

Influence of rare-earth ionic radius on the properties of Ni- and Fe-substituted $R\text{Ba}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$ systems ($R=\text{Y,Nd,Eu,Gd,Ho,Tm}$; $M=\text{Ni,Fe}$)

V. N. Narozhnyi* and V. N. Kochetkov

*Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk, Moscow Region, 142092, Russia
and International Laboratory of High Magnetic Fields and Low Temperatures, Gajowicka 95, 53-529 Wroclaw, Poland*

(Received 12 June 1995)

The crystal structure parameters, temperature dependences of resistance $R(T)$, and concentration dependences of superconducting transition temperature $T_c(x)$ for the Ni- and Fe-substituted $R\text{Ba}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$ systems based on Y and several rare earths ($R=\text{Y,Nd,Eu,Gd,Ho,Tm}$; $M=\text{Ni,Fe}$) have been investigated. It was found that the $|\partial T_c/\partial x|$ parameter for both kinds of substitution depends mainly on the value of R^{3+} ionic radius of the host matrix. As R changes from Tm to Nd the value of $|\partial T_c/\partial x|$ increases by approximately three and four times for Ni and Fe substitutions correspondingly. No correlations of the $|\partial T_c/\partial x|$ value with R^{3+} localized magnetic moment were observed. The prime role of R^{3+} ionic radius variation on the properties of $R\text{Ba}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$ systems as well as the same effect observed earlier for $R_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ systems are discussed. The essentially different shapes of superconducting transitions for the Ni- and Fe-substituted systems are pointed out.

I. INTRODUCTION

Significant attention was devoted to the investigation of the influence of different kinds of substitution on the properties of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ -type compounds (Y-123), see the review in Ref. 1. It was established that $3d$ metals (Ni, Fe, Co, Zn) can partially replace Cu in both CuO_2 plane and CuO chain positions in Y-123 structure. As expected the preferable positions for Ni and Zn are CuO_2 planes but Fe and Co occupy mainly the CuO chain sites.¹

The investigations of $\text{YBa}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$ systems have revealed that the Cu substitution by $3d$ metals leads to resistance increase and lowering of superconducting critical temperature T_c , see, e.g., Refs. 1–4. It is interesting that the highest rate of T_c depression among $3d$ metals substitutions was observed for $M=\text{Zn}$ that does not have magnetic moment.²

In several works^{5–8} the $3d$ substitutions for rare earth based R-123 systems were investigated. It was pointed out that for $\text{GdBa}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$ systems ($M=\text{Ni,Fe}$) the influence of these substitutions is stronger than for $\text{YBa}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$.^{6–8} This result was connected in Refs. 7 and 8 with the interaction between Gd and M magnetic moments (Gd³⁺ has the maximum localized spin magnetic moment among rare earths but Y³⁺ has no one). However the possible influence of the ionic radius difference between Y³⁺ and Gd³⁺ was not taken into account in Refs. 7 and 8.

This possibility was verified in our previous work⁹ devoted to the investigation of $R\text{Ba}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$ systems based on Y, Gd and Eu [Gd³⁺ and Eu³⁺ have close ionic radii values but Eu³⁺ contrary to Gd³⁺ has a nonmagnetic ground state ($J=0$)]. The measurements on the Gd- and Eu-based systems have revealed that the influence of Ni substitution on the temperature dependence of resistance and T_c in these compounds is very similar, at the same time it is significantly stronger than for Y-based system. This fact shows

that the influence of Ni substitutions on $R(T)$ and T_c of $R\text{Ba}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$ essentially depends on the R^{3+} ionic radius of the host matrix but not on its localized magnetic moment.

It should be noted that the distinct correlation of the T_c sensitivity to R substitution by Pr on R^{3+} ionic radius of the host matrix was found in the recent investigations of $R_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ systems based on Y and a wide range of rare earths (Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm).^{10–13} The $|\partial T_c/\partial x|$ value for Pr-substituted compounds increases by nearly three times as the R^{3+} ionic radius rises when R goes from Tm to Nd.

All this motivated us to make a systematic study of the influence of R^{3+} ionic radius on the properties of Ni- and Fe-substituted $R\text{Ba}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$ systems based on Y and several rare earths, $R=\text{Y, Nd, Eu, Gd, Ho, Tm}$ with larger variation of R^{3+} ionic radius than in Refs. 9 and 14. The preliminary results for $R=\text{Y, Gd, Eu}$ have been published in Refs. 9 and 14.

