of T_N in K_2CuF_4 with 10 at.% substitution of Zn. This suggests that nearly all of the Ni ions occupy a Cu(2) position. Actually, for a sample $YBa_2Cu_3O_{6.85}$ with 10 at.% Ni the neutron scattering results of Ref. 7 gave a site preference of 100% Cu(2) for Ni.

In order to derive the effective magnetic moments of the Ni spins in the $YBa_2Cu_3O_6$ matrix, we neglect in a first approximation any interaction of the Ni spins and the Cu spins, i.e., we regard the two spin systems as independent. Then the paramagnetic susceptibility of Ni can be derived by subtracting the susceptibility of pure $YBa_2Cu_3O_6$ from the measured susceptibility of Ni-substituted $YBa_2Cu_3O_6$.

The reciprocal magnetic susceptibility of the Ni spins thus derived is given in Fig. 14. At low temperatures one obtains a Curie-Weiss law with the values for the effective magnetic moments and paramagnetic Curie temperatures as given in Table I. The effective moments thus derived are consistent with a high-spin state of Ni^{2+} with a theoretical $\mu_{\text{eff}}=2.83\mu_B$. The moment which results for the 7 at.% Ni sample is definitely lower; we suppose that in this sample impurity phases containing Ni exist.

The paramagnetic Curie temperatures, which are a measure of the interaction between the Cu spins and the Ni spins, are close to 0 K, thus the superexchange interaction between the Cu and Ni spins is astonishingly weak; the Cu spins and Ni spins are nearly decoupled in the $YBa_2Cu_3O_6$ lattice. This result implies that the Ni $3d^8$ orbitals do not mix with the neighboring oxygen p orbitals; the Ni $3d^3$ electrons do not take part in the covalent p-σ bond.

For a determination of the Pauli susceptibility of Ni-doped $YBa_2Cu_3O_{6.9}$ we again assume that the paramagnetic contribution of Ni does not change when going from the insulating to the metallic state. This assumption is supported by the concentration dependence of the measured susceptibility shown in Fig. 15. The Pauli susceptibility is then obtained by a subtraction of the measured susceptibility in the superconducting state at high temperatures and the paramagnetic term determined for the Ni spins, and is shown in Fig. 5.

In Fig. 16 we depict the susceptibility measured for the Fe-substituted samples in the insulating, antiferromagnetic state (oxygen concentration $O_{6.2}$ or $O_{6.3}$). The Fe spins contribute a paramagnetic moment down to low temperatures, but contrary to the Ni-spins order at 5 K, independent of the Fe concentration (Fig. 13).

The antiferromagnetic ordering temperature of the Cu lattice can be derived from the $d\chi/dT$ curves in Fig. 10 for the 3 at.% and the 7 at.% sample only. For higher Fe concentrations we cannot resolve a structure in the $d\chi/dT$ curve, probably because of a strong smearing of the transition. With the same reasoning as above, i.e., taking into consideration the weak coupling of the Cu spins and the Fe spins and the different influence for a substitution on

TABLE I. Paramagnetic Curie temperatures and effective magnetic moments of the samples derived from the fit in Figs. 14, 17, and 18.

Sample	Θ (K)	$\mu_{\text{eff}}(\mu_B)$
$YBa_2(Cu_{0.97}Ni_{0.03})_3O_6$	−5(±5)	2.70(±0.1)
$YBa_2(Cu_{0.93}Ni_{0.07})_3O_6$	−10(±5)	2.10(±0.1)
$YBa_2(Cu_{0.90}Ni_{0.10})_3O_6$	0(±5)	2.57(±0.1)
$YBa_2(Cu_{0.85}Ni_{0.15})_3O_6$	−5(±5)	2.59(±0.1)
$YBa_2(Cu_{0.97}Fe_{0.03})_3O_{6.2}$	−150(±20)	5.77(±0.2)
$YBa_2(Cu_{0.93}Fe_{0.07})_3O_{6.2}$	−125(±20)	5.01(±0.2)
$YBa_2(Cu_{0.90}Fe_{0.10})_3O_{6.3}$	−120(±20)	4.67(±0.2)
$YBa_2(Cu_{0.97}Fe_{0.03})_3O_{7.0}$	−40(±40)	5.83(±0.2)
$YBa_2(Cu_{0.93}Fe_{0.07})_3O_{7.1}$	−5(±20)	4.98(±0.2)
$YBa_2(Cu_{0.90}Fe_{0.10})_3O_{7.2}$	−10(±40)	4.68(±0.2)

