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INVESTIGATION OF THE SAMARIUM ROLE IN THE PHYSICAL PROPERTIES OF $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ COMPOUNDS IN THE ORTHORHOMBIC AND TETRAGONAL STRUCTURES

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Perovskites of type $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ (Re=Y, La, Nd, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu) have been investigated by XRD, magnetic and EPR measurements in both orthorhombic and tetragonal phases. In the former case the usual superconducting phase transition in the range 90 to 95 K has been detected. In all the compounds an EPR spectrum of Cu^{2+} ions has been observed. In the tetragonal phase, the EPR spectra of trivalent rare earth ions have been recorded for some members of the series. The observation of a broad EPR signal, tentatively attributed to superexchange interaction over the oxygen bridges (O_2), has also been recorded. Furthermore, the intensity of low-field microwave absorption has been found to depend strongly on the nature of the substituted rare earth ion at the sites of Y ions of the $YBa_2Cu_3O_{7-\delta}$ type compounds.

1. Introduction

Different modifications of high-T_c superconductors based on the $YBa_2Cu_3O_{7-\delta}$ material, produced by introduction of divalent or trivalent dopants to partially replace the Y, Ba, or Cu ions, have been extensively investigated by various experimental techniques in the last years. As it is well known the rare earths can substitute successfully for the Y ions and the lighter of them can substitute partially for the Ba ions too.[1,2] However, there is no strong evidence that such superconducting properties at T_c depend significantly on the Re ion, while other physical properties particularly those of a magnetic character exhibit substantial variations with the Re ion.[3,4]

EPR is a very sensitive method to study the various properties of superconductors. This method, which is thought to provide the most detailed data on the paramagnetic centers and their ligand structures, has been systematically used to study the rare earth ions in various crystal lattices.

Up to now extensive research has come out on the EPR spectrum of Gd^{3+} ions in high-T_c superconductors (either the $GdBa_2Cu_3O_{7-\delta}$ or compounds with gadolinium partially substituting for Y ions) which is easily observable up to RT (room temperature) because of its long spin lattice reaction time.[1,5–8]

Great interest has been attracted in the literature to the EPR spectrum of Cu^{2+} ions, which is attributed by many authors to impurity phases,[9,10] while others believe[4,11,12] that it is due to the parent phase of the superconductor and may thus provide useful information about the copper's interactions.

In this work, a whole series of type $Sm_{0.5}Re_{0.5}Ba_2Cu_2O_{7-\delta}$ materials was very carefully prepared and characterized by XRD and magnetic measurements. The latter measurements have revealed rather high T_c's for all the members, an indication of good quality samples. EPR studies were carried out, both in orthorhombic and tetragonal phases, for all the members of the above series. In the orthorhombic phase the EPR signal of the Cu^{2+} ions was observed in all the samples. In the tetragonal phase an EPR signal attributed to the rare earth ions was detected in a number of samples at high temperature.

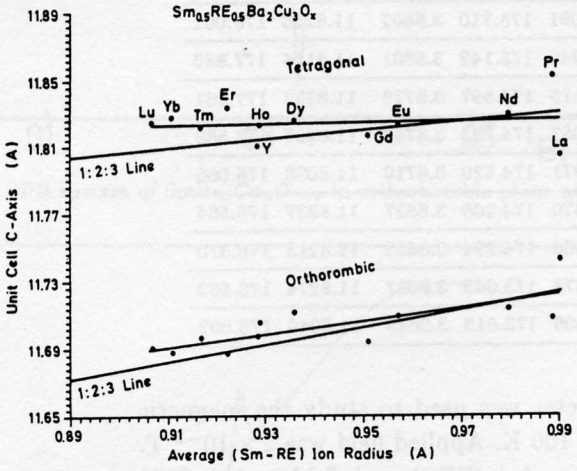
2. Experimental Results

$Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ ceramics were prepared by the standard solid state reaction technique. Appropriate amounts of Sm_2O_3, Re_2O_3, Cu and $BaCO_3$ were thoroughly mixed and pellets were formed under a pressure of about 10 bars. The pellets were annealed in flowing oxygen in a sequence of four steps, of 20 hour duration each, at temperatures 920, 925, 930 and 940°C with intermediate grinding. Afterwards, the samples in powder form were re-calcined in oxygen at 940°C in two successive steps of 12 hours each. To increase the oxygen content of the samples, after the last pulverization the powders were introduced into an already hot furnace (920°C) under flowing oxygen. After attainment of thermal equilibrium the temperature was reduced to 450°C where the samples remained for 6 hours, and then for another 6 hours at 400°C. Finally the furnace was brought to RT, always in an oxygen atmosphere.

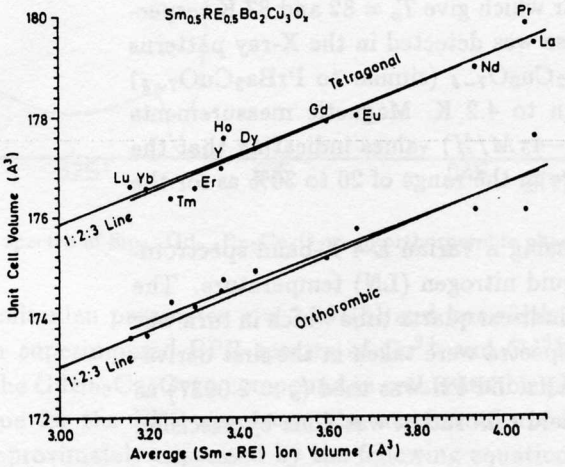
To obtain the tetragonal phase, part of the oxygenated powders were annealed at 650°C in flowing He for 6 hours following fast cooling to RT in an reducing atmosphere.