II. EXPERIMENTAL DETAILS

The polycrystalline samples of nominal composition $R\text{Ba}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-y}$ ($R=\text{Y,Nd,Eu,Gd,Ho,Tm}$; $M=\text{Ni,Fe}$; $x=0.000, 0.025, 0.050, 0.075, 0.100, 0.150$) were prepared by solid state reaction method from thoroughly mixed powders of high purity $R_2\text{O}_3$, BaCO_3 , CuO , NiO , Fe_2O_3 taken in stoichiometric ratios. Initially mixtures were synthesized on air at $\approx 920^\circ\text{C}$ for 2 days with careful intermediate grinding. Then the samples were annealed on air at about 940°C with intermediate grinding. The temperatures of synthesis were variable, being slightly higher for the compounds based on R with larger ionic radius. Final annealing was performed at 450°C for 1–2 days in oxygen flow following with slow cooling. Further annealing did not change the T_c value. Since the annealing procedure is exactly the same for all series of the samples, the oxygen content of the compounds with equal Ni (or Fe) concentrations is assumed to be close for the

TABLE I. Crystal structure parameters for $\text{GdBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_{7-y}$ and $\text{GdBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$ systems.

x	$\text{GdBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_{7-y}$			$\text{GdBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$		
	$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$
0.000	3.832	3.894	11.700	3.832	3.894	11.700
0.025	3.849	3.900	11.698	3.847	3.895	11.640
0.050	3.844	3.900	11.692	3.845	3.885	11.670
0.075	3.842	3.897	11.686	3.862	3.886	11.610
0.100	3.868	3.912	11.737	3.889	3.889	11.676
0.150	3.889	3.911	11.734	3.892	3.892	11.676

systems based on different R . [Earlier our iodometric titration measurements of the oxygen content of the undoped R -123 compounds, prepared as described above, have shown that the y values are nearly identical ($y=0.05 \pm 0.05$) for the systems based on $R=\text{Nd, Eu, Gd, Y, Ho, Tm}$.^{13]}

Samples quality and the lattice structure parameters were controlled by x-ray diffraction method using Geigerflex diffractometer with $\text{Cu } K_\alpha$ radiation. All investigated samples were found to be practically single phase up to maximum investigated M concentration $x=0.15$.

The electrical resistance for 4.2–300 K temperature range was measured for by four-terminal dc or ac methods with 0.2–10 mA current flow. Temperature was measured using Cu-Cu(Fe) thermocouple. For several samples the resistance measurements were also carried out in high magnetic fields (up to 150 kOe). The measurements were performed partially in the International Laboratory of High Magnetic Fields and Low Temperatures, Wroclaw, Poland.

III. EXPERIMENTAL RESULTS

A. Crystal structure

The example of crystal structure parameters for Gd-based Ni- and Fe-substituted samples is given in Table I. The slight decrease of orthorhombic distortion was observed with the rise of Ni concentration for all $\text{RBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_{7-y}$ systems in a good agreement with previous studies.^{1–4,6,7} These compounds remained orthorhombic at $x=0.15$.¹⁵

On the other hand, the influence of Fe, occupying primarily the Cu-chain sites, on the crystal structure of investigated compounds was more pronounced. The value of orthorhombic distortion decreased significantly more rapidly with increase of Fe concentration. Approximately at $x=0.1$ the tetragonalization was observed for all systems. It should be noted that for Fe substitution the parameter b (chains direction) was almost unchangeable. Only increase of parameter a led to decrease of orthorhombic distortion. Such behavior can be explained by taking into consideration the possible occupation by oxygen the position O(5) (between CuO chains) which was pointed out in Refs. 16 and 17 for Fe substitution of Cu-chain sites. The systems with other R (Y, Nd, Eu, Ho, Tm) were observed to have the similar behavior of crystal structure parameters. For more detail, the crystal structure parameters of the investigated systems is described in our previous work.⁹

B. Resistance

Normalized temperature dependences of resistance $R(T)/R(300 \text{ K})$ for Ni- and Fe-substituted $\text{RBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-y}$ systems based on Nd, Y, Ho, Tm are shown in Fig. 1 (the results of Gd- and Eu-based systems were represented by us in Ref. 9). In all the investigated systems Ni and Fe impurities lead to the increase of resistance. In the case of Ni substitution the $R(T)$ dependence for $\text{TmBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_{7-y}$ system remains “metal-like” even at $x=0.15$. With the increase of R^{3+} ionic radius the influence of Ni substitution on $R(T)$ dependence gradually becomes stronger. So the “semiconductinglike” behavior near the superconducting transition is clearly seen at $x \geq 0.05$ for $\text{NdBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_{7-y}$ system with the largest value of R^{3+} ionic radius.

The same tendency also occurs in the case of Fe substitution. For $\text{TmBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$ system the small region with “semiconductinglike” $R(T)$ dependence followed by superconducting transition appears only at $x=0.15$. The same Fe concentration in Nd-based systems fully suppresses superconductivity, the $R(T)$ dependence being strongly “semiconductinglike” at $4.2 < T < 300 \text{ K}$. It should be noted that for all investigated systems the influence of Fe substitution on $R(T)$ dependence is stronger than the Ni one (compare the corresponding parts of left and right panels of Fig. 1).

