Физика низких температур, 1995, т. 21, № 7, с. 752–756 УДК 538.945

EPR studies of Mn-doped $YBa_2Cu_3O_{7-\delta}$ composites

A. A. Stepanov[1,2], B. Gaillard[1], S. Regnier[3], and J. Marfaing[3]

1. *Laboratoire d'Electronique des Milieux Condensés, Université de Provence, 13397-Marseille Cedex 20, France*

2. *B. I. Verkin Institute for Low Temperature Physics and Engineering, Ukrainian National Academy of Sciences, 47 Lenin Ave., 310164 Kharkov, Ukraine*

3. *Laboratoire MATOP -URA CNRS 1530-D, Case 151,13397-Marseille Cedex 20, France*

Submitted March 9, 1995

The preliminary results of EPR experiments on superconducting Mn-YBaCuO composites are reported. The measurements were done in X band in the temperature range 4–300 K. Three distinct EPR components were observed possessing different g-factors and a rather different temperature behavior. For similar nonsuperconducting samples, only two signals were observed. The nature of the different components is discussed from the comparison of the results. It is shown that, among the superconducting samples, two of them originate from Mn^{2+} paramagnetic centers while the third one presumably comes from Cu^{2+} paramagnetic center. For the nonsuperconducting samples, a magnetic phase transition in an ordered state has been revealed at 25 K. This transition seems to be stimulated by the presence of Mn ions or clusters, probably located in the CuO chains.

I. Introduction

The magnetic properties of high-T_c cuprates have been extensively investigated during recent years because it has been suggested that antiferromagnetic interaction between Cu ions in the CuO_2 layers plays an important role in the superconductivity. Different methods, including neutron scattering, NMR, muon rotation and magnetic susceptibility have been successfully used for the high-T_c compounds studies. The idea of Cu substitution by of other ion from the transition-metal group provides new possibilities for probing the magnetic interactions of high-T_c cuprates. The structural, magnetic, transport and superconducting properties of $YBa_2Cu_{3-x}M_xO_{7-\delta}$ and $La_{2-x}Sr_xCu_{1-y}M_yO_4$, where M = Ni, Co, Fe, Zn have been reported [1]. The problem in question, in experiments of this type, is how the doping affects the Cu electronic state in the CuO_2 planes. By increase in the doping element, the way in which the T_c is suppressed can be studied. This provides additional information on the electronic state of Cu ions and the charge mobility in CuO_2 planes [2–4]. Also, incorporation of paramagnetic ions serve as a probe in EPR experiments, giving evidence of the low frequency spin dynamics of superconducting cuprates [5,6].

Recently a new, unexpected aspect of the substitution technique has been discovered [7–9]. It was found that doping of $YBa_2Cu_3O_{7-\delta}$ (noted YBCO) materials by a small amount of Mn or Nb atoms stimulates, instead of suppressing, the superconductivity. In the presence of small Mn concentration the temperature of superconducting phase transition of YBCO reaches 94–95 K [7,8] while in the case of Nb doping, T_c increases up to 97 K [9].

In this communication, preliminary results concerning the EPR investigation of the superconducting Mn-YBCO composites are reported. The results are compared with similar nonsuperconducting Mn-YBCO samples, in order to analyze and interpret the different observed signals.

II. Sample preparation and characterizations

Composites were formed by mixing the two microns-sized YBCO and Mn powders, varying the Mn weight from 2 to 7%. The thermal cycle consisted in heating the samples under argon flow, up to temperatures, T_{sint}, in the range 820–980 °C. The nonsuperconducting samples were obtained by quenching from T_{sint} down to 77 K. The superconducting samples were prepared using the same thermal cycle up to T_{sint} and then the sintering was decreased down to 200 °C, in oxygen atmosphere, with a step at 450 °C for two hours. Systematically, different characterizations were carried out on the samples: i) alternative resistance measurements in a classical, closed-cycle helium cryostat, in the range 20 to 300 K, $R(T)$; ii) Scanning Electron Microscopy study with energy diffraction spectroscopy analysis; iii) x-rays diffraction measurements. Variations of the sample sintering temperature, from 820 to 970 °C, provide information concerning the evolutive electrical and chemical behavior