Structure characterization of the samples was carried out using a Phillips X-ray powder diffractometer utilizing Co–K_a radiation at RT. Table 1 shows the lattice parameters for all the compounds $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ in orthorhombic and tetragonal phases. Figure 1 presents the crystallographic constants of the unit cells of the compounds $ReBa_2Cu_3O_{7-\delta}$ and $Sm_{0.5}Re_{0.5}Ba_2Cu_2O_{7-\delta}$ for both the orthorhombic and tetragonal structures. The values of the various ion radii

have been taken from Ref. 11. In this series, the ionic radius of the ion in the rare earth site is taken as the average Sm^{3+}-Re^{3+} ion radius. Based on this assumption, it can be seen from Fig. 1 that the unit cell *c*-axis and the unit volume versus the average Sm-Re ionic radius show similar variations as for the Re123 compounds. The XRD patterns are typical of the Re123 perovskites and no impurities were detected by the X-rays. This means that the substitution of the Sm atoms for half the atoms of the Re in the Re123 perovskites does not affect the general trends of the crystallographic constants. Thus the Sm-Re system could be considered as a single continuous lattice.



(a)



(b)

Fig. 1. (a) Length of unit cell along *c*-axis. (b) unit cell volume vs. average Sm-Re ionic radius for the series $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$.

Table 1. Crystallographic constants of the unit cell of members of the series $Sm_{0.5}Re_{0.5}Ba_2Cu_2O_{7-\delta}$ for both orthorhombic and tetragonal phases (IR and IV represent the average Ionic Radius and the average Ionic Volume respectively).

			Orthorhombic					Tetragonal		
Pair	IR	IV	T_c	a	b	c	V cell	$a=b$	c	V cell
	[A]	[A^3]	[K]	[A]	[A]	[A]	[A^3]	[A]	[A]	[A^3]
SmLa	0.990	4.073	82	3.8659	3.9120	11.7413	177.576	3.8987	11.8036	179.413
SmPr	0.989	4.053	–	3.8533	3.9034	11.7077	176.095	3. 8951	11.8511	179.803
SmNd	0.980	3.939	94	3.8468	3.9083	11.7135	176.106	3.8895	11.8282	178.934
SmEu	0.957	3.672	95	3.8447	3.9031	11.7091	175.710	3.8802	11.8226	178.001
SmGd	0.951	3.605	94	3.8391	3.9012	11.6940	175.142	3.8801	11.8156	177.886
SmDy	0.936	3.444	93	3.8329	3.8962	11.7115	174.897	3.8728	11.8252	177.361
SmHo	0.929	3.373	92	3.8324	3.8950	11.7057	174.733	3.8757	11.8227	177.589
SmY	0.928	3.368	94	3.8331	3.8924	11.6971	174.520	3.8710	11.8098	176.966
SmEr	0.923	3.308	87	3.8291	3.8928	11.6870	174.206	3.8627	11.8337	176.564
SmTm	0.917	3.255	91	3.8283	3.8924	11.6966	174.294	3.8626	11.8213	176.370
SmYb	0.911	3.199	91	3.8175	3.8922	11.6878	173.663	3.8637	11.8274	176.562
SmLu	0.907	3.162	90	3.8202	3.8874	11.6906	173.613	3.8646	11.8246	176.602

A PAR 155 vibrating sample magnetometer was used to study the magnetic properties of the samples in the range 4.2 to 100 K. Applied field was 2×10^{-2} T. Measurements were performed in zero-field-cooled (ZFC) and field-cooled (FC) modes. The magnetic data revealed a T_c onset greater than 90 K (Table 1) for all the members of the series except for La and Er which give $T_c = 82$ and 87 K respectively. Significantly enough, no impurity phase was detected in the X-ray patterns of the latter two samples. For $Sm_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$ (similar to $PrBa_2CuO_{7-\delta}$) no superconducting state was observed down to 4.2 K. Magnetic measurements employing FC mode give for the ratio $L = (-4\pi M/H)$ values indicating that the percentage of the superconducting phases were in the range of 20 to 30% as for the Re123 series.[4]

The EPR measurements were performed using a Varian E-4 X-band spectrometer operating at $\nu = 9.3$ GHz at RT and liquid nitrogen (LN) temperature. The powdered sample (30 mg) was inserted in a cylindrical quartz tube which in turn was placed in a quartz finger Dewar at LN. EPR spectra were taken in the first derivative mode with modulation frequency of 100 kHz. DPPH was used ($g = 2.0037$) as a reference for the g value and the magnetic field calibration was done by precision NMR gaussmeter.

