Electron Paramagnetic Resonance of High-T_c Superconducting Composites $YBa_2Cu_{3-x}Sc_xO_{6\pm\delta}$

P. Baňacký,[†,‡] P. Pelikán,[*,‡,§,∥] M. Valko,[§] Š. Buchta,[‡,×] F. Hanic,[‡,×] and A. Cigaň[×]

Faculty of Natural Science, Institute of Chemistry, Chemical Physics Division, Comenius University, Mlynská dolina CH2, SK-842 15 Bratislava, Slovakia, Faculty of Chemistry, Department of Physical Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovakia, Faculty of Chemistry, University of Technology Brno, Purkyňová 118, CZ-612 00 Brno, Czech Republic, Institute of Measurement Science, Slovak Academy of Sciences, Dúbravská cesta 9, SK-842 19 Bratislava, Slovakia, and S-Tech a.s., Uršulinska 3, SK-801 11 Bratislava, Slovakia

Received: May 24, 2000; In Final Form: October 27, 2000

The EPR spectra of high-T_c superconducting composites with the formula $YBa_2Cu_{3-x}Sc_xO_{6.5\pm\delta}$ ($x = 0-1.1$) over the temperature range 300−77 K are reported. The study reveals that unusually large-scale substitution of Sc^{3+} for Cu^{2+} results in high-T_c superconducting materials with paramagnetic phases which are well resolved above T_c. Paramagnetism is suppressed below T_c with the dominance of the diamagnetic -superconducting phase which is EPR-silent. However, the composite with the nominal formula $YBa_2Cu_2ScO_{7\pm\delta}$ is the exception. For this sample, the EPR spectrum remains well resolved also below T_c, exhibiting only a local symmetry change of a paramagnetic center when decreasing the temperature below T_c. The study presented in this paper has revealed that the paramagnetic signal over T_c corresponds to the impurity phases and the EPR signal recorded below T_c, for $x = 0.8-1.1$, is due to the dominance of the spinellike $Ba(CuSc)O_{3.5}$ phase.

Introduction

The absence of an electron paramagnetic resonance (EPR) signal in the high-T_c cuprate superconductors in their normal state, despite the presence of the paramagnetic ions Cu^{2+} ($3d^9$), remains still unresolved. Soon after the discovery of $YBa_2Cu_3O_{7-\delta}$ superconductor, it was shown that EPR Cu^{2+} signals registered with this material are due to the presence of the impurity phases, namely of the "green phase" Y_2BaCuO_5 and $BaCuO_{2+x}$.[1,2] So far, there is not a direct EPR registration of paramagnetism due to Cu^{2+} ions pertaining to the superconducting structure of a pure phase.

It is worth to mention, however, that EPR evidence of paramagnetism of ions that are introduced (substituted) into positions different from that of Cu ions in a superconducting structure of a pure phase remains well resolved even below T_c. Substitution of the magnetic rare-earth ions (Gd, Er, Ho) for Y yields a pure superconducting 1−2−3 phase without a dramatic decrease of T_c. Magnetic susceptibility measurements show that above T_c the susceptibility obeys Curie−Weiss law with Curie constant scaling accurately with the effective moment for the isolated rare-earth ions. The Curie contributions are weakened for $T < T_c$ due to diamagnetic screening of superconducting state while local moments appear to have no effect on it.[3] For Eu^{3+} at relatively high-field $H = 2.17$ kG, the susceptibility never goes to a negative value which is attributed to the domination of the remnant paramagnetic tail of the Er^{3+} ion. In contrast, for the pure Y compound the susceptibility never goes positive at fields up to $H = 6$ kG and temperatures down to 4 K. The EPR spectra of Er^{3+}-substituted $Y_{1-x}Er_xBa_2O_{7\pm\delta}$ confirm this observation. For the range from room temperature down to 4 K, only the EPR signal of the Er^{3+} is obtained.[4] Similar results have been obtained for $GdBa_2Cu_3O_7$ where a very strong EPR signal has been obtained which is attributed to the presence of paramagnetic Gd^{3+} ions.[5]