For clarity the normalized temperature dependences of resistance for $\text{RBa}_2(\text{Cu}_{0.9}\text{M}_{0.1})_3\text{O}_{7-y}$ systems based on different rare earths with the same Ni and Fe concentration $x=0.1$ are represented in Fig. 2 [pay attention to the different scale along the $R(T)$ axis]. As can be seen the influence of M substitution on resistance of the considered systems essentially depends on the R^{3+} ion type of the host matrix. Taking also into account the fact that for Gd- and Eu-based systems with close values of ionic radii the character of $R(T)$ dependences are similar to each other and are substantially different from the Y-based system (see Fig. 2 in Ref. 9), one can see the correlation between the size of the R^{3+} ion and the influence of M substitution on the resistance of $\text{RBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-y}$ systems. At the same time no correlation is observed in the influence of Ni and Fe substitutions on the resistance of $\text{RBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-y}$ systems with R^{3+} localized magnetic moment value.

The correlation with the R^{3+} ionic radius is also clearly seen for the $3d$ metal concentration dependences of critical temperature discussed below.

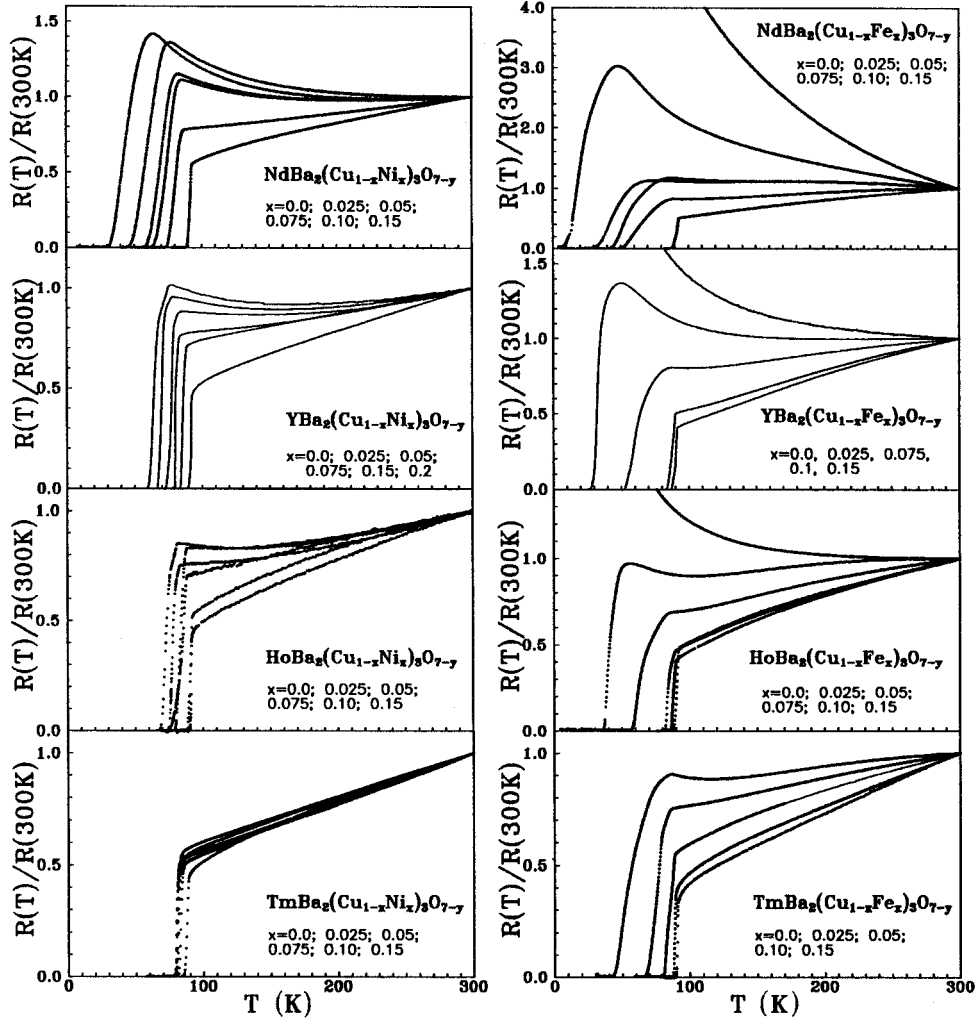


FIG. 1. Normalized resistance as a function of temperature for $RBa_2(Cu_{1-x}M_x)_3O_{7-y}$ systems ($R=Nd, Y, Ho, Tm$; $M=Ni, Fe$).

C. Critical temperature

Superconducting critical temperature dependences on M concentration $T_c(x)$ are shown on Fig. 3 for $RBa_2(Cu_{1-x}M_x)_3O_{7-y}$ ($R=Tm, Ho, Nd$) systems both for Ni and Fe substitutions. The value of T_c was determined at the middle of resistive transition, $R(T_c) = 0.5R_n(T_c)$, where R_n is extrapolated normal state resistance. The width of superconducting transitions (from $0.1R_n$ to $0.9R_n$) is also shown.

