Influence of magnetic scattering centers in the insulator component of the composite HTSC+$Cu_{1-x}Ni_xO$ on its resistive properties

M. I. Petrov, D. A. Balaev, K. A. Shaĭkhutdinov, and S. G. Ovchinnikov

L. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

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We present results of an experimental study of the effect of magnetic scattering centers (nickel) in the insulator component (cuprous oxide) of the composite HTSC+$Cu_{1-x}Ni_xO$ on its transport properties. A suppression of the superconducting properties of this system is observed to take place with increasing nickel content. The results are analyzed within the framework of the model of strong electron correlations. © *1998 American Institute of Physics.* [S1063-7834(98)00609-1]

Weak bonds in materials based on HTSC's are presently under intense study, both theoretically and experimentally, motivated by the fact that they display most strikingly carrier-pairing regularities.[1] A study of the transport properties of two-component composite samples, one whose components is a HTSC and the other is either an insulator (I) or semiconductor (Sm) or normal metal (N), is tantamount to a study of the transport properties of an artificially created network of weak bonds of given type ($S-I-S$, $S-Sm-S$, $S-N-S$, where S is a superconductor).[2–8] Despite the fact that the weak bonds in such composites are distributed randomly with respect to geometrical dimensions, the transport characteristics [temperature dependence of the critical current $J_c(T)$ and resistance $R(T)$, current–voltage characteristics (CVC)] reflect the primary regularities of supercurrent flow through an effective contact of the corresponding type. We prepared composites based on the classical HTSC $Y_{3/4}Lu_{1/4}Ba_2Cu_3O_7$ and CuO.[8,9] We showed that such a system is an example of a network of weak bonds of $S-I-S$ type. Current–voltage characteristics of quasitunneling type and thermally activated phase slippage (TAPS) are characteristic of such a system below T_c (Ref. 10). When CuO is transformed by lithium doping into a superconductor, composites based on it manifest the characteristics of a network of weak $S-Sm-S$ bonds — specifically, we are looking here at a transformation of the CVC from quasitunneling to metallic and the appearance of a plateau in $J_c(T)$ in the low-temperature region as a result of increased carrier concentration in the superconductor constituent.[7,11] A study of HTSC+$BaPbO_3$ composites with paramagnetic impurities introduced in the normal metal $BaPbO_3$ (Ref. 12) motivated us to examine the influence of magnetic scattering centers introduced in the insulator component of the HTSC+CuO composite. The choice of CuO is based on the experimental observation of an absence of chemical interaction between the HTSC with $1-2-3$ structure and the cuprous oxide, as was shown by electron microscopy[13] and x-ray diffraction studies.[8,13] Although CuO is a semiconductor, at temperatures below 100 K its resistivity (ρ) is 15 orders of magnitude larger than the resistivity of the HTSC;[14] for this reason CuO can be taken to be an insulator in our case. Doping of CuO by isovalent nickel should not, in our opinion, lead to the induction of valence and the appearance of impurity carriers in contrast to nonisovalent doping of CuO by Li (CuO:Li), which gives rise to a substantial growth in the conductivity and even a change in its character with increasing concentration of impurity carriers.[7,15] In Refs. 16–18 it was theoretically shown that magnetic impurities introduced into the insulting barrier also suppress the Josephson supercurrent. The present paper reports an experimental study of the influence of a nickel impurity in a CuO matrix on the resistive properties of HTSC+$Cu_{1-x}Ni_xO$ composites.

1. EXPERIMENT

Composite samples having the formula HTSC+$Cu_{1-x}Ni_xO$ were prepared in the following way. First, the initial components of the composite to be prepared were synthesized: $Y_{3/4}Lu_{1/4}Ba_2Cu_3O_7$ and $Cu_{1-x}Ni_xO$. The standard ceramic technique was used to synthesize $Y_{3/4}Lu_{1/4}Ba_2Cu_3O_7$. $Cu_{1-x}Ni_xO$ was prepared by the ceramic technique from CuO and NiO at 950 °C. The synthesis time was ~40 h with several intermediate grindings.