Figure 2 shows the EPR spectra of $SmBa_2Cu_3O_{7-\delta}$ compound in orthorhombic phase at RT which consists of a characteristic line of Cu^{2+} ions in orthorhombic local symmetry. All members of the series in the orthorhombic phase exhibited similar EPR spectra of Cu^{2+} ions but with different intensities. For the Sm-Gd sample, besides the Cu^{2+} line, a very wide line has been observed which arises from Gd^{3+}

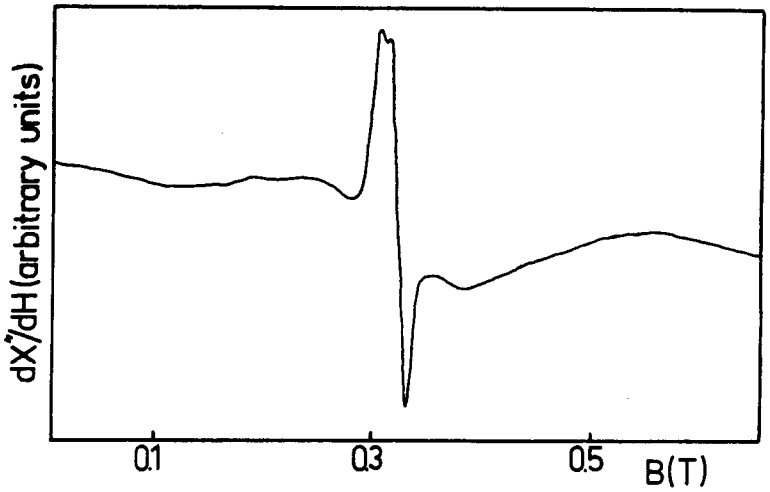


Fig. 2. EPR spectra of $SmBa_2Cu_3O_{7-\delta}$ in orthorhombic phase at RT.

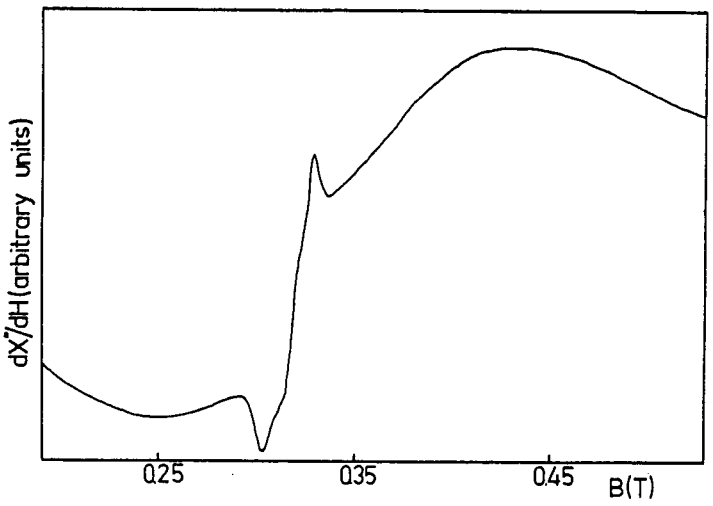


Fig. 3. EPR spectra of $Sm_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$ in orthorhombic phase at RT.

ions with spin-Hamiltonian parameter $g = 2.091(5)$ and linewidth $\Delta H = 0.211(5)$ T (Fig. 3). Similar superimposed EPR spectra of Cu^{2+} and Gd^{3+} ions have also been recorded for the $GdBa_2Cu_3O_{7-\delta}$ compound in orthorhombic phase. Assuming Lorentzian lineshape for the EPR spectrum, the number of unpaired spins in a sample could be approximately expressed by the following equation: $N \sim I(\Delta H)^2$ (N is the number of the paramagnetic centers). In the case of $GdBa_2Cu_3O_{7-\delta}$ in the orthorhombic phase, the linewidth was $\Delta H = 0.30(1)$ T and the lineshapes of the Gd^{3+} signal in both cases were almost Lorentzian. Using the previous relation and taking into account the fact that the intensity of the signal is similar for the two samples, the ratio $N_1/N_2 = (\Delta H_1/\Delta H_2)^2$ was estimated and found equal to 2,

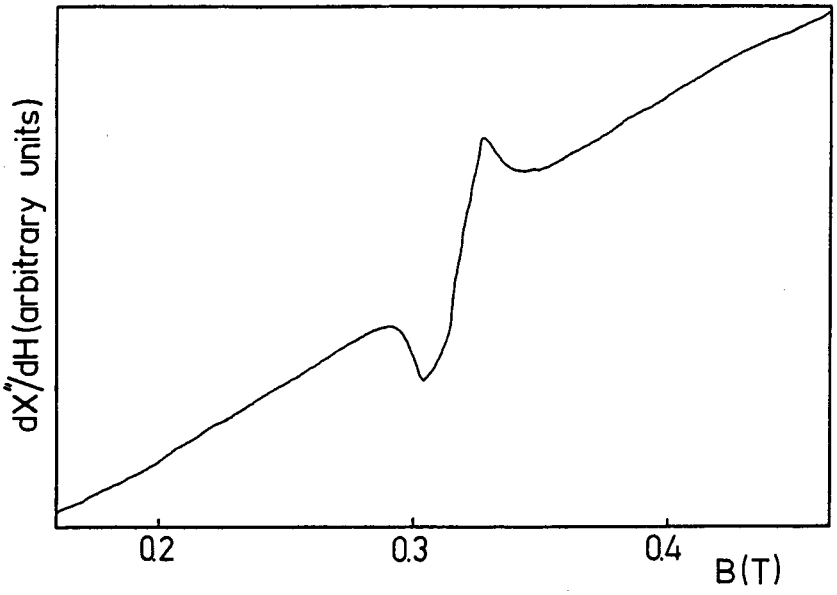


Fig. 4. EPR spectra of $Sm_{0.5}La_{0.5}Ba_2Cu_3O_{7-\delta}$ in orthorhombic phase at LN.