The $T_c(x)$ dependences are close to linear for Ni and Fe substitutions at $x \leq 0.1$ and $x \leq 0.075$, correspondingly (some deviation from linearity occurs for $HoBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$ system). In the case of Fe substitution the value of T_c decreases far more rapidly than for $M=Ni$. It is clearly seen from Fig. 3 that the influence of both Ni and Fe substitutions are significantly stronger for the Nd-based than for Ho- and Tm-based systems. For Fe-substituted compounds based on Nd and Ho with $x=0.15$ no sign of superconductivity was found at $T \geq 4.2$ K. At the same time $TmBa_2(Cu_{0.85}Fe_{0.15})_3O_{7-y}$ system are superconducting with $T_c \approx 55$ K. The values of critical concentration at which superconductivity disappears equal approximately 0.11 and 0.13 for Nd- and Ho-based Fe-substituted systems.

To have the possibility to quantitatively characterize the effect of R^{3+} ionic radius influence on T_c of Ni- and Fe-substituted systems the values of $|\partial T_c / \partial x|$ were determined from the experimental data represented in Fig. 3 for $x \leq 0.15$ and $x \leq 0.075$ in the case of $M=Ni$ and Fe, correspondingly. These results added by ones for $R=Y, Gd$, and Eu are represented on the upper and middle panels of Fig. 4 as the dependences of $|\partial T_c / \partial x|$ on the value of R^{3+} ionic radius. As can be seen the value of $|\partial T_c / \partial x|$ increases substantially with rising R^{3+} ionic radius of the host matrix (approximately three and four times for $M=Ni$ and Fe).

As mentioned above, earlier the strong $|\partial T_c / \partial x|$ dependence on the value of R^{3+} ionic radius was also found for $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ systems.¹⁰⁻¹³ For comparison our results for $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ from Ref. 13 are shown on the down panel of Fig. 4. The $|\partial T_c / \partial x|$ value for $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ also raises with the size of R^{3+} ion and increases from 90 K for $R=Tm$ to 230 K for Nd, i.e., almost three times.

The obvious correlation of $|\partial T_c / \partial x|$ parameter with R^{3+} ionic radius value for both 3d and Pr substitutions in 123 systems should be taken into account. At the same time close

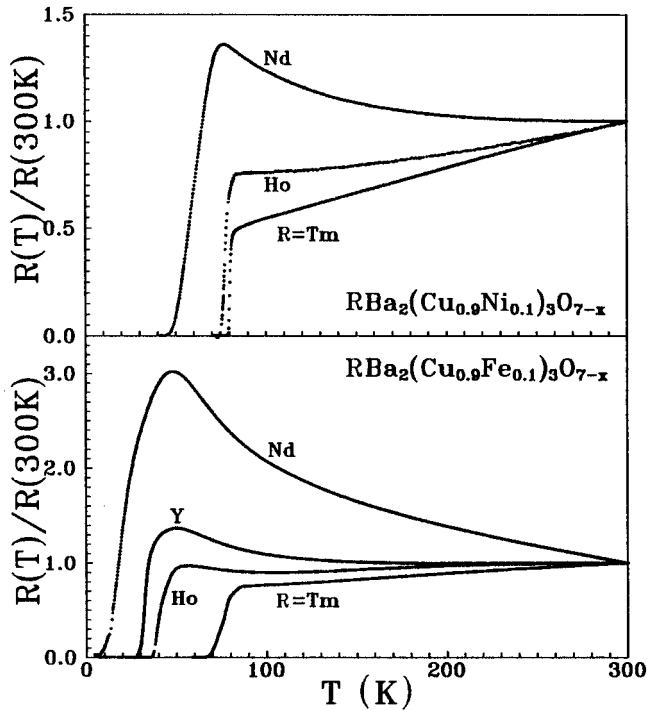


FIG. 2. Normalized resistance vs temperature for several $\text{RBa}_2(\text{Cu}_{0.9}\text{M}_{0.1})_3\text{O}_{7-y}$ (upper) and $\text{RBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{7-y}$ (down) systems with the same M concentration.