A Debyegram of the sample with the largest x—$Cu_{0.94}Ni_{0.06}O$ (samples with $x<0.06$ were not investigated since the standard x-ray technique does not give reliable results in this case)—revealed the presence of two crystallographic phases in which a solid solution the system $(CuO)_{1-x}(NiO)_x$ can exist. These results are in full agreement with the conclusions of Ref. 19. Magnetic measurements were performed in the components of the composite $Cu_{1-x}Ni_xO$ with $x=0$, 0.01, 0.03, 0.06 using a vibrating magnetometer.[20] Figure 1 plots the magnetization dependence on the temperature of the samples in the interval 4.2 -300 K, measured in a field $H=5$ kOe. A monotonic increase of the absolute value of the magnetization with increase of the nickel content is evident in the samples, as well as a decrease of the Néel temperature with increase of x (for

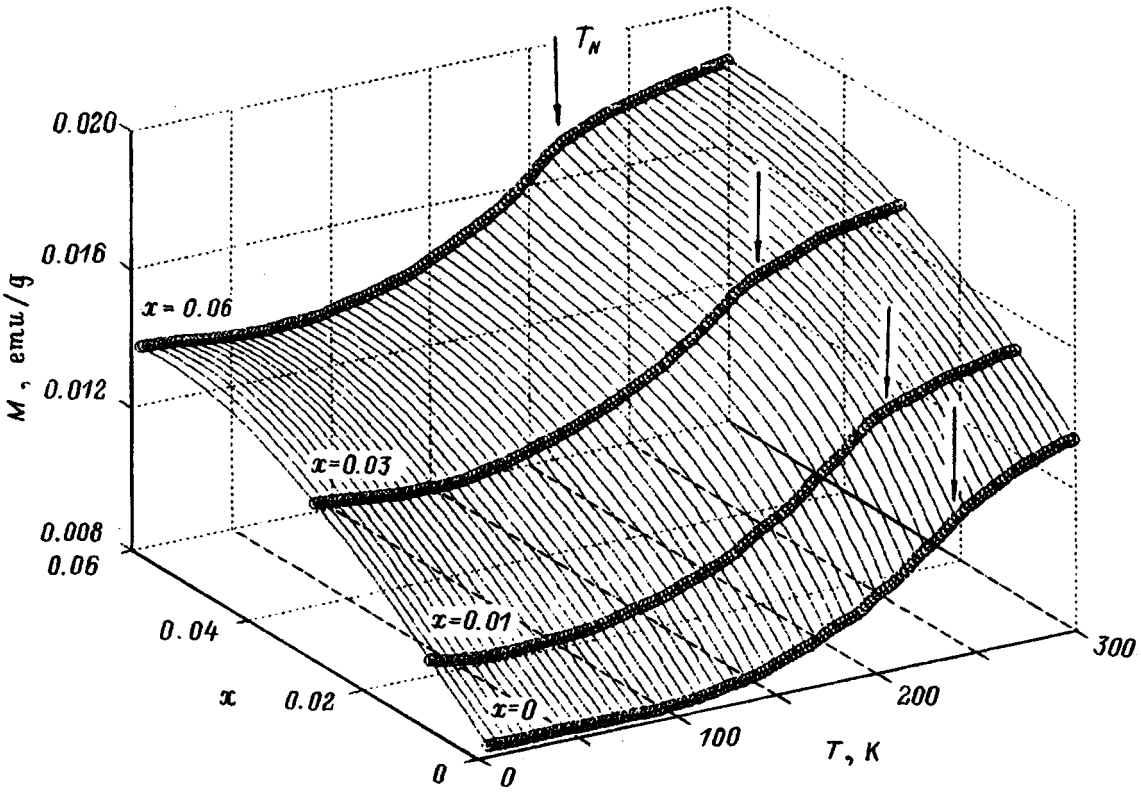

FIG. 1. Temperature dependence of the magnetization M of $Cu_{1-x}Ni_xO$ as a function of x. $x=0$, 0.01, 0.03, 0.06. Isotherms are drawn with a 5 K step. Arrows indicate the Néel temperature.

CuO T_N is $\sim$250 K, which is in qualitative agreement with the data of Refs. 14 and 21). Although this value is somewhat larger than the value measured by other authors and is probably due to impurities and a possible oxygen nonstoichiometry, what is more important in the given case is the relative variation of the Néel temperature with doping of CuO with nickel. Measurements of the magnetization $M(H)$ of the components of the composites were performed in fields up to 60 kOe at $T=4.2$ K. All of the dependences turned out to be linear, their slopes increasing monotonically with growth of x. Analysis of these measurements showed that the magnetization is additive in the nickel concentration. On the basis of magnetic measurements and x-ray diffraction studies, we can describe the $Cu_{1-x}Ni_xO$ system as an antiferromagnetic CuO matrix in which copper atoms are randomly replaced by nickel atoms. These atoms can enter as additional magnetic scattering centers for carriers of the superconducting current in a network of weak $S-I-S$ bonds with a barrier formed from such material.

