

XRD EPR Studies of Ceramics $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ in the Orthorhombic and Tetragonal Phase

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EPR, XRD, and magnetic studies are presented for $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds (Re = La, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Tm, Yb, and Lu) in the orthorhombic and tetragonal (large oxygen deficiency) phase. For the samples with Re = Dy, Ho, Y, Er, Tm, Yb, and Lu in the orthorhombic phase, the transition to the superconducting state has been observed in the temperatures range T_c between 18 and 40 K. For the samples with Nd and Yb in the tetragonal phase, EPR spectra coming from trivalent rare earth ions have been recorded. In the nonoxygenated sample $\text{Pr}_{0.5}\text{La}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ the EPR spectrum arising from the non-Kramers trivalent praseodymium ion has been observed. A broad EPR line appearing in all our samples was attributed to superexchange interaction between copper ions over oxygen (O_2^-) bridges. Interestingly, for the $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (Re = Er and Lu) compounds in the tetragonal phase at liquid-nitrogen temperature, a nonresonant microwave absorption in low magnetic fields has been detected.

KEY WORDS: Superconductivity; EPR; XRD; $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds.

1. INTRODUCTION

Recently, $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (Re = rare earth ions) have been extensively studied [1-3]. Among the magnetic rare earth systems, those which are based on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, Pr-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and the isomorphic compound $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ stand out as anomalous. Praseodymium doping suppresses the superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ while the pure $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, although crystallographically identical to all the other 123 superconductors, is an antiferromagnetic semiconductor ($T_N = 17$ K) [1]. Possible reasons for the

lack of superconductivity were suggested to be Pr valence fluctuations, the detected Pr-Ba substitution, and/or differences in the charge carrier density [3].

In the present work the EPR method was used to investigate the materials $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (Re = La, Ce, Nd, Sm, Eu, Gd, Dy, Y, Er, Tm, Yb, and Lu) both in the orthorhombic and tetragonal phase in order to obtain detailed EPR data for all the members of the series which may provide an insight into the origin of their behavior. Structural and magnetic characterization of the material has also been done.

2. EXPERIMENTAL RESULTS

Samples were very carefully prepared by the solid-state reaction technique. Appropriate amounts of Re_2O_3 , Pr_6O_{11} , CuO, and BaCO_3 were thoroughly mixed, and pellets were formed under pressure of about 10 bars. The whole procedure has been described elsewhere [4].

Structure characterization of the samples was done using a Philips X-ray powder diffractometer

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(XRD) utilizing Co $K\alpha$ radiation. For all the members of the series $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, the Bragg peaks of the XRD spectrum revealed single orthorhombic (for samples without oxygen deficiency) and tetragonal (for samples with large oxygen deficiency) phases. The XRD spectra of both phases for all the Pr-Re compounds are consistent with the standard XRD patterns obtained from the 123 type. Only the $\text{Pr}_{0.5}\text{La}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound exhibited different behavior. Characteristically, the most intense peaks (110), (103), and (013) of the XRD spectrum for the orthorhombic phase were not separated, a fact also observed in $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds [8]. In Table I the lattice constants are cited for all the compounds of the series $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ in the orthorhombic and tetragonal phase. In this series, the ionic radius of the ion in the rare earth site is taken as the average Pr^{3+} - Re^{3+} ion radius. The unit cell c -axis and the unit volume vs. the average Pr-Re ionic radius do not show similar variations as for the (Sm, Re)123 and (Gd, Re)123 compounds [9,10]. It seems that the substitution of the Pr atoms for half the Re atoms in the Re123 perovskites affects the general trends of the crystallographic constants.

A PAR155 vibrating sample magnetometer was used to study the transition temperatures of the samples in the range 4.2 to 100 K and in an applied magnetic field of 2×10^{-2} T. Magnetization measurements revealed superconductivity for the compounds with Re=Ho, Tm, Yb, and Lu with a T_c around 40 K (Table I and Fig. 1). In these compounds the obtained superconducting phase from the field-cooled mode lines using the ratio $L = -4\pi M/H$ is of order 4%. Recently, Latka *et al.* [4] have shown that for the $(\text{Eu}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system, for x close to 0.4 the

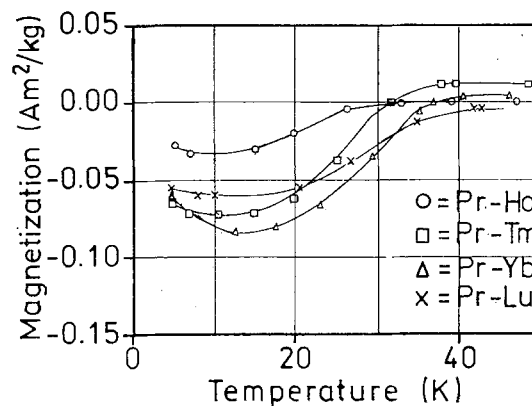


Fig. 1. Magnetic measurements for $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds in the tetragonal phase (Re=Ho, Tm, Yb, and Lu) in the field-cooled mode.

superconductivity has disappeared, in comparison with analogous systems containing samarium [9] and gadolinium atoms [10], which exhibit the superconducting stage for x values around 0.5.

Resistivity measurements were also performed. Semiconducting behavior was observed in the orthorhombic phase of the samples in the whole temperature range (except in the superconducting state). For the samples with Dy, Y, and Er the values of T_c were obtained by resistivity measurements (Table I).

The oxygen content of the materials was determined by the iodometric method [11]. As is seen from Table I, the phase transition to the superconducting state is independent of small variations in the oxygen content. It is found that the superconducting state does not exist for compounds with Re ions of large ionic radius (Table I).

Table I. Lattice Constants of $\text{Pr}_{0.5}\text{Re}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ Compounds in the Orthorhombic and Tetragonal Phase

Compound	Ionic radius $10^{-1} R$ (nm)	T_c (K)	δ	Orthorhombic			Tetragonal	
				$10^{-1} a$ (nm)	$10^{-1} b$ (nm)	$10^{-1} c$ (nm)	$10^{-1} a=b$ (nm)	$10^{-1} c$ (nm)
Pr, La	1.015	—	—	3.8740	3.9077	11.7566	3.9131	11.8327
Pr, Nd	1.004	—	0.20	3.8579	3.9105	11.7390	3.9037	11.8511
Pr, Sm	0.989	—	—	3.8533	3.9034	11.7077	3.8951	11.8513
Pr, Eu	0.982	—	0.21	3.8479	3.9067	11.7091	3.8943	11.8264
Pr, Gd	0.976	—	0.21	3.8359	3.9018	11.7122	3.8863	11.8302
Pr, Dy	0.961	18	0.19	3.8440	3.9055	11.7093	3.8936	11.8172
Pr, Ho	0.954	33	0.22	3.8337	3.8978	11.6911	3.8783	11.8255
Pr, Y	0.953	25	0.23	3.8373	3.8963	11.6996	3.8830	11.8339
Pr, Er	0.947	20	0.19	3.8321	3.8927	11.6818	3.8795	11.8210
Pr, Tm	0.942	33	0.26	3.8293	3.8946	11.6792	3.8771	11.8210
Pr, Yb	0.936	37	0.23	3.8259	3.8927	11.6759	3.8729	11.8259
Pr, Lu	0.932	40	0.25	3.8262	3.8912	11.6831	3.8717	11.8115

EPR spectra were obtained at 77 K and at room temperature using a standard Varian E-4 X-band ($\nu = 9.3$ GHz) spectrometer with magnetic field modulation of 100 kHz. EPR measurements were performed in powder samples of cylindrical shape (