The absence of Cu^{2+} EPR signals of cuprates has recently been discussed in a review paper of Pannoose and Singh.[6] One of the first proposed models[7] is based on the idea of a "resonating valence bond" (RVB) theory.[8] The absence of an EPR signal is attributed to a singlet ground state constructed from the RVB ±1/2 spin states. However, the excited triplet state is easily accessible at high temperatures but Cu^{2+} EPR of cuprates has never been observed up to 1150 K,[9] which is inconsistent with the above model. A second possibility for the lack of an observed EPR Cu^{2+} signal might be signal broadening by 2D antiferromagnetic correlations as proposed by Chakravarty and Orbach.[10]

On the other hand, there are studies advocating the observance of EPR Cu^{2+} intrinsic spectra of superconducting phase in the normal state. Weak EPR signals were detected[11−13] for oxygen-deficient $YBa_2Cu_3O_{7\pm\delta}$ samples, which are attributed[13] to Cu−O chain fragments in oxygen-deficient Cu(1) phases. Interesting is also the Al^{3+}-doped $YBa_2Cu_3O_7$ spectrum. The authors[14] assign the EPR spectrum to the triplet state of Cu^{3+} ions in the Cu(1) position, while Al^{3+} is assumed to replace Cu(2) positions. Recently the hole-doping effect on Tl-doped 2−1−2 cuprates has been studied by means of EPR spectroscopy.[15] The authors have simulated EPR spectra on the basis of the model of highly correlated spin fluctuations incorporating variations of the magnetic field according to antiferromagnetic resonance at the interpretation of the high asymmetry of the shapes of spectral

* Author to whom correspondence should be addressed at Slovak University of Technology. Fax: ++421-7-524 93 198. E-mail: pelikanp@chelin.chtf.stuba.sk.

† Comenius University.

‡ S-Tech a.s.

§ Slovak University of Technology.

∥ University of Technology Brno.

× Institute of Measurement Science, Slovak Academy of Sciences.

10.1021/jp0019198 CCC: $20.00
Published on Web 02/17/2001

lines. The authors rule out the possibility that the observed EPR spectra are due to paramagnetic impurities and advocate the intrinsic Cu^{2+} signal of the superconducting phase.

In relation to this problem, the results of papers[16,17] and mainly the interpretation of the EPR spectral characteristics of underdoped $La_{2-x}Sr_xCuO_4$ superconducting cuprate[16] should be mentioned. On the basis of the study of spin dynamics in this compound, the authors have concluded that observed EPR signals could be related neither to paramagnetic surface defects nor to Cu^{2+} centers in a disturbed octahedral environment but to magnetic centers created by *p*-holes doped either by excess oxygen or by Sr ions. The authors suppose that isolated paramagnetic centers exist in the regions with a poor concentration of Sr, and the results are then interpreted within the model of "three-spin polarons" (TSP) formed in the hole-doped CuO_2 planes. The TSP consists of two Cu^{2+} ions and one oxygen *p*-hole and is distorted due to a dynamic Jahn−Teller (JT) effect. The final conclusion is that observed paramagnetism is intrinsic to superconducting structured of $La_{2-x}Sr_xCuO_4$.

Interesting, in this respect, is also the paper of Gotor et al.[18] The observed EPR spectrum of the sample of oxide carbonated YBCO ($YBa_2Cu_{2.95}(CO_3)_{0.35}O_{6.6}$) is assigned by the authors to Cu^{2+} ions in an orthorhombic local crystal symmetry of the modified Cu(1) site of the YBCO 1−2−3 structure. The possibility that the spectrum could pertain to an impurity phase, particularly to $BaCuO_2$, has been ruled out by the authors since they have measured a different spectrum for synthesized $BaCuO_2$ compared to the one of the studied oxide carbonates.