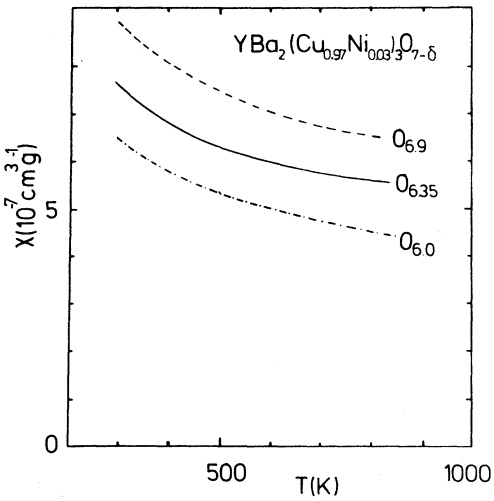

FIG. 15. Magnetic susceptibility vs temperature for the sample $YBa_2(Cu_{0.97}Ni_{0.03})O_{7-\delta}$ at different oxygen content.

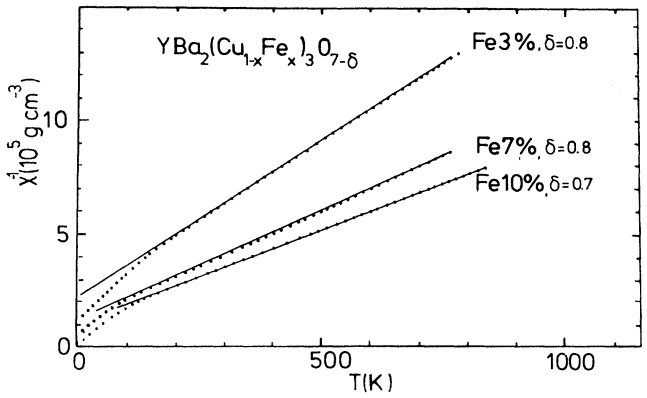

FIG. 17. Reciprocal magnetic susceptibility vs temperature for antiferromagnetic $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. The parameters of the fit by the Curie-Weiss straight line are given in Table I.

Cu(1) and Cu(2), the concentration-independent T_N in Fig. 11 indicates a site preference for the Cu(1) position, consistent with the interpretation of the Mössbauer spectra in the insulating state[12–14] of Fe-doped $YBa_2Cu_3O_{7-\delta}$.

For the determination of the effective magnetic moments of Fe in the matrix of $YBa_2Cu_3O_{7-\delta}$ we proceed as for the Ni system above, i.e., we subtract the susceptibility of pure $YBa_2Cu_3O_6$ from the measured susceptibility of Fe-doped $YBa_2Cu_3O_6$. The reciprocal susceptibility follows a straight line from about 100 to 800 K (Fig. 17). The magnetic moments derived from this straight line are given in Table I. For the sample with 3 at.% Fe one finds $\mu_{\text{eff}}=5.77\mu_B$, in good agreement with a Fe^{3+} ion in the high spin state ($\mu_{\text{eff}}=5.9\mu_B$). But the effective magnetic moment decreases with the Fe concentration, although the valence state of Fe does not change.

The paramagnetic Curie temperature Θ is about -130 K and independent of the Fe concentration within the accuracy of the experiment. In addition, one should note that independent of the Fe concentration the reciprocal susceptibility deviates from the Curie-Weiss straight line at about 100 K, indicating the onset of magnetic short-range order.

We conclude that the negative paramagnetic Curie temperature is due to a weak antiferromagnetic exchange interaction between the Fe^{3+} spin in the nonmagnetic Cu(1) position and the two neighboring Cu spins in the Cu(2) position. This explains consistently the concentration-independent ordering temperature of the Fe spins in Fig. 13, the concentration-independent paramagnetic Curie temperature, and the onset of magnetic short-range order at 100 K for all three samples. From the standard mean-field result $\Theta=2/3JzS(S+1)$ with the number of magnetic neighbors z and the spin of the Fe^{3+} $s=\frac{5}{2}$, one gets an antiferromagnetic exchange interaction between the Cu and Fe spins of $J\simeq 4$ K.