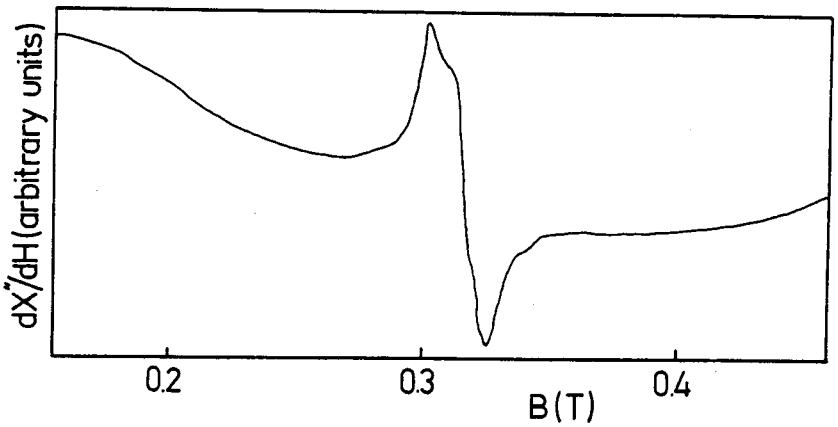
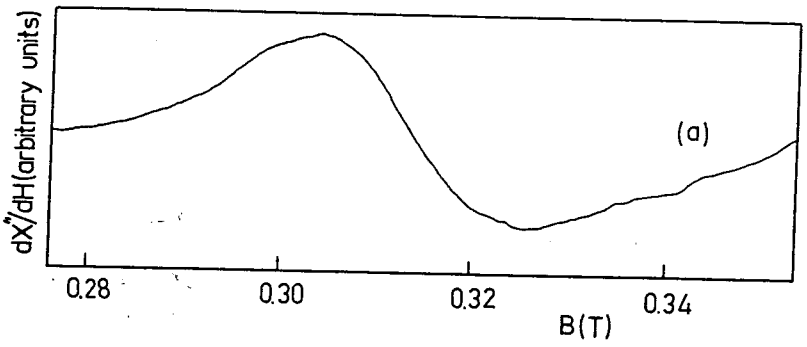


Fig. 5. EPR spectra of $Sm_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$ in orthorhombic phase at LN.

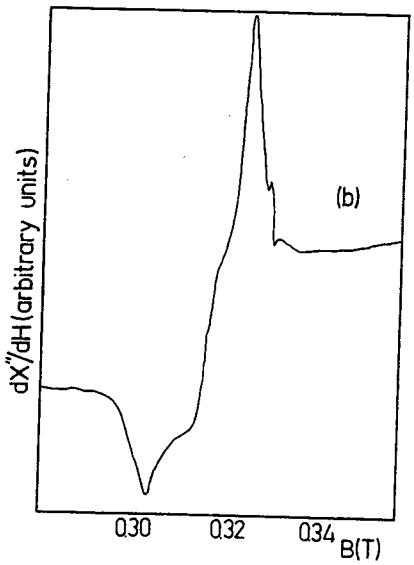
as is expected from the stoichiometric composition of the compounds.

At LN the observed EPR spectra of the samples $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ in orthorhombic phase could be divided into three categories: (I) those exhibiting a very intense EPR signal of Cu^{2+} ions (Re = Ho, Y and Yb), (II) those that consist of a superposition of the Cu^{2+} signal with a very broad line (Re = La, Dy and Er) (Fig. 4), and (III) those where only this broad line occurs but with a large intensity (Re = Eu, Tm and Lu). For the case $Sm_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$ the EPR spectrum consists of a superposition of lines coming from Cu^{2+} and Gd^{3+} ions (Fig. 5). For the $SmBa_2Cu_3O_{7-\delta}$ sample only this broad line has been observed. The broad line is centered at $g = 2.05(1)$ and has a linewidth $\Delta H \sim 0.4$ T.

In the following, the EPR spectra of the samples in the tetragonal phase at RT are presented and discussed. Some of them exhibit the characteristic Cu^{2+} signal, same as in the orthorhombic phase. However, in general, their EPR spectra appear different. For the $SmBa_2Cu_3O_{7-\delta}$ compound a single EPR line from Cu^{2+} at RT has been observed with $g_{\text{eff}} = 2.15(1)$ and linewidth $\Delta H = 0.022(1)$ T (Fig. 6a). Figure 6b presents the EPR spectrum of $Sm_{0.5}La_{0.5}Ba_2Cu_3O_{7-\delta}$ compound. As it is seen the spectrum consists of a superposition of the Cu^{2+} signal with another line having a spin Hamiltonian parameter $g_{\text{eff}} = 1.99(1)$ and linewidth $\Delta H = 14(1) \times 10^{-4}$ T. According to Abragam and Bleaney[14] the open shells with $4d^1$ configuration give values of g parameter in the range of 1.90 to 2.00, which are in good agreement with the obtained experimental value. Therefore, this line could have originated from