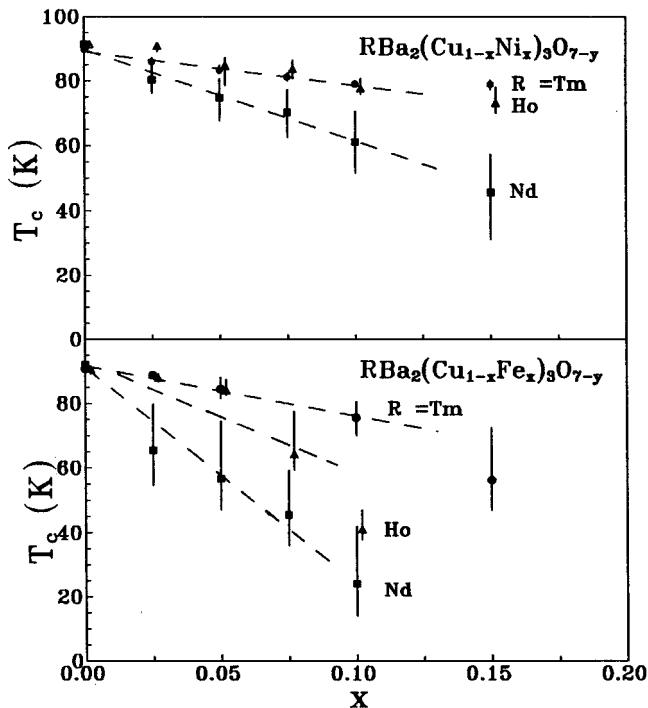


FIG. 3. T_c vs Ni and Fe concentrations for $\text{RBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-y}$ systems ($R=\text{Nd}, \text{Ho}, \text{Tm}$; $M=\text{Ni}, \text{Fe}$). The width of superconducting transitions from $0.1R_n$ to $0.9R_n$ is also shown.

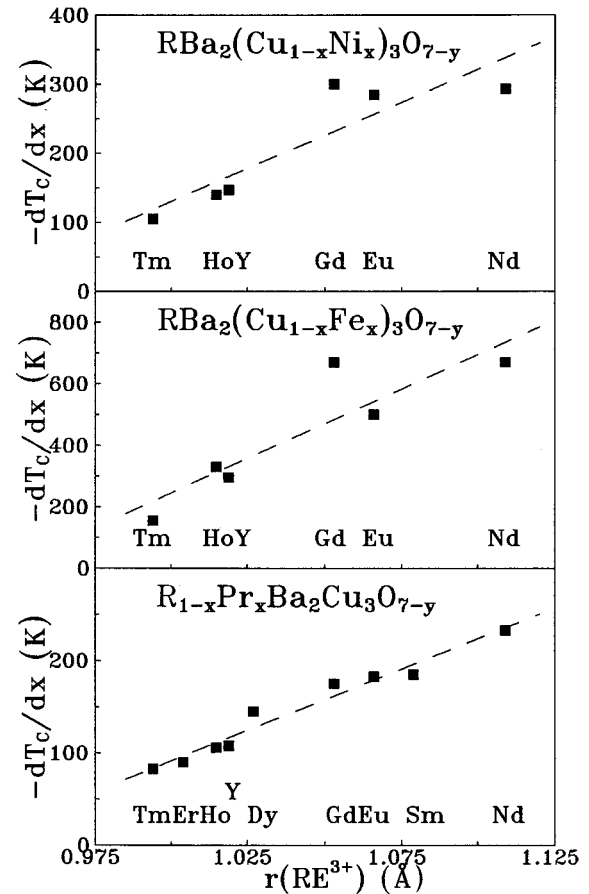


FIG. 4. The values of $|\partial T_c / \partial x|$ vs R^{3+} ionic radius for $\text{RBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-y}$ (upper and middle panels) and $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ (down panel, the data from Ref. 13) systems.

numerical values of the $|\partial T_c / \partial x|$ variation for $3d$ - and Pr -substituted compound may be the result of the occasional coincidence. It should be emphasized that no correlation was found in the properties of $\text{RBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_{7-y}$ as well as $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ systems¹⁰⁻¹³ with the value of R^{3+} localized magnetic moment. This fact is probably connected with well-known magnetic “isolation” of R^{3+} ion in 123-type structure, see, e.g., Ref. 1 This rare earth magnetic moment “isolation” leads to practical independence of the T_c value of fully oxidized undoped superconducting R -123 compounds on the value of R^{3+} magnetic moment.¹

IV. DISCUSSION

The obtained results show that the influence of the different types of substitutions ($\text{Ni}, \text{Fe}, \text{Pr}$), occupying different positions (CuO_2 plane, CuO chain and R site, correspondingly) on the superconductivity, depends strongly on the R^{3+} ionic radius of the host matrix and does not display any correlation with the value of the R^{3+} localized magnetic moment.

These facts give an evidence for high sensitivity of the properties of investigated systems to the details of crystal structure. Comparison of the results for $3d$ metals substitution in Y -123 and $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y -124) systems gives an additional argument for the important role of the crystal structure details on the properties of these structurally very closely

related compounds. As has been shown in Ref. 18 the rate of T_c depression for Y-124 are significantly larger than the corresponding rates for the Y-123 system for Fe, Ni, Zn, and Ga substitutions. Moreover, while the effect of Zn substitution is strongest in Y-123 it is weaker in Y-124 than that of the effect of Fe and Ni substitutions.