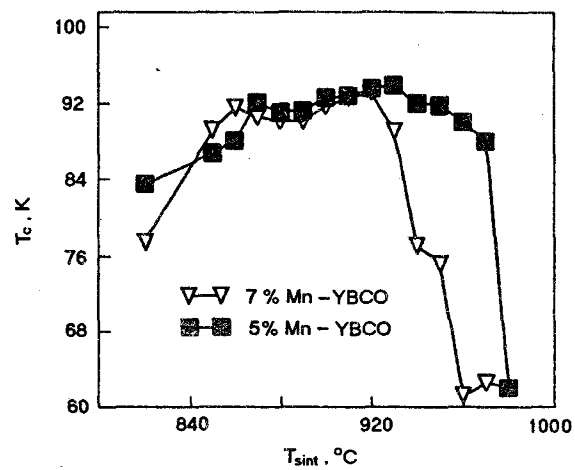

Fig. 1. Evolution of T_c (zero resistance) versus sintering temperature T_{sint}, in the range 820–980 °C for two different Mn concentrations of the Mn-YBCO composites. The T_c of pure YBCO was measured at 91 K.

of the material, especially by changing its stoichiometry.

The $R(T)$ curves of the superconducting Mn-YBCO composites are characterized by: a metallic behavior and small R_{300} value in the normal state; a sharp superconducting transition (width of about 2 K) with *a zero resistance temperature* varying up to T_{cmax} = = 94 K; the reference of pure YBCO ceramic exhibited a zero resistance at 91 K.

The total evolution of the T_c of the Mn-YBCO composites vs. T_{sint} for two different Mn concentrations is presented in Fig. 1. From this Figure it can be seen that a similar behavior is observed whatever the Mn concentration is. It is clear that: i) T_c is increasing for sintering temperature up to 860 °C, whatever the value of x; ii) T_c is stabilizing from 860 °C and up to a T_{sint} value dependent on the x-Mn content; the corresponding measured T_{cmax} are 93.8 and 93 K for composites with 5 and 7% Mn (sintered at 930 and 920 °C, respectively). Compared with pure YBCO, one improvement of T_c is obtained for each x value; iii) T_c is decreasing, in a more pronounced manner, when both x and T_{sint} increase. Figure 1 shows that the higher Mn content is, the lower the T_{sint} necessary to optimize T_{cmax}.

III. Results and discussion

EPR experiments in X band were performed with a Bruker ESP 300 spectrometer, using a gas-flow cryostat (Oxford ESR9) and Varian rectangular dual cavity (TE1O4). The spectra of the two types of samples, using the 5% Mn concentration, were collected from 300 to 4 K.

Though the Mn-doped YBCO materials are very rarely discussed in the literature, it seems that Mn^{2+} is the most promising substitution candidate for EPR purpose, having a S-ground state with a well defined g-factor that is very close to 2. We took advantage of the Mn ions presence in YBCO ceramic, trying to shed more light on the unusual effect of the T_c stimulation by a small Mn concentration.

a) Superconducting samples

Figure 2,*a* shows the typical shape of EPR spectra collected at room temperature for the superconducting 5% Mn-YBCO sample, sintered at 930 °C. The observed signal, represented by the solid line, has two distinct components and can be fitted by two Lo-