The declared appearance of the EPR Cu^{2+} spectra of the superconducting phase in the normal state has always been assigned to formation of structural fractions with some Cu^{2+} ions that are magnetically decoupled, while such structural fractions are magnetically isolated from the main part of antiferromagnetic copper phases. Assuming that behind the nonobservance of the EPR spectra of copper oxide superconductors in the normal state is strong magnetic interaction of Cu^{2+} ions resulting in broadening and smearing-out of the spectral line, then a diamagnetic dilution of Cu^{2+} ions should be a proper way for recovering the EPR spectra. The most ideal method would be the direct substitution of a diamagnetic cation for Cu^{2+} ion of cuprates. The problem is, however, that substitution for Cu^{2+} ions in cuprates is too sensitive and can destroy high-T_c superconductivity, or strongly decrease T_c.[19−21]

Recently we have studied the effect of the substitution of Sc^{3+} on the superconducting properties of YBCO.[22] It has been found that Sc^{3+} can be stoichiometricaly substituted for any metal element of $YBa_2Cu_3O_7$ in an astonishingly large scale without the loss of high-T_c superconductivity. For an investigation of the magnetic properties this aspect is very important since Sc^{3+} in the singlet state is extremely stable, which enables a study of the effect of diamagnetic dilution on the magnetic properties of high-T_c superconducting cuprates. The results obtained by means of the EPR spectroscopy are presented in this paper.

Experimental Section

Sc^{3+}-substituted YBCO composites, $YBa_2Cu_{3-x}Sc_xO_{6.5\pm\delta}$, for $x = 0$, 0.05, 0.1, 0.2, 0.4, 0.8, 1.0, and 1.1, and the single-phase paramagnetic standard related to studied composites, i.e., $Ba_2(ScCu_3)O_{6.5}$, have been synthesized by the method of solid-state reaction between the corresponding oxides and barium−carbonate at the desired stoichiometric conditions. After the first-step decarbonization of the mixture (940 °C), the homogenized samples were pressed into cylindrical pellets at 200 MPa (diameter 12 mm) and sintered at 1050 °C for 72 h in an O_2 atmosphere with the final oxidizing phase at 580 °C for 24 h. Single-phase paramagnetic compounds that often form the impurity phases of YBCO, i.e., Y_2BaCuO_5 and $BaCuO_2$, have also been synthesized and sintered in the form of pellets by standard solid-state procedure in the air atmosphere at the stoichiometric conditions from the corresponding oxides/carbonates, as the standards for the EPR study. The $R-T$ characteristics were measured by a standard four-point method. The phase compositions of the sintered samples were determined by X-ray powder diffraction (XRPD) method using Philips Analytical PW 1710 goniometer and Cu Kα radiation.

The EPR spectra were recorded on a Bruker SRC 200D spectrometer operating at X-band equipped with a variable-temperature unit (Bruker). Cylindrical quartz sample tubes with 3.5 mm o.d. (ca. 3.0 mm i.d.) were used for measurements. DPPH was used as internal reference standard. The temperature-dependent EPR spectra were studied using a variable-temperature unit. The EPR spectra at 77 K, well below T_c, were measured using a Dewar vessel. All spectra were recorded under the same experimental conditions. Measured EPR spectra exhibit either axial or rhombic **g** tensor and could be interpreted using a spin Hamiltonian

$$H = g_xB_xS_x + g_yB_yS_y + g_zB_zS_z \qquad (1)$$

where all symbols have their usual meanings.[23,24] The EPR computer simulation and spin Hamiltonian parameter optimization were done using a computational method and program described elsewhere.[25]

Results

From the standpoint of the solid-state chemistry, for the studied reaction mixtures of nominal composition $YBa_2Cu_{3-x}Sc_xO_{6.5+0.5x}$, the following phases-formation reaction scheme can be proposed:

$$B \rightarrow A_1 + uA_2 + 0.5uA_3 + 0.5uA_4 \qquad (2)$$

Here, u is the stoichiometry coefficient balancing the reaction 2 with respect to following chemical compositions: B, $YBa_2Cu_{3-x}Sc_xO_{6.5+0.5x}$ (initial reaction mixture: $YBa_2Cu_{3-x}O_{6.5+0.5x} + 0.5xSc_2O_3$); A_1, $Y_{1-u}Ba_{2-2u}(Cu_{3-2u-x}Sc_{x-u})O_{6.5-7u+0.5u}$ (superconducting phase); A_3, Y_2BaCuO_5 (nonsuperconducting-green phase/paramagnetic; Figure 1); A_4, $BaCuO_2$ (nonsuperconducting-brown phase/paramagnetic; Figure 1).