The mixture of powdered components of the composite to be formed, taken in the required proportions (85 vol% HTSC and 15 vol% $Cu_{1-x}Ni_xO$), were pressed into pellets which were then loaded into the working zone of a furnace heated to 910 °C. The pellets were kept at this temperature for 2 min and then loaded into a second furnace at 350 °C, where they were kept for 3 h, after which they were allowed to cool in the furnace. All of the samples investigated in this work were prepared from a single series of initial ingredients to avoid random deviations of their physical properties associated with possible impurities and variations in their stoichiometry and particulars of their preparation.

Figure 2 plots the resistivity of samples of the composite HTSC+$Cu_{1-x}Ni_xO$ as a function of temperature and composition, normalized to ρ (93.5 K) for $x=0$, 0.01, 0.03, 0.06. The absolute values of ρ (93.5 K) of the composites were 0.055 $\Omega\cdot$cm for $x=0$, 0.069 $\Omega\cdot$cm for $x=0.01$, 0.061 $\Omega\cdot$cm for $x=0.03$, and 0.059 $\Omega\cdot$cm for $x=0.06$, i.e., within the limits of measurement error the values of the resistivity at 93.5 K [ρ (93.5 K)] for all samples of the composite HTSC+$Cu_{1-x}Ni_xO$ can be taken to be identical. Hence we conclude that nickel is not an additional scattering center for ordinary current carriers as they tunnel through the insulating interlayer. The form of the $\rho(T)$ curves is the same as for HTSC + CuO composite samples:[8] they have a quasisemiconductor character up to the superconducting transition temperature of the HTSC grains (93.5 K) (not shown in Fig. 2), which is followed by an abrupt decrease in the resistance corresponding to transition to the superconducting state of the HTSC grains (the invariance of this temperature for all x and its equality to T_c of the starting HTSC point to an absence of nickel diffusion into the HTSC), and they have a smooth ''tail'' reflecting the transition to the superconducting state of the weak bonds. This part of the dependence for $x=0$ has been attributed to thermal fluctuations (TAPS)[10] in a network of Josephson junctions.[8]

It is explicitly clear from Fig. 2 that the temperature of the transition to the state of zero resistance falls as the nickel content in the insulator component of the composite is in-

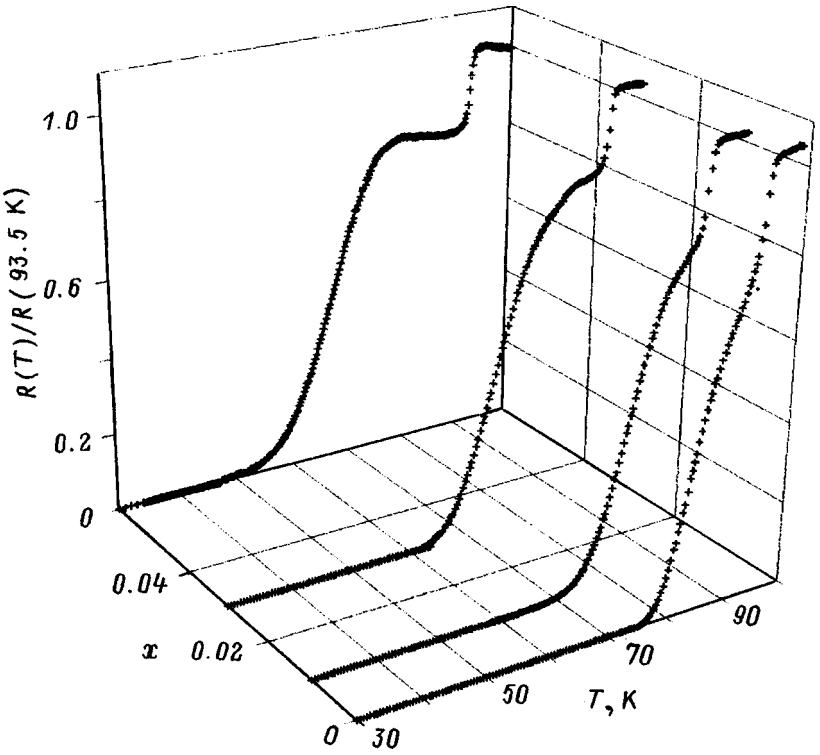

FIG. 2. Temperature dependence of the normalized electrical resistance $R(T)/R$ (93.5 K) as a function of x for composite samples 85 vol.% $Y_{3/4}Lu_{1/4}Ba_2Cu_3O_7$ + 15 vol% $Cu_{1-x}Ni_xO$. $x=0$, 0.01, 0.03, 0.06.

creased. Since the volume fraction of $Cu_{1-x}Ni_xO$ in all the composite samples was the same (15 vol%), and likewise the particulars of their preparation, the decrease in the temperature at which the resistance vanishes can be explained only by an additional (besides TAPS) magnetic scattering of the supercurrent carriers in the insulating interlayer.