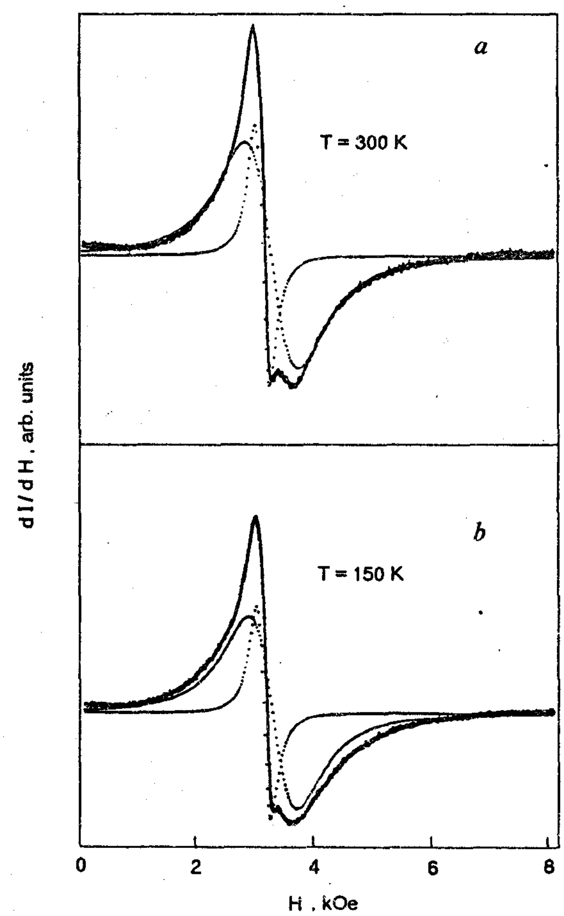

Fig. 2. EPR spectra of 5% Mn-YBCO superconducting composite sintered at 930 °C at ν = 9.38 GHz. The solid line represents the observed signal. The two Lorentzian components used in the fitting procedure are also shown (dashed lines). *a)* T = 300 K; *b)* T = = 150 K. The narrow line (noted as the *a*-component in the text) corresponds to the Cu^{2+} signal and the broad one (noted as the *b*-component) — to the Mn^{2+} signal.

rentzian lines, with the following parameters: $g_a = 2.11$, $\Delta H_a = 160$ Oe and $g_b = 2.02$, $\Delta H_b = 660$ Oe, respectively (here and in the discussion that follows, ΔH stands for the peak-to-peak linewidth). Taking into account the *g*-factor values of the detected components we can identify them, respectively, as a Cu signal (noted *a*-component, narrow line) and a Mn signal (noted *b*-component, broad line). It is worth noting that the relative amplitude of the observed components I_a/I_b depends on the sintering temperature in a similar way as T_c: the $I_a/I_b(T_{sint})$ dependence exhibits a maximum around $T_{sint} \approx 930$ °C and two deep minima around 830 and 970 °C. This observation can give some indications on the distinct line origin.

When temperature decreases, the observed EPR spectrum undergoes the following transformations. The first line (*a*-component) displays changes in the position and linewidth when temperature approaches T_c, and disappears below T_c. The initially broad component (*b*-component) presents a linewidth that decreases substantially, passing through a minimum near T_c, and then increases very rapidly (Fig. 3). Its position, which, at first, changes only slightly down to T_c, then becomes strongly temperature-dependent, reaching a *g*-factor value ≈ 3.1 (Fig. 4). Finally, this EPR component disappears completely below 10 K, due to a strong broadening effect.

A detailed analysis of the line shape temperature variations of the *b*-component of the observed spectra shows that it deviates progressively from a Lorentzian shape when temperature decreases below 250 K. Figure 2,*b* shows the EPR signal pattern at 150 K (solid line) and examples of the simulated spectra (dashed

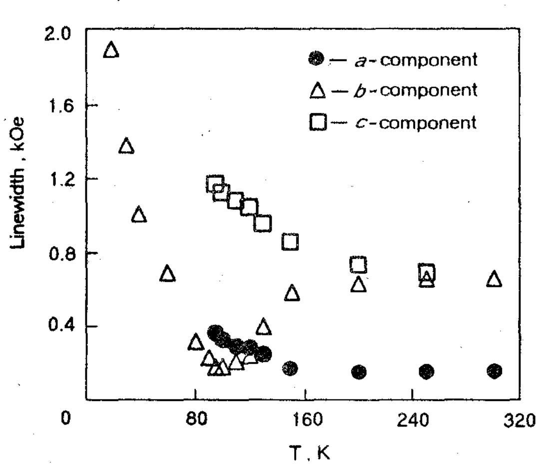

Fig. 3. Temperature dependence of the linewidths of the comporting of the observed EPR signal in the superconducting sample sintered at 930 °C, T_c(zero resistance) = 94 K.

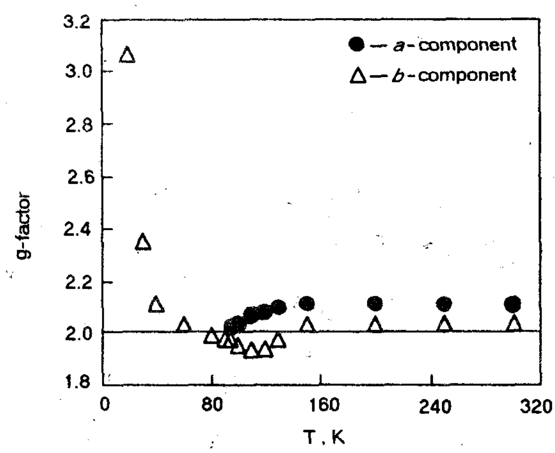

Fig. 4. Temperature dependence of the effective *g*-factor of the components comprising the observed EPR signal in the superconducting sample sintered at 930 °C, T_c(zero resistance) = 94 K.