From the XRPD patterns of the composites studied, in addition to the diffractions characteristic for superconducting phase A_1 and nonsuperconducting phases A_3 and A_4, it was possible to identify diffraction lines characteristic of a compound with a cubic unit cell parameter $a = 16.873(3)$ Å. We have assigned this to the following: A_2, $Ba(CuSc)O_{3.5}$ (nonsuperconducting-spinellike phase/paramagnetic phase; Figure 1), which should be of the same spinellike structure as $Ba_2(ScCu_3)O_{6.5}$. We have synthesized the latter compound as the pure phase at total substitution of Sc for Y. The compound is characteristic by a cubic unit cell parameter $a = 16.872(3)$ Å, i.e., the same as exhibited by the new phase of the studied composites. This phase is nonsuperconducting−paramagnetic with an EPR spectrum exhibiting a singletlike line shape (Figure 2).

On the basis of the stoichiometry of the reaction scheme (2), for a studied molar value x of Sc, the ratios of individual phases are calculated (as functions of u) and presented in Table 2. From the ratios of experimental integral intensities of the diffraction lines of particular phases in the XRPD patterns, with respect to

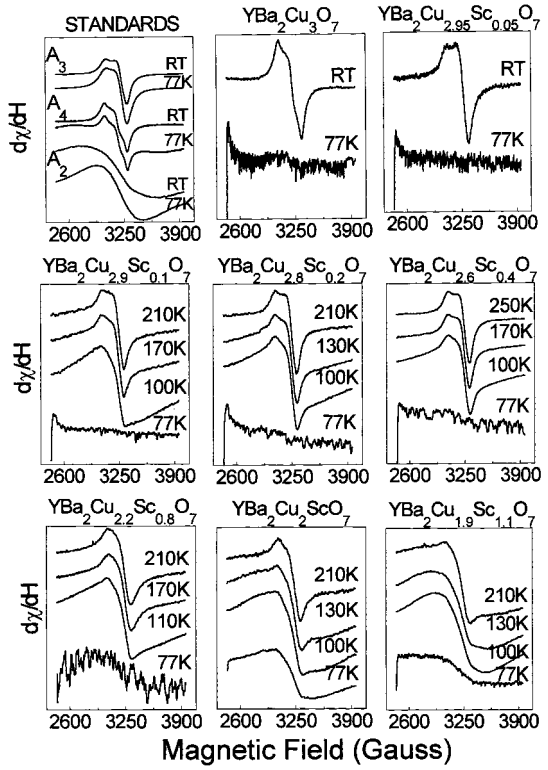

Figure 1. EPR spectra of standards (spinel-$Ba(ScCu)O_{3.5}$, A_2; Y_2BaCuO_5, green phase, A_3; $BaCuO_2$, A_4) and superconducting composites of the formula $YBa_2Cu_{3-x}Sc_xO_{6.5\pm\delta}$ ($x = 0-1.1$) over the temperature range 300−77 K.

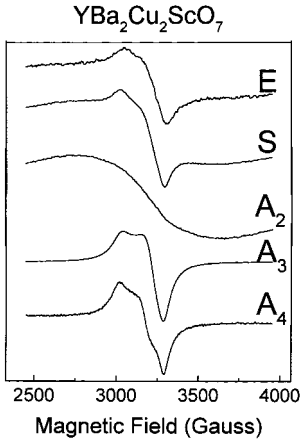

Figure 2. EPR spectrum of $YBa_2Cu_2ScO_7$ measured at 210 K, E, and simulated-composed spectrum, S. The simulated spectrum is composed from the following: spinel, $Ba(ScCu)O_{3.5}$, A_2 (weight factor 0.22); Y_2BaCuO_5, green phase, A_3 (weigh factor 0.17); $BaCuO_2$, A_4 (weight factor 0.085). Weight factors were taken as the calculated percentage of the particular phases in a superconducting composite, based on the XRPD integral intensities for the molar amount x of Sc (see also Table 3).

results of Table 2, it was possible to calculate the stoichiometry coefficient u and the percentage of particular phases in a composite for an actual molar amount x of Sc substituted. From the standpoint of the EPR study, the most interesting are data for $x = 0.8$, 1.0, and 1.1 (see Table 3).