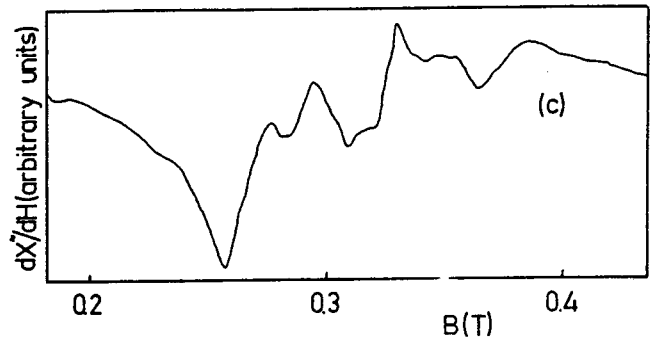


6(a)

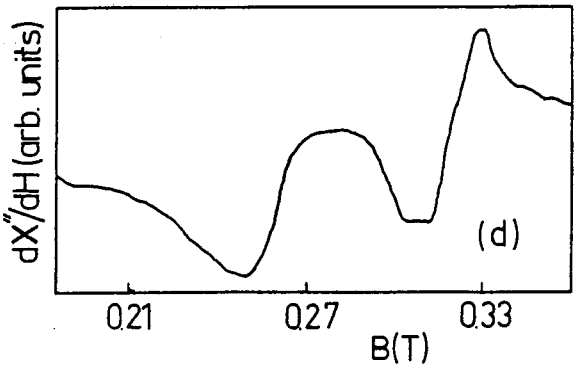


6(b)

La^{2+} ions. One could assume that a fraction of the La ions may be in the divalent state. This assumption is consistent with the suggestion[15,16] that La and Ba ions are partially substituting each other. Remarkably, the same line has also been observed in the $LaBa_2Cu_3O_{7-\delta}$ compound at LN in the tetragonal phase.[2]



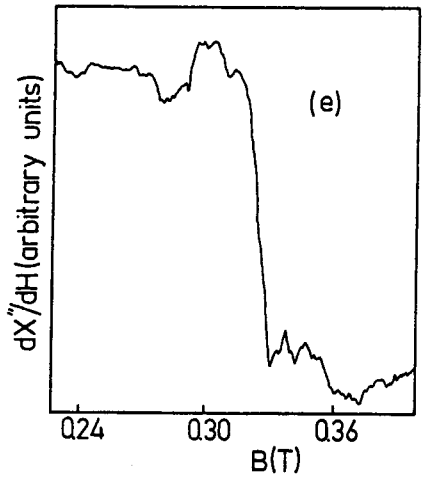
6(c)



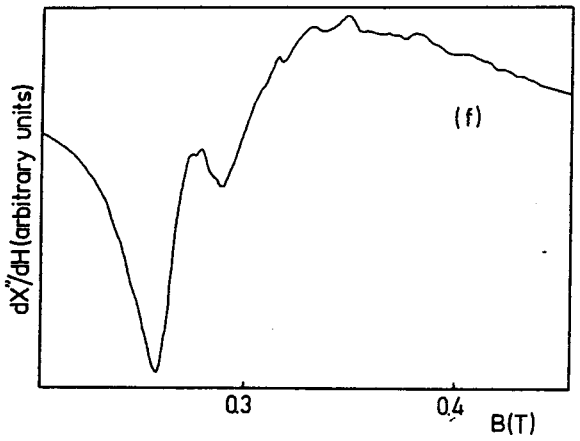
6(d)

Figure 6c shows the EPR spectrum of $Sm_{0.5}Eu_{0.5}Ba_2Cu_3O_{7-\delta}$ compound in tetragonal phase at RT. This spectrum comes from the superposition of a very wide line with another one exhibiting fine structure. As it has been reported previously[1] some of the europium ions may replace barium ions. Based on this assumption it is suggested that the observed spectrum comes from the Eu^{2+} ions which have $^8S_{7/2}$ ground state and their EPR spectrum exhibits a fine structure of seven lines.

The EPR spectrum of $Sm_{0.5}Tm_{0.5}Ba_2Cu_3O_{7-\delta}$ compound in tetragonal phase at RT is presented in Fig. 6d. Apart from the signal due to Cu^{2+} ions another clear signal is observed which may be ascribed to Tm^{2+} ions ($g = 2.7(1)$). These results are consistent with previous reports[17] concerning the EPR spectra of Tm^{2+} ions in $TmBa_2Cu_3O_{7-\delta}$ in tetragonal phase. The signal may be due to divalent thulium ion



6(e)