lines). It is clear that while the sum of two Lorentzians fits the central part of the observed spectrum rather well, a systematic deviation between them in the wings of the spectrum cannot be accounted for by two Lorentzian approximations. Analysis of the intensity temperature dependence of the observed spectra leads to the same conclusion: below 250 K, there is a systematic redistribution of the signal intensity from center to the wings of the signal. The difference between the observed signal and the sum of the two Lorentzian curves can be treated like a third Lorentzian component (noted *c*-component, see Fig. 3), with a *g*-factor close to 2.0 ± 0.1. Considering this *g*-factor value, we ascribe this component to a Mn^{2+} signal. Such a deconvolution provides a satisfying fit of the temperature dependence of the results. An additional point in favor for introduction of a new EPR component has been found by investigating the nonsuperconducting Mn-YBCO samples (see below).

Since the absence of EPR signal from Cu ions in pure YBCO compound is now widely recognized, a basic problem of EPR spectroscopy in high-T_c materials is the EPR signals assignment. Whether the signals are due to spurious phases or not is the most important question to be resolved. While it is possible, in principle, that the observed signals come from impurities, several features argue for their YBCO lattice origin. The first remark we can make is that, in our Mn-YBCO samples, we have not found any trace of the so called «green phase» which was observed with pure YBCO material.

We shall start to discuss the problem of the lines origin from the *b*-component of the spectra. Several characteristics are of importance for this line assignment. First, a quasi-one-dimensional low-temperature behavior exhibiting both strong line shift and line broadening in the large temperature interval can be due to a growing role of antiferromagnetic fluctuations. This shows that we are dealing with a magnetically concentrated system of Mn^{2+} ions, with a strong exchange interaction that geometrically is one-dimensional. Second, a significant correlation exists between T_c and the observed linewidth and line position. This fact has been checked on samples presenting a lower T_c to avoid an coincidence; it demonstrates that the one-dimensional Mn^{2+} clusters somehow «see» the supeconducting phase transition. Third, the *b*-component signal crosses T_c without changing its intensity and this gives an indication concerning the place of the Mn-clusters in YBCO crystals. Presumably, we assume that this signal comes from one-dimensional Mn clusters located in the walls between the different crystallographic twins, which usually demonstrates an oxygen deficit and, therefore, can give a dielectric response without a screening effect.

A strong correlation have been observed for the *a*- and *c*-components between the signals intensity and the onset of superconductivity in the metallic samples. This argument cannot usually be used in favor of a bulk origin of the signals; however, in combination with the observed broadening of the *a*-component in the metallic phase, which starts at 150 K, this correlation strongly proves the bulk origin of the signals (see Fig. 3). We identify them as copper and manganese signals for the *a*- and *c*-components, respectively, probably belonging to the CuO chains in the YBCO lattice. Justification of this assignment is given by the measurements of the EPR signals of nonsuperconducting YBCO samples.

b) Nonsuperconducting samples

Their EPR spectra are presented in Fig. 5. They look different from those of the superconducting samples. Two Lorentzian lines fit the detected EPR spectra quite well for all temperatures, except for the low-temperature region, below the magnetic phase transition near $T_m = 25$ K. Slight changes in the room temperature *g*-factor values of the two Lorentzian components, $g_a = 2.11$ and $g_c = 2.01$, have been seen when the temperature decreased, in the region above T_m. Below T_m, the two EPR components exhibit both line narrowing and line shape distortion. At $T = 4$ K, the average effective *g*-factors are $g_a = 2.13$ and $g_c = 2.18$. Note that the *g*-factor values and the temperature dependence of the *a*- and *c*-components of the nonsuperconducting sample (Fig. 6), in the range 100–300 K, are very similar to those of the *a*- and *c*-components of the superconducting samples. This gives an a posteriori justification for introducing the *c*-component in the superconducting case and gives