EPR Spectroscopy of Standards. The EPR spectra of standards Y_2BaCuO_5 (green phase), $BaCuO_2$, and spinel $Ba(ScCu)O_{3.5}$ are shown in Figure 1. The spectrum of Y_2BaCuO_5 is axially symmetric, while that of $BaCuO_2$ is of rhombic symmetry[26] and $Ba(ScCu)O_{3.5}$ exhibits a broad singlet line EPR spectrum. The EPR data obtained by computer simulation are

TABLE 1: EPR Data for Standards and Composites $YBa_2Cu_{3-x}Sc_xO_{6.5\pm\delta}$ ($x = 0-1.1$) Measured at Room Temperature (RT) and at 77 K Obtained by Computer Simulation[a]

system	temp	g_y ($g_\perp$)	g_x (g_{eff})	g_z ($g_{||}$)
standards				
Y_2BaCuO_5 (A_3)	RT	2.048		2.213
	77 K	2.048		2.213
$BaCuO_2$ (A_4)	RT	2.046	2.091	2.229
	77 K	2.042	2.086	2.229
spinel $Ba(ScCu)O_{3.5}$ (A_2)	RT		2.107	
	77 K		2.107	
$YBa_2Cu_{3x}Sc_xO_{6.5\pm\delta}$				
$x = 0$	RT	2.045	2.090	2.229
$x = 0.05$	RT	2.046		2.212
$x = 0.1$	RT	2.045		2.213
$x = 0.2$	RT	2.046		2.212
$x = 0.4$	RT	2.046		2.212
$x = 0.8$	RT	2.046		≈2.211
	77 K		2.102	
$x = 1.0$	RT	2.045		2.212
	77 K		2.103	
$x = 1.1$	RT		2.101	
	77 K		2.103	

[a] For more details, see ref 25.

TABLE 2: Calculated Dependence of the Ratios of the Resulting Phases on the Molar Amount x of Sc According to the Stoichiometry of the Reaction Scheme (2) (See Text)

x	A_2/B	A_3/B	A_4/B	A_5/B
0.05	$1 - 0.984\,72u$	$0.458\,94u$	$0.348\,73u$	$0.177\,05u$
0.1	$1 - 0.985\,51u$	$0.459\,31u$	$0.349\,01u$	$0.177\,19u$
0.2	$1 - 0.987\,10u$	$0.460\,05u$	$0.349\,57u$	$0.177\,48u$
0.4	$1 - 0.990\,29u$	$0.461\,54u$	$0.350\,70u$	$0.178\,05u$
0.8	$1 - 0.996\,74u$	$0.464\,55u$	$0.352\,99u$	$0.179\,21u$
1.0	$1 - u$	$0.466\,06u$	$0.354\,14u$	$0.179\,80u$
1.1	$1 - 1.001\,6u$	$0.466\,83u$	$0.354\,72u$	$0.180\,10u$

TABLE 3: Stoichiometry Coefficient u and Percentages of the Particular Phases in a Superconducting Composite, Resulting from the Experimental XRPD Integral Intensities and Table 2, for the Particular Molar Amount x of Sc

x	u	% A_1	% A_2	% A_3	% A_4
0.8	0.42	58.1	19.5	14.8	7.5
1.0	0.47	53.0	21.9	16.6	8.4
1.1	0.5	50.0	23.3	17.7	9.0

presented in Table 1. The spectra do not exhibit any significant changes in their line shapes within the temperature range room temperature−77 K.

The observed Cu^{2+} EPR signal is due to the presence of the phase(s) possessing a greater number of localized Cu^{2+} d electrons. Kobayashi et al.[27] have reported very similar g values for signal corresponding to a phase with increased oxygen vacancies.