In Fig. 18 we have plotted for comparison with Fig. 17 the paramagnetic contribution of Fe in the superconducting state at higher oxygen content. For the derivation of the moments we have assumed that the Pauli susceptibility changes with the Fe concentration similar to the change derived for the substitution of Zn and Ni (Figs. 4 and 5). This assumption is not very critical, since the paramagnetic contributions from the Fe spins are large. One finds that the effective magnetic moments remain unchanged, but the paramagnetic Curie temperatures have lower absolute values. Thus, the exchange interactions for Fe ions in the superconducting state are definitively lower than in the insulating, antiferromagnetic state.

This result correlates well with the observed strong change of the Mössbauer spectrum of Fe when going from the metallic to the insulating state.[12–14] Most authors interpret the Mössbauer spectra by assuming that in the metallic state Fe ions reside on Cu(1) and Cu(2) positions with an approximately equal probability, and in the insulating state they are mainly in the Cu(1) position. By adopting this interpretation, the change of the paramagnetic Curie temperature would indicate that the exchange interaction between the Cu spins and the Fe spins in the Cu(2) planes are very weak in the superconducting state.

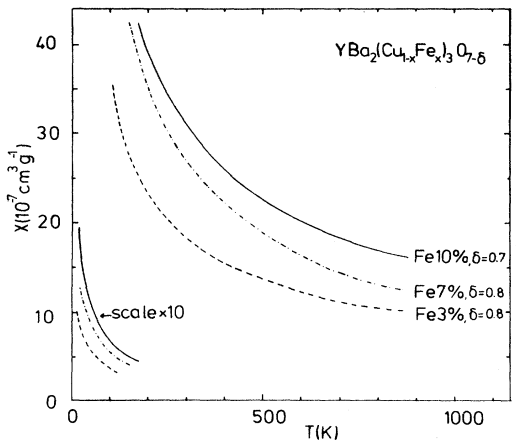

FIG. 16. Magnetic susceptibility vs temperature for antiferromagnetic $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$.

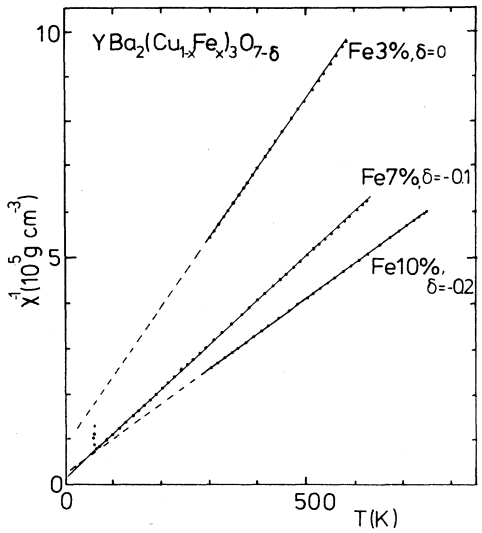

FIG. 18. Reciprocal magnetic susceptibility vs temperature for superconducting $YBa_2(Cu_{1-x}Fe_3)_3O_{7-\delta}$. The parameters of the Curie-Weiss straight line are given in Table I.

However, we cannot exclude from the present measurements that the origin of the different paramagnetic Curie temperature is simply a change of the oxygen coordination within the Cu(1) plane.

One problem concerning the Fe substituted $YBa_2Cu_3O_{7-\delta}$ concerns the value of the magnetic moments that decrease with increasing Fe concentration (see Table I). This behavior has also been observed by other authors,[1,5] although they use a different method for separating the paramagnetic contribution from Fe and the intrinsic susceptibility of the matrix. We suggest that this behavior might indicate that the Fe ions are not distributed at random on the Cu positions but have a tendency to form pairs or larger clusters at higher concentrations. The covalent bonding of the Fe ions within these clusters might reduce the effective magnetic moment compared to the value of one single isolated Fe spin.