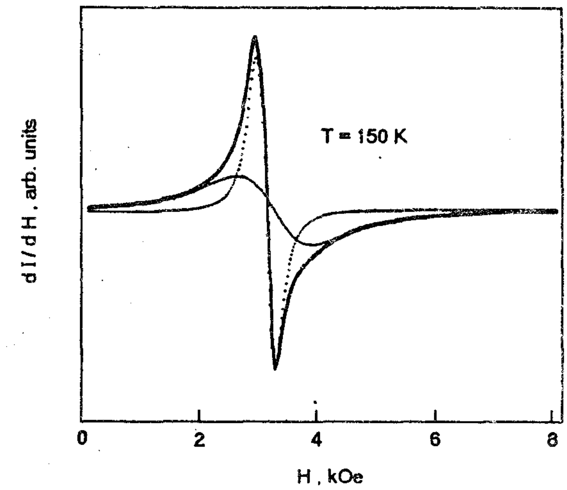

Fig. 5. EPR spectra of 5% Mn-YBCO nonsuperconducting composite sintered at 930 °C at $\nu = 9.38$ GHz and $T = 150$ K. The solid line represents the observed signal. The two Lorentzian components used in the fitting procedure are also shown (dashed lines).

strong indications about the out-of-CuO_2-plane origin of the two components. A gradual increase in the *c*-component linewidth when temperature decreases, behavior which is typical for one-dimensional antiferromagnetic systems and the strong linewidth narrowing of both components (*a*- and *c*-), observed below T_m, support the idea of their CuO chain origin. The results observed at $T < T_m$ and also the observed parallelism in the two components behavior indicate an ordering process in the antiferromagnetic CuO chains in the YBCO lattice [10]. In this case T_m is the ordering temperature of the CuO

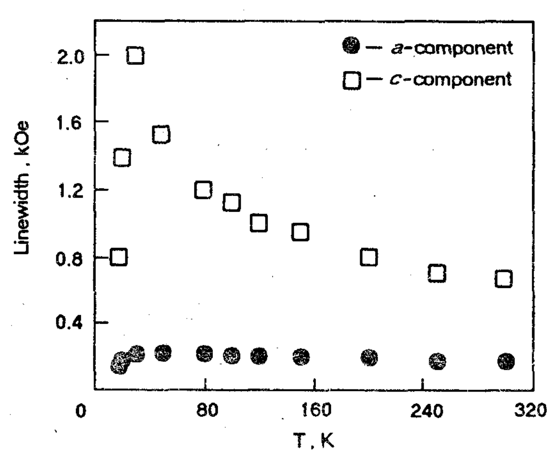

Fig. 6. The linewidth temperature dependence of the two components of the EPR spectra in nonsuperconducting sample of the 5% Mn–YBCO composite.

chains, which can be the Neel temperature of these chains.

IV. Conclusion

In conclusion, using EPR experiments on superconducting and nonsuperconducting Mn-YBCO composites, it is possible to analyze the dopant behavior. Our important finding concerns the Mn^{2+} position in the YBCO lattice. Most probably, the Mn^{2+} ions enter the CuO chains in YBCO lattice and somehow control the sample oxygenization process and also some structural oxygen ordering. This question should be clarified in the experiments on single crystals which are currently being carried out. Another important observation is that, in the Mn-YBCO samples, prepared by the composite technology, we have not found any trace of the so called «green phase» which, evidently, plays a negative role in the sample oxygenization and Cu stoichiometry of the YBCO material.

Acknowledgments

We are grateful to Dr. J. P. Boucher for fruitful and stimulating discussions.

1. D.M. Ginsberg, *Physical properties of high temperature superconductors I*, World Scientific, Singapore (1989), p. 266 and references therein.
2. P. Strobel, C. Paulsen,and J.L. Tholence, *Solid State Commun.* **65**, 585 (1988).
3. R. F. Jardim, S. Gama, S. F. de Lima, and I. Torriani, *Phys. Rev.* **B38**, 4580 (1988).
4. N. L. Saini and K.B. Garg, *Solid State Commun.* **82**, 895 (1992).
5. A. Moto, A. Morimoto, M. Kumeda, and T. Shimizu, *Supercond. Sci. Technol.* **3**, 579 (1990).
6. M. Z. Cieplak, A. Sienkiewicz, F. Mila, S. Guha, G. Xia, J. Q. Xiao, and C. L. Chien, *Phys. Rev.* **B48**, 4018 (1993).
7. S. Regnier and J. Marfaing, *Physica* **C235–240**, 1513 (1994).
8. I. Dhingra, S.C. Kashyap, and D. K. Das, *J. Mater. Res.* **9**, 2771 (1994).
9. M. H. Abdullah and B.T. Tan, *Solid State Commun.* **93**, 93 (1995).
10. T. Tamaki, T. Komai, A. Ito, Y. Maeno, and T. Fujita, *Solid State Commun.* **65**, 43 (1988).

The article was submitted in English.
Edited by R. T. Beyer.