EPR Spectroscopy of Sc-Substituted Ceramics. For samples of general composition $YBa_2Cu_{3-x}Sc_xO_7$ with zero-content of Sc ($x = 0$, $YBa_2Cu_3O_7$) a well-resolved rhombic spectrum (Figure 1) with g-factors summarized in Table 1 was observed. For samples with stoichiometrically substituted Sc^{3+} ($0.5 > x > 0$), axially symmetric EPR spectra were recorded. Increase in symmetry of EPR line shape occurs for $x > 0.5$. For those samples ($YBa_2Cu_{2.2}Sc_{0.8}O_7$, $YBa_2Cu_2ScO_7$, and $YBa_2Cu_{1.9}Sc_{1.1}O_7$) a pseudoisotropic asymmetric singlet line and significant drift in baseline of the line shape were observed (see Figure 1).

For ceramics ($YBa_2Cu_{3-x}Sc_xO_7$) with $0 < x < 0.8$, temperature-dependent EPR spectra above T_c reveal no significant change in their line shapes. Below T_c at 77 K, only microwave absorption with no features corresponding to paramagnetic signal

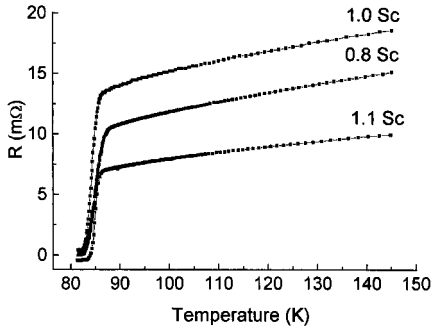

Figure 3. Temperature dependence of resistivity for $YBa_2Cu_{3-x}Sc_xO_{6.5\pm\delta}$ ($x = 0.8$, 1, 1.1) composites.

was observed. However, for ceramics with a Sc content $0.8 \leq x \leq 1.1$, strong temperature-dependent EPR signals were registered. Most significant is that, in addition to microwave absorption, a singletlike paramagnetic signal is superimposed (Figure 1). The paramagnetic signal reaches maxima for $x = 1$ ($YBa_2Cu_2ScO_7$). Further increase in Sc content leads to a decrease in intensity of coexisted paramagnetic phase(s).

Discussion

For studied composites, computer simulation, with respect to percentage of abundance of individual phases (Table 3), provides a good match between the experimental and simulated EPR spectra (see Figure 2). This urged us to suppose that the observed EPR signals correspond to composed signals of individual nonsuperconducting phases of the ceramics in their relative abundance. Residual singlet (best resolved for $x = 1$) observed below T_c at 77 K correlate well with the dominant contribution of spinellike $Ba(CuSc)O_{3.5}$ phase. It is worth noting that although the ratio of the superconducting phase (A1) has decreased on the level of 50−58%, the composites still exhibit superconducting properties, as can be seen from $R-T$ measurements (see Figure 3).

The TSP model[16,17] can be neither confirmed nor ruled out by the results of this study. The composites we have studied are multiphase systems, and even if the spin-dynamics were analyzed, it would be basically impossible to make a spin-dynamics assessment for a particular phase. In this respect it should be clear whether the sample studied in ref 16 was a single or multiphase system. If the results[16] correspond to a single-phase sample, then the conclusions concerning the TSP model are of the key importance for understanding of superconductivity mechanism, and it would appear to be very important experimental evidence supporting the nonadiabatic−polaron theory of superconductivity which has been elaborated some years ago.[28,29]

Conclusions

The temperature-dependent EPR spectra of superconducting composites of the general formula $YBa_2Cu_{3-x}Sc_xO_{6.5\pm\delta}$ are presented. In contrast to the conclusions of some authors who claimed that the EPR signal of superconductors over T_c is due to the "intrinsic phase" (see for example the recent work of Gotor et al.[18]) we have reached different results. The study presented in this paper has revealed that the paramagnetic signal over T_c corresponds to the impurity phases and the EPR signal recorded below T_c, for $x = 0.8-1.1$, is due to the dominance of the spinellike $Ba(CuSc)O_{3.5}$ phase. Increase in intensity of paramagnetic signal correlates well with decrease of abundance of superconducting phase. In general, below T_c an increase of exchange interaction between copper centers through oxygen bridges results in broadening of the EPR signals observed.

Acknowledgment. The authors express cordial thanks to S-Tech., a.s., for synthesis of the samples and arrangement of computational facilities as well to the Slovak Grant Agency VEGA (Grants A-13/99 and 1/4012/99) for partial financial support.

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