2. DISCUSSION

According to the phase diagram of the system $Cu_{1-x}Ni_xO$ (Ref. 19), for $x<0.05$ a solid solution with monoclinic CuO structure exists, i.e., the substitution Cu $\rightarrow$ Ni can be considered as isostructural. Changes in the electronic structure and magnetic properties caused by such a substitution were treated for the system $La_2Cu_{1-x}Ni_xO$ in Ref. 22 with the aid of exact diagonalization of the microelectronic Hamiltonian of the $p-d$ model for CuO_4 and CuO_6 clusters. Since the immediate environment of the copper and nickel atoms in $Cu_{1-x}Ni_xO$ is almost the same, the calculated results of Ref. 22 can also be applied to this system.

According to Ref. 22, the substitution Cu$\rightarrow$Ni in oxides does not result in the formation of the bivalent configuration $Ni^{2+}(d^8)$ with spin $s=1$, which is energetically unfavored because of the strong intra-atomic electron correlations of the $3d$ electrons. It is more favorable for the two holes (relative to the filled $3d^{10}$ shell) not to be localized in the $3d^8$ state, but to be partly ''smeared'' over the nearest neighbors, that is, oxygen ions, so that the wave function of the two-hole state can be written as a superposition of the $3d^9L$ and $3d^{10}L^2$ configurations

$$|2\rangle = u_0|p^5d^{10}p^5\rangle - v_0(|p^6d^9p^5\rangle + |p^5d^9p^6\rangle)/\sqrt{2}, \qquad (1)$$

where the coefficients u_0 and v_0 are determined by such parameters of the Hamiltonian of the $p-d$ model as the charge transfer energy, the copper–oxygen Coulomb interaction, and the energies of the p and d levels in the crystal field. Thus, because of covalency effects the nickel ion is found in the diamagnetic state d^{10} with probability u_0^2 and in the state d^9 with spin $s=1/2$ with probability v_0^2. The weight of the configuration d^8 with spin $s=1$ is small ($\sim 1\%$); therefore it can be neglected. All these conclusions are valid only for low concentrations of the substituent atoms, i.e., for $x \ll 1$.

Let us apply these ideas to an analysis of the magnetic and electrical properties of the composites described above. In an antiferromagnetic CuO matrix, according to Eq. (1), the substitution Cu $\rightarrow$ Ni with probability v_0^2 conserves the $s=1/2$ spin, and with probability u_0^2 leads to diamagnetic dilution. The suppression of antiferromagnetism can be explained by diamagnetic dilution, where the falloff of T_N is proportional to the concentration of diamagnetic centers, $dT_N/dx \sim u_0^2 x$. From the data of Fig. 1, for $Cu_{1-x}Ni_xO$ we have $dT_N/dx \cong -5$ K/at. %, which is quite close to the value $dT_N/dx = -5.5$ K/at. % in the system $La_2Cu_{1-x}Ni_xO$ (Ref. 23).

The electrical properties of the system $Cu_{1-x}Ni_xO$ are configured by the fact that with the appearance of the two-hole states (1), deep impurity levels are formed in the one-electron spectrum,[24] which by virtue of their large depth (~ 1 eV) do not affect the carrier concentration (at room temperature and below), which is determined by the intrinsic defects in CuO. Therefore, the resistance for $T>T_c$ of the

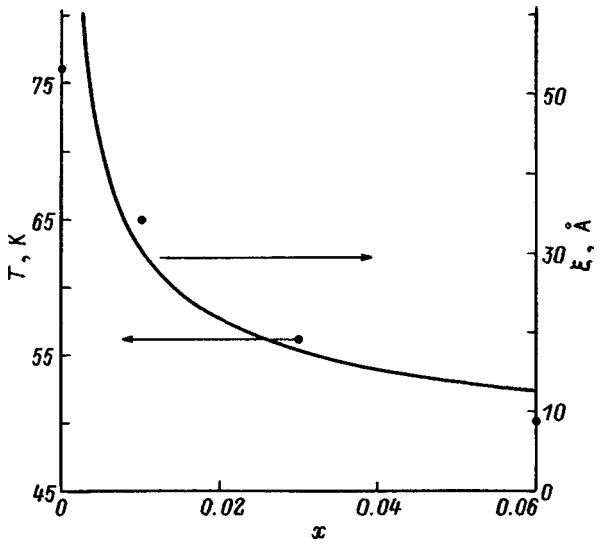

FIG. 3. Concentration dependence of the antiferromagnetic correlation length ξ_A for $Cu_{1-x}Ni_xO$ (solid line) and the temperature at which the resistance of the HTSC+$Cu_{1-x}Ni_xO$ composites goes to zero (filled circles).