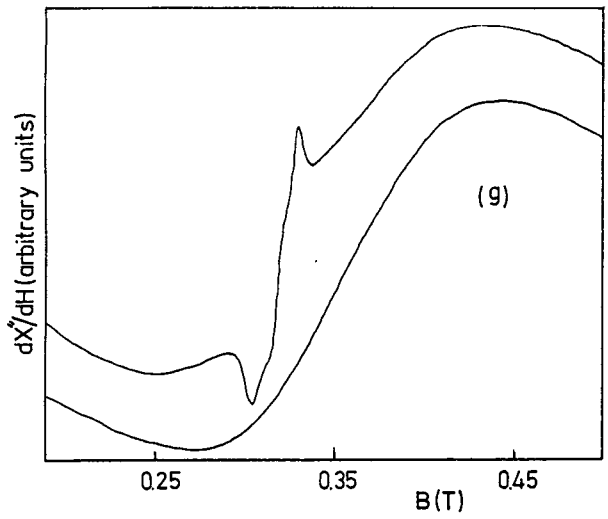


6(f)

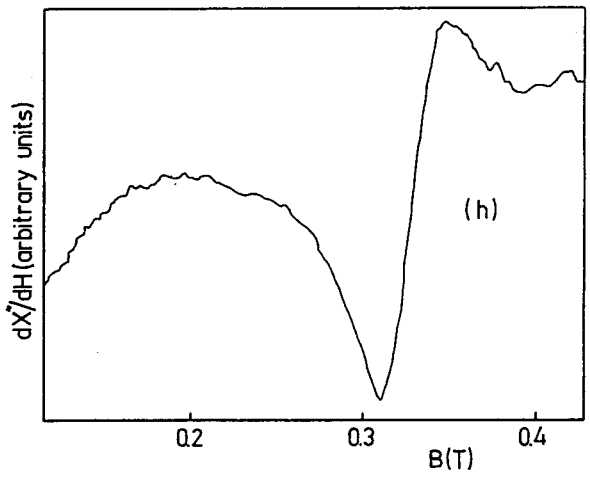
($4f^{13}$; $F^2_{7/2}$) ground state under the condition that it results from the Γ_7 doublet and that the reduction of the orbital angular momenta is quite large. This phenomenon, arising from covalent effects and dynamic coupling to the lattice, was also found to play an essential role in the case of Nd^{3+} ions in the $NdBa_2Cu_3O_{7-\delta}$ compound in tetragonal phase.[18]

Figure 6e presents the EPR spectrum of the polycrystalline $Sm_{0.5}Y_{0.5}Ba_2Cu_3O_{7-\delta}$ in tetragonal phase at RT. The spectrum is the superposition of a very broad line with a signal of weak intensity arising from the divalent copper ions.

The EPR spectrum of $Sm_{0.5}Dy_{0.5}Ba_2Cu_3O_{7-\delta}$ material in tetragonal phase at RT is shown in Fig. 6f. This spectrum consists of the superposition of a very wide



6(g)



6(h)

Fig. 6. EPR spectra of (a) $SmBa_2Cu_3O_{7-\delta}$, (b) $Sm_{0.5}La_{0.5}Ba_2Cu_3O_{7-\delta}$, (c) $Sm_{0.5}Eu_{0.5}Ba_2Cu_3O_{7-\delta}$, (d) $Sm_{0.5}Tm_{0.5}Ba_2Cu_2O_{7-\delta}$, (e) $Sm_{0.5}Y_{0.5}Ba_2Cu_3O_{7-\delta}$, (f) $Sm_{0.5}Dy_{0.5}Ba_2Cu_3O_{7-\delta}$, (g) $Sm_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$, and (h) $Sm_{0.5}Nd_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds in tetragonal phase at RT.

line with another one probably due to Dy^{3+} ions. The values of the spin Hamiltonian parameters of Dy^{3+} in CaF single crystal and in tetragonal crystal field symmetry were[2] found to be $g_{||} = 1.7(1)$ and $g_{\perp} = 2.82(5)$ which are centered in the range of the observed EPR spectra.[19]

For the case of $Sm_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$ compound in tetragonal phase at RT only a single, very wide, line coming from Gd^{3+} ions has been observed (Fig. 6g). It has the same spin Hamiltonian parameter with the Gd^{3+} signal arising from the orthorhombic phase but a different linewidth $\Delta H = 0.16(1)$ T. The EPR signal of Cu^{2+} ions has not been detected.

Figure 6h presents the EPR spectrum of $Sm_{0.5}Nd_{0.5}Ba_2Cu_3O_{7-\delta}$ compound in tetragonal phase at RT. The observed line is centered at $g = 2.00(1)$ and has a linewidth $\Delta H = 0.037(1)$ T. The Nd^{3+} ions have the $^4I_{9/2}$ ground state of the $4f^3$ configuration which transforms according to Γ_6, $\Gamma_8^{(1)}$ and $\Gamma_8^{(2)}$ irreducible representations of the cubic group. For the $\Gamma_8^{(2)}$ representation the quartet can be built from the following two doublets[20]:

$$a_1|^{\pm}9/2\rangle + a_2|^{\pm}1/2\rangle + a_3|^{\mp}7/2\rangle \ , \tag{1a}$$

and

$$\cos\theta|^{\pm}5/2\rangle - \sin\theta|^{\mp}9/2\rangle \ . \tag{1b}$$

In a previous experiment we have reported the EPR spectra of the $NdBa_2Cu_3O_{7-\delta}$ material in tetragonal phase at LN. The two observed lines were ascribed to Nd^{3+} ions.[18] Significantly enough, their g-values ($g_{||} = 3.60$, $g_{\perp} \sim 2.13$) are very similar to those determined by Eq. 1a. The spin Hamiltonian parameter $g_{\perp}$ for that case is in very good agreement with the results of this experiment, suggesting that the recorded line comes from Nd^{3+} ions.