The first thing one should take into account in understanding the R^{3+} size effect in substituted R -123 systems is an essentially *nonuniform deformation* suffered by R -123 lattice when the ionic radius of R^{3+} increases.¹⁹ One part of the unit cell is expanded while the other can be compressed. Namely the separation of the CuO_2 planes, between which R^{3+} ions are placed, increases. On the contrary, the CuO_2 plane-apical oxygen and the CuO_2 plane-CuO chain distances decrease to some extent. The strong properties sensitivity of pure R -123 compounds to these parameters, e.g., on the CuO_2 plane-apical oxygen distance, was noted in a number of papers (see, e.g., Ref. 20). It is quite probable that the increase of the R -123 system properties sensitivity for the substitutions of different types of (Ni,Fe,Pr) can be connected with the nonuniform deformation of the R -123 unit cell when R goes from Tm to Nd. Note also that the nonuniform deformation of the R -123 crystal lattice with the changing of the ionic radius of R^{3+} may lead to opposite effects of hydrostatic and chemical pressure applying to these systems.²¹

The next fact that should be considered is the *effect of disordering*. In the case of Pr substitution, as has been shown in Ref. 22 using data of K -edge x-ray absorption fine structure, the oxygen atoms around Pr become disordered and/or distorted. In Ref. 23 the study of $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ system revealed the strong analogy between this system and ion beam damaged $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. More exactly, the effect of increasing concentration of Pr is similar to increasing of ion damage dose for the resistivity behavior. The very important role of the oxygen site disorder on T_c is underlined in Ref. 24 for several $R_2\text{Ba}_4\text{Cu}_7\text{O}_{14+y}$ systems. Oxygen reduced compound with good ordering can have higher T_c value than one with higher oxygen concentration that reveals a strong disordering.²⁴

It should be emphasized that for the systems based on R^{3+} ion with larger ionic radius the extent of disordering may be more pronounced. In Ref. 5 the progressive structural disordering in Fe-substituted $\text{LaBa}_2\text{Cu}_3\text{O}_{7-y}$ was found. This effect is partially reflected in: (a) the partial occupancy of O(6) sites; (b) the occurrence of O(2) vacancies; (c) cation disorder between the La and Ba ions; (d) shifts in the z coordinates of Ba and apical oxygen towards the values expected for a completely disordered perovskite structure. It is interesting that no similar disorder in Fe-substituted $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ was observed.

Such strong dependence of disordering in perovskite-like cuprates of R^{3+} ionic radius may be connected with above-mentioned unit cell nonuniform deformation of considered systems. In that case the same impurities concentration can lead to higher extent of disordering in more initially deformed host lattice based on R^{3+} with larger ionic radius.

As is well known the disordering can lead to *localization effects*. These effects have been also observed in perovskite-like cuprates in several papers. Soft-x-ray absorption near-edge structure²⁵ and electron-energy-loss spectroscopy studies²⁶ of $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ system have shown that the

whole number of holes in the CuO_2 planes does not change with Pr concentration while normal-state Hall effect measurements (see, e.g., Ref. 27) shows decreasing in the number of *mobile holes* due to the localization effects with increasing Pr concentration. Moreover the variation of the Hall coefficient was found to be two times greater for $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ than for the Y-based system.²⁸

As mentioned above for the investigated systems the $R(T)$ dependence gradually transforms from “metal” to “semiconductinglike” behavior with increasing concentration of $3d$ impurities. The analysis of the $R(T)$ dependences obtained for all investigated type substitutions (Ni,Fe) in the framework of different models [activation conductivity, influence of Kondo effect, and variable range hopping model (VRH)] has shown that although it is difficult to unambiguously distinguish between all these models the experimental data as a whole are best described three-dimensional VRH model, see Fig. 3 of Ref. 9. It gives an additional evidence for the significant role of the localization effects in the investigated systems. Earlier the same conclusion was made for several Pr-substituted systems.^{29,30}

It seems very surprisingly that the substitution of different atoms in different positions leads to the very close results (compare three panels of Fig. 4). The possible explanation of this fact is to assume that the different substitutions influence superconductivity in investigated systems through the common mechanism. The strengthening of localization effects due to increasing extent of disorder of M - and Pr-substituted systems based on larger R^{3+} ions is one of the possible candidates for this mechanism.

It should be noted that several models were proposed to describe the properties of Pr-substituted systems $R_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ itself, including first-principle calculations of electronic structure, see for review Refs. 31 and 32. It is not excluded, of course, that properties of Pr- and $3d$ metals-substituted systems are driven by different mechanisms. In that case the striking similarity of the obtained results for these two systems, see Fig. 4, should be considered only as an accidental coincidence.

One more effect we would like to point out in this paper is the difference in superconducting transition shapes for Ni- and Fe-substituted systems. As can be seen from Fig. 1, Ni substitution has a “conventional” broadening effect on the superconductivity transition: the parts of resistive transitions with positive and negative curvature are comparable in size. On the other hand, Fe substitution results in substantially wider superconducting transition and in the negative curvature for the most part of superconducting transition. This effect was observed for all systems investigated by us. Such results were also reported recently in Ref. 33 for $\text{ErBa}_2(\text{Cu}_{0.995}\text{M}_{0.005})_3\text{O}_{7-y}$ ($M = \text{Ni, Zn, Fe, Co, and Ga}$). The larger width of superconducting transitions for the CuO-chain substitutions (Fe, Co, and Ga) were connected in Ref. 33 with the weakening of the coupling between CuO_2 planes in c direction. As expected in Ref. 33 this transforms the systems to be more two dimensional, thereby enhancing the contribution of fluctuations. Another mechanism for the difference in the in-plane and out-of-plane substitutions influence can be proposed based on the electrical current redistribution due to the M substitution. As was established by the measurements on twin-free Y-123 single crystals³⁴ the elec-

trical current flows through CuO_2 planes as well as CuO chains but superconducting fluctuations manifest mainly in CuO_2 plane. At Ni substitution the current should primarily flow through CuO chains (the planes are disordered in that case and hence have large resistance), so the superconducting fluctuation is hardly seen. On the other hand, at Fe substitution the current should mainly flow through CuO_2 planes where the superconducting fluctuations broaden the superconducting transition.