The effective magnetic moments we gave in Table I for Ni and Fe are larger than the moments usually given in the literature, e.g., $\mu_{\text{eff}}=3.7\mu_B$ for 10 at.% Fe in $YBa_2Cu_3O_7$.[1] The procedure usually applied in the literature to determine μ_{eff} is a fit of the measured total susceptibility by the standard formula $\chi_{\text{tot}}=\chi_0+C/(T-\Theta)$ and calculating μ_{eff} from the Curie constant C. Using this formula one neglects, however, the temperature dependence of the intrinsic susceptibility χ_0 and thus underestimates the magnetic moments. We think that the method we applied here, starting with realistic assumptions about the intrinsic susceptibility, gives more realistic values for the effective moments.

SUMMARY AND CONCLUSIONS

In the first part of this paper we have studied the basic properties of the superconductor $YBa_2Cu_3O_{6.9}$ doped with Ni, Fe, and Zn. From the change of the resistivity and the Pauli susceptibility we have concluded that the number of free charge carriers decreases with increasing concentration of the substitutional atoms. This is one important electronic effect which suppresses the transition temperature. However, a comparison of the Ni and Zn systems shows that the number of charge carriers alone cannot explain the T_c shift. We have pointed out that the mechanism which shifts the Fermi level towards the mobility edge might be different for the substitution of Zn with a site preference for Cu(1), and Ni with a site preference for Cu(2). With the substitution of Zn the internal charge balance between the Cu(1) and Cu(2) planes determines the number of mobile holes in the Cu(2) plane. With the substitution of Ni directly in the conducting planes Cu(2) two-dimensional localization induced by the random potential of Ni is conceivable. Thus, although the total number of mobile holes decreases in a similar manner in the Zn and Ni systems the microscopic process and the T_c shift might be different.

Alternatively, of course, the substitution of Zn might directly suppress the superconducting coupling mechanism either of excitonic or magnetic origin.[28,29]

A problem which is common for $YBa_2Cu_3O_{6.9}$ with any substitution for Cu is the gradual decrease of the superconducting volume with increasing concentration of the substitutional atoms. We know of only two exceptions in the literature, where the superconducting volume is close to 100% and the transition remains sharp even at higher concentrations. This is the Co system of Ref. 1 and the Ga system of Ref. 8. It seems that the preparation-dependent distribution of the substitutional atoms determines the superconducting volume and the width of the transition. A homogeneous distribution with nearly random occupancy of the Cu positions leaves the transition sharp and the superconducting volume close to 100%. An inhomogeneous distribution with formation of clusters, on the other hand, broadens the transition and decreases the superconducting volume. With the three systems studied here, the distribution of Fe seems to be rather inhomogeneous even at low concentrations, and the homogeneity of the Zn and Ni distribution is much better.

In the second part of this paper we mainly studied the high-temperature paramagnetic susceptibility of the antiferromagnetic $YBa_2Cu_3O_6$ samples with substitution of Ni, Fe, and Zn. We found clear evidence for a very weak exchange coupling of the Ni spins and the Cu spins in the $YBa_2Cu_3O_6$ matrix. The Fe spins in the Cu(1) positions are coupled antiferromagnetically to the Cu(2) spins with an exchange interaction of about 4 K and order magnetically at $T=5$ K. The very weak exchange interactions between the Cu spins and the Fe and Ni spins indicate that the Ni and Fe d-orbitals are well isolated in the $YBa_2Cu_3O_{7-\delta}$ matrix and do not mix with the oxygen p orbitals. In the superconducting state this will mean that conventional pair-breaking scattering on the local Ni or Fe moments, if it exists at all, will be weak and difficult to detect.

We have shown that the Néel temperature of the Cu matrix can be derived from the high-temperature susceptibility measurements even for the compounds with higher degrees of substitution and rather smeared transitions.

Since the two Cu positions are very different magnetically, it is straightforward to draw some conclusions about the site preference of the substitutional elements from the concentration dependence of T_N. We have concluded that Zn resides on Cu(1), Fe resides on Cu(1), and Ni on Cu(2). This is in good agreement with the site preference determined in the superconducting state by neutron scattering. Thus, it seems that during the change of the oxygen content the site occupancy of the metal positions is not changed. The effective magnetic moments for Fe and Ni in $YBa_2Cu_3O_{7-\delta}$ are consistent with a high spin value at low concentrations. At higher concentrations the Fe moment decreases, which we tentatively have explained by the formation of Fe clusters.

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