For all the other samples of this series no EPR spectrum was detected in the tetragonal phase at RT.

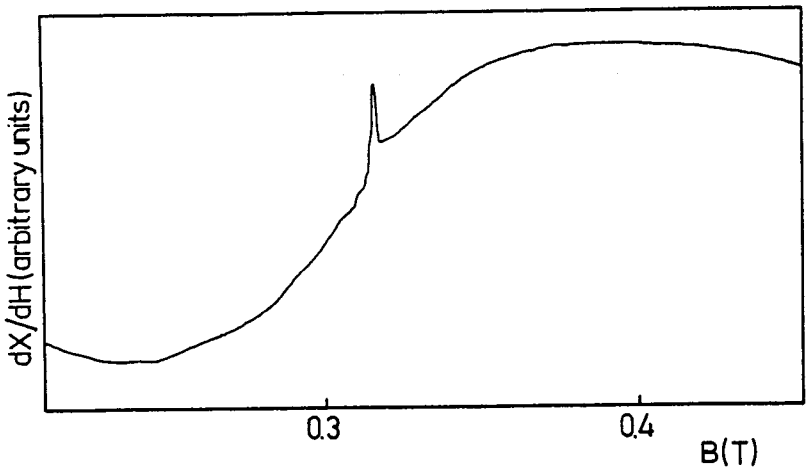


Fig. 7. EPR spectra of $SmBa_2Cu_3O_{7-\delta}$ compound in tetragonal phase at LN.

At LN, $SmBa_2Cu_3O_{7-\delta}$ in tetragonal phase gave a single EPR line with spin Hamiltonian parameter $g = 2.03(1)$ and linewidth $\Delta H = 0.15(1)$ T. Interestingly, superimposed on the center of this line was another feature of unknown origin (Fig. 7). For $Sm_{0.5}Gd_{0.5}Ba_2Cu_3O_{7-\delta}$ at LN the same single line as at RT coming from trivalent gadolinium ions was detected but with increased intensity due to the skin effect.[4,8]

For all the other samples of the investigated ceramics a very wide line has been observed with g-values between 2.03 and 2.06 and linewidth varying from 0.35 to 0.42 T.

In case of $Sm_{0.5}Er_{0.5}Ba_2Cu_3O_{7-\delta}$ compound an additional EPR signal arising from the divalent copper ions, superimposed on the wide line, has been recorded. As it is seen from Table 1, for this sample in the orthorhombic state the temperature phase transition is lower than 90 K (in contrast with the values of T_c for the other members of the series) indicating oxygen deficiency. As it is known, the oxygen content in these compounds has essential influence on the valence of the copper ions. The fact that we also see the signal from Cu^{2+} ions in tetragonal phase may indicate a possible role of oxygen in the valence of these ions. The broad line observed above could be considered[21] as arising from a superexchange interaction between copper ions over oxygen bridges (O_2^-). The same broad line was also observed in the orthorhombic phase at LN as mentioned above. This is in agreement with previous reports on $YBa_2Cu_3O_{7-\delta}$.

2.1. *Skin effect*

As it has been reported previously[4] the intensity of the characteristic Cu^{2+} signal was found to depend strongly on the rare-earth ions of the lanthanide series which were substitutionally introduced into the host lattice of $YBa_2Cu_3O_{7-\delta}$ in orthorhombic phase at Y-ions site. The results for the various $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds are summarized in Table 2. The variation of the EPR line intensity could be ascribed to the influence of the "skin effect". As a result of this effect the volume of the sample which could be penetrated by the microwave radiation decreases as electrical conduction increases. These materials in the orthorhombic phase are known to exhibit metallic behavior above T_c. Furthermore, a 50% substitution of the Re site by different ions changes the conductivity of the samples, which leads, through the skin effect, to changes in the intensity of the EPR signal according to the relation[22,23]

$$I/I_0 = \{2\exp(-w) + [1 - \exp(-2w)]/w\}/[1 - \exp(-w)]^2 , \qquad (2)$$

where $w = d/\delta$ (d being the thickness of the conducting sample), $\delta = (1/\mu_0\omega\sigma)^{1/2}$ is the skin depth, ω is the microwave frequency and σ is the electrical conductivity.

Table 2. The results for the various $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds.