HTSC, i.e., for ordinary carriers in the composite HTSC+$Cu_{1-x}Ni_xO$, is not a function of nickel doping. Nor is the onset point of the transition T_c, which is determined by the superconducting transition inside the HTSC grains, since the probability of nickel diffusion into the HTSC grains is exceedingly small in view of the short annealing time of the composite. As for the depression of the temperature of the transition to zero resistance in the sample, it is necessary to consider tunneling in a composite with antiferromagnetic insulating interlayers.

Since even in optimally doped HTSC's, antiferromagnetic correlations exist on scales ξ_A larger than the coherence length of a Cooper pair, ξ_S, motion of such a pair takes place, as it were, against a background of antiferromagnetic order. Therefore, for tunneling in the system HTSC + CuO, the presence of antiferromagnetic order in CuO will scarcely lead to additional breaking of Cooper pairs. A different situation arises in the case of $Cu_{1-x}Ni_xO$, where the antiferromagnetic structure contains $d^{10}L^2$ diamagnetic centers.

It is well known that in an antiferromagnet containing diamagnetic substitutions, because of the nonequivalency of one of the sublattices, an uncompensated moment appears in the vicinity of the diamagnetic impurity. Such moments were detected by measurements of the static magnetic susceptibility in $La_2Cu_{1-x}A_xO_4$, A=Zn, Ga, Al (Refs. 23 and 25) and from NMR data in $YBa_2(Cu_{1-x}Zn_x)_3O_7$ (Ref. 26). Scattering by such impurity magnetic moments suppresses superconductivity in the usual way according to BCS theory. Figure 3 plots the dependence of the antiferromagnetic correlation length ξ_A in $Cu_{1-x}Ni_xO$, calculated according to the formula $\xi_A = q_0/\sqrt{x}$ (Ref. 27) for $a_0 = 3.08$ Å, where a_0 is the nearest-neighbor Cu–Cu distance in CuO (right axis). Figure 3 also plots the dependence of the temperature at which the resistance of the HTSC+$Cu_{1-x}Ni_xO$ composites becomes equal to zero, as a function of x (left axis). The correlation between these two dependences is obvious.

The additional salient point in the $R(T)$ curves in Fig. 2 appearing below T_c with growth of x can be compared to an analogous salient point in the $R(T)$ curves in $YBa_2Cu_3O_7/Pr_{0.7}Sr_{0.3}MnO_3/Ag$ and $YBa_2Cu_3O_7/Pr_{0.7}Sr_{0.3}MnO_3/YBa_2Cu_3O_7$ sandwiches with a ferromagnetic barrier layer.[28] Apparently, scattering by the magnetic moments in the magnetically ordered barrier layer is responsible for the indicated salient points.

In high-temperature superconductors, phase layering is often observed,[29] where the non-conducting and superconducting phases can form ordered one-dimensional superstructures.[30,31] The composite systems HTSC+CuO that we have investigated can be considered as artificially created systems with phase layering where, in contrast to natural layering, we have the possibility of intentionally introducing magnetic impurities into the non-conducting layers and studying their effect on the tunneling of Cooper pairs.

In the system $Y_{3/4}Lu_{1/4}Ba_2Cu_3O_7+Cu_{1-x}Ni_xO$ we discovered three important experimental facts: 1) independence of the transition temperature T_c and the resistance above the transition temperature of the level of nickel doping, 2) a lowering of the temperature at which the resistance vanishes with growth in the nickel concentration, and 3) the appearance of special features in the $R(T)$ curves below T_c. All of these facts are qualitatively explained by peculiarities in the electronic structure of CuO and changes in it wrought by substitution of nickel for copper. The appearance of magnetic moments in the insulating interlayer is caused not only by the states $Ni^{2+}(3d^8)$ with spin $s=1$, which have a very high energy due to effects of strong electron correlations, but also by the diamagnetic configurations $d^{10}L^2$. The uncompensatedness of the CuO antiferromagnetic sublattices in the vicinity of the diamagnetic spin hole also gives a magnetic moment with effective spin $<1/2$ per impurity atom. The reduction of the superconducting properties of HTSC+$Cu_{1-x}Ni_xO$ composites with increasing x correlates with the decrease in the antiferromagnetic correlation length in $Cu_{1-x}Ni_xO$, where the latter fulfills the role of a tunneling interlayer in the network of $S-I-S$ bonds of these composites.

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