The difference in the shape of resistive superconducting transitions at Ni and Fe substitutions are much more clearly seen for the results of the measurements in high magnetic fields, see Fig. 5, where the examples of Eu-based systems are shown. The complete results of the measurements for Ni- and Fe-substituted $\text{RBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-y}$ systems in magnetic fields will be published elsewhere.³⁵

V. CONCLUSION

Distinct and strong dependence of $|\partial T_c/\partial x|$ parameter for $\text{RBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-y}$ systems on the value of R^{3+} ionic radius of the host matrix was found. Taking into account that the sensitivity of the properties of R-123 system for R substitution by Pr is also defined by the size of R^{3+} ion; the value of R^{3+} ionic radius can be considered as a parameter determining the properties both 3d- and Pr-substituted R-123 compounds. The strengthening of the localization effects due to the higher extent of disordering of M- and Pr-substituted systems based on larger R^{3+} ions is the possible explanation for the observed correlations. During the preparation of this

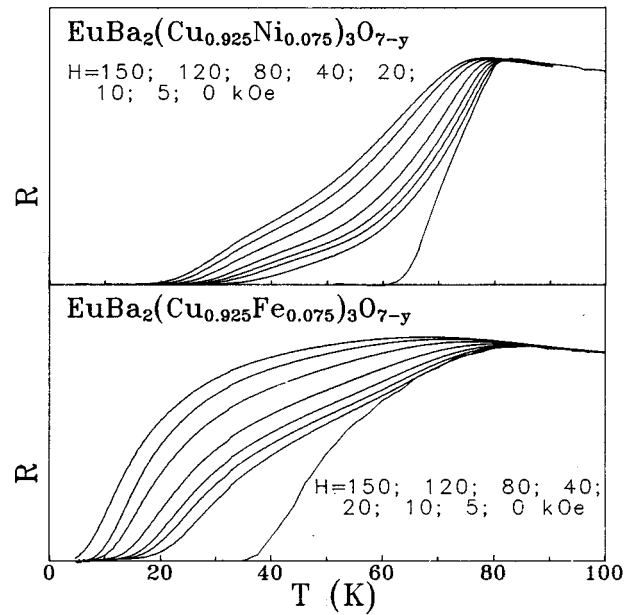


FIG. 5. Superconducting transitions in various magnetic fields for $\text{EuBa}_2(\text{Cu}_{0.925}\text{M}_{0.075})_3\text{O}_{7-y}$ compounds ($M=\text{Ni,Fe}$).

paper for publication we have known that the correlation with the R^{3+} ion size was found for the properties of $\text{RBa}_2\text{Cu}_{3-x}\text{Ga}_x\text{O}_{7-y}$ systems (Ga substitutes the CuO-chain sites).³⁶

*Author to whom correspondence should be addressed. FAX No.: 7-(095)-334-00-12. Electronic address: narozh@ns.hppi.troitsk.ru

¹J. T. Markert, Y. Dalichaouch, and M. B. Maple, in *Physical Properties of High-Temperature Superconductors I*, edited by D. M. Ginsberg (World Scientific, Singapore, 1989).

²K. Westerholt, H. J. Wuller, H. Bach, and P. Stauche, *Phys. Rev. B* **39**, 11 680 (1989).

³J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschut, and S. A. Sunshine, *Phys. Rev. B* **37**, 7458 (1988).

⁴J. F. Bringley, T. M. Chen, B. A. Averill, K. M. Wong, and S. J. Poon, *Phys. Rev. B* **38**, 2432 (1988).

⁵P. R. Slater, A. J. Wright, and C. Greaves, *Physica C* **183**, 111 (1991).

⁶B. Ullmann, R. Wordenweber, K. Heinemann, and H. C. Freyhart, *Physica C* **170**, 71 (1990).

⁷H. Shimizu, T. Kiyama, and J. Arai, *Physica C* **196**, 329 (1992).

⁸T. G. Chen, Z. Xianyu, and Y. Zhuo, *J. Magn. Mater.* **140-144**, 1323 (1995).

⁹V. N. Narozhnyi, V. N. Kochetkov, E. P. Khlybov, and N. E. Alekseevskii, *Phys. Met. Metallogr.* **78**, 173 (1994) [*Fiz. Met. Metalloved.* **78**, 75 (1994)].