Compound	I/I_0	w	δ [mm]	σ [$\Omega^{-1}cm^{-1}$]	ρ [$10^{-4}\Omega cm$]
Y–Ba–Cu–O	0.0281	35.7	0.056	500	20
Sm–Ba–Cu–O	0.0154	64.0	0.031	1600	6
(Sm, La)–Ba–Cu–O	0.0365	27.4	0.073	300	33
(Sm, Nd)–Ba–Cu–O	0.0112	89.3	0.022	3200	3
(Sm, Eu)–Ba–Cu–O	0.0174	57.5	0.035	1300	8
(Sm, Gd)–Ba–Cu–O	0.0194	52.4	0.038	1100	9
(Sm, Dy)–Ba–Cu–O	0.0310	32.2	0.062	401	25
(Sm, Ho)–Ba–Cu–O	0.0337	29.7	0.067	305	33
(Sm, Y)–Ba–Cu–O	0.0217	46.0	0.044	908	11
(Sm, Er)–Ba–Cu–O	0.0292	34.3	0.058	407	25
(Sm, Tm)–Ba–Cu–O	0.0270	37.0	0.054	504	20
(Sm, Yb)–Ba–Cu–O	0.0150	64.5	0.030	170	6
(Sm, Lu)–Ba–Cu–O	0.0393	24.1	0.077	205	49

We used this relation to estimate the electrical conductivity σ from the relative intensities of the EPR signals for different samples. The dimension of the samples was $d = 2$ mm. A value of $\sigma = 500\Omega^{-1}$ cm^{-1} was deduced for the electrical conductivity at RT of the high-T_c superconductor.[24] The corresponding ratios I/I_0 was then estimated by introducing this value in relation (2). Assuming now that I_0 is the same for all the $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds, the electrical conductivities were obtained by introducing the values of I as measured from the EPR signals (Table 2). These results are in good agreement with previous reports in the literature.[25,26]

2.2. *Low field microwave absorption*

One of the most interesting features of the high-T_c superconducting copper oxides is the existence of a strong nonresonant absorption (MA) in low magnetic field. This MA has been the subject of intense studies using a standard EPR X-band spectrometer mainly for powdered samples and recently for single crystals. It can be used efficiently to probe the superconducting phase, transition temperature, grain size, etc.[27,28] Various models have been proposed to explain MA in low magnetic fields, most of them based on the existence of superconducting grains weakly coupled through intrinsic Josephson junctions.[29–31] In the following, we present our results of the usual EPR experiment on ceramic samples of the series $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ and discuss the obtained signals arising from MA. The differences observed when the substitution Re ions change are reported. All the samples of this series, with the exception of $Sm_{0.5}La_{0.5}Ba_2Cu_3O_{7-\delta}$, exhibited huge (as compared with the strength of EPR signals) peaks at very low fields. However, the intensities of the signals received under identical experimental conditions for the different members

of the series varied significantly. The shape of the peak is similar to that observed by other workers.[32] The positions of the peaks for all the samples were the same while the intensities of the signals were quite different. Taking as reference the intensity of the signal of the $SmBa_2Cu_3O_{7-\delta}$ compound, the intensity ratios obtained from our measurements for the various members at LN are summarized in Table 3. Evidently, the intensity of the signal depends strongly upon the Re ion. A very striking fact was that in the case of $Sm_{0.5}La_{0.5}Ba_2Cu_3O_{7-\delta}$, a well-characterized sample by XRD and magnetic measurements with $T_c = 82$ K, no signal arising from MA was detected, even when larger quantities of the material were used. On the

Table 3. The intensity ratios for the various members at LN.

Re	Sm	Tm	Lu	Ho	Yb	Er	Nd	Gd	Eu	Y	Dy
J/J_0	1	14.05	9.21	4.39	3.45	2.12	0.45	0.44	0.48	0.18	0.08

contrary, when the non-superconducting oxygen deficient $Sm_{0.5}La_{0.5}Ba_2Cu_3O_{7-\delta}$ material (tetragonal phase) was measured, the characteristic signal arising from MA was observed. The mass of the sample was 165 mg and the microwave power used was 50 mW. The signal's intensity was weaker in comparison with those obtained from the superconducting samples. The observation of the characteristic signal implies the existence of superconducting phase inside the tetragonal sample which is not detectable by magnetic measurements. This unexpected behavior of the $Sm_{0.5}La_{0.5}Ba_2Cu_3O_{7-\delta}$ sample, which is in contradiction with the current explanations of MA, is possibly closely related to the role of La ions when placed as substitutes at Y-sites in the high-T_c superconductors $YBa_2Cu_3O_{7-\delta}$. So far the existence of La ions at the sites of Y resulted in a lower phase transition temperature as compared with other high-T_c superconductors. Previous EPR investigations of the oxygen-deficient $LaBa_2Cu_3O_{7-\delta}$ revealed the presence of some dynamical fluctuations at LN, which were independent of the applied external magnetic field.[2] Since EPR is sensitive to small percentage of superconducting phase it might be assumed that this behavior resulted from a fraction of the sample being superconducting at LN not detectable by magnetization measurements. Furthermore, EPR measurements have shown some kind of exchange interaction between copper ions in $LaBa_2Cu_3O_{7-\delta}$ which could have significant influence on the transport processes in this material. However, the exact behavior of the La ions is not yet clear and the question concerning the disappearance of MA in the superconducting sample is still open.

3. Conclusion

Our EPR investigations of the series $Sm_{0.5}Re_{0.5}Ba_2Cu_3O_{7-\delta}$ have shown that some of the Re ions are in the trivalent state and some others such as La, Eu, and Tm may exist in the divalent state. Similar conclusions for Gd^{3+} and Eu^{2+} have also been reported in the literature. There the results are clearer in the tetragonal

phase characterized by large oxygen deficiency. Evidently, the content of oxygen influences essentially the valence state of copper and Re ions. We believe that a systematic investigations on the tetragonal phase in this kind of materials could provide additional information on the creation of the superconducting states.

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