¹⁰Yunhui Xu and Weiyan Guan, *Phys. Rev. B* **45**, 3176 (1992).

¹¹V. N. Narozhnyi and E. P. Khlybov, in *Proceedings of the 29th Conference on Low Temperature Physics, Kazan'*, 1992, edited by A. A. Makarova (Kazan' State Univ. Publ., Kazan', 1992), Pt. **1**, C50 (in Russian).

¹²Weiyan Guan, *Chin. J. Phys.* **31**, 849 (1993).

¹³V. N. Narozhnyi, E. P. Khlybov, V. N. Kochetkov, and T. G. Uvarova, *Physica C* **235-240**, 1349 (1995).

¹⁴V. N. Narozhnyi, V. N. Kochetkov, E. P. Khlybov, J. Warchulska, and N. E. Alekseevskii, in *Proceedings of the 30th Conference on Low Temperature Physics, Dubna, 1994*, edited by Yu. V. Taran (Joint Inst. Nucl. Res., Dubna, 1994), Pt. **1**, 187 (in Russian).

¹⁵We also prepared $\text{YBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_{7-y}$ samples with $x=0.2$ and 0.3 . The x-ray diffraction analysis shows that the maximum solubility of Ni nearly corresponds to $x=0.2$, the concentration at which impurity-phase lines appear in the x-ray patterns. The sample with $x=0.3$ is essentially multiphase. However, even at this large concentration, the crystal symmetry was far from tetragonal and the samples remained superconducting.

¹⁶M. Iliev, Y. Atanassova, L. Bozukov, J. Tihov, and V. G. Hadjiev, *Physica C* **191**, 419 (1992).

¹⁷C. Blue, K. Elgaid, I. Zitkovsky, P. Boolchand, D. McDaniel, W. C. H. Joiner, J. Oostens, and W. Huff, *Phys. Rev. B* **37**, 5905 (1988).

¹⁸Ratan Lal, S. P. Pandey, A. V. Narlikar, and E. Gmelin, *Phys. Rev. B* **49**, 6382 (1994).

¹⁹M. Guillaume, P. Allenspach, J. Mesot, B. Roessli, U. Staub, P. Fischer, and A. Furrer, *Z. Phys. B* **90**, 13 (1993).

²⁰R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, and L. W. Rupp, *Physica C* **165**, 419 (1990).

²¹A. A. R. Fernandes, J. Santamaria, S. L. Bud'ko, O. Nakamura, J. Guimpel, and I. K. Schuller, *Phys. Rev. B* **44**, 7601 (1991).

²²C. H. Booth, F. Bridges, J. B. Boyce, T. Claeson, and Z. X. Zhao, *Phys. Rev. B* **49**, 3432 (1994).

- ²³A. G. Sun, L. M. Panlins, D. A. Gajewski, M. B. Maple, and R. C. Dynes, *Phys. Rev. B* **50**, 3266 (1994).
- ²⁴D. B. Currie, M. T. Weller, P. C. Lanchester, and R. Walia, *Physica C* **224**, 43 (1994).
- ²⁵U. Neukirch, C. T. Simmons, P. Sladeczek, C. Laubschat, O. Strebel, G. Kaindl, and D. D. Sarma, *Europhys. Lett.* **5**, 567 (1988).
- ²⁶J. Fink, N. Nicker, H. Romberg, M. Alexander, M. B. Maple, J. J. Neumeier, and J. W. Allen, *Phys. Rev. B* **42**, 4823 (1990).
- ²⁷Wu Jiang, J. L. Peng, S. J. Hagen, and R. L. Greene, *Phys. Rev. B* **46**, 8694 (1992).
- ²⁸V. N. Narozhnyi, *J. Magn. Magn. Mater.* **140-144**, 1325 (1995); *Superconductivity* **7**, 589 (1994) [*Sverkhprovodimost' (KIAE)* **7**, 589 (1994)].
- ²⁹Wu Jiang, J. L. Peng, J. J. Hamilton, and R. L. Greene, *Phys. Rev. B* **49**, 690 (1994).
- ³⁰V. N. Narozhnyi and E. P. Khlybov, *Superconductivity* **5**, 928 (1992), [*Sverkhprovodimost' (KIAE)* **5**, 923 (1992)].
- ³¹R. Fehrenbacher and T. M. Rice, *Phys. Rev. Lett.* **70**, 3471 (1993).
- ³²A. I. Liechtenstein and I. I. Mazin (unpublished).
- ³³A. K. Bandyopadhyay, Deepak Varandani, E. Gmelin, and A. V. Narlikar, *Phys. Rev. B* **50**, 462 (1994).
- ³⁴B. Billon, R. Gagnon, and L. Taillefer, *Physica C* **235-240**, 1917 (1995).
- ³⁵V. N. Narozhnyi and J. Warchulska (unpublished).
- ³⁶Yunhui Xu, Weiyan Guan, Y. F. Chen, S. R. Sheen, and M. K. Wu, *Phys. Rev. B* **50**, 1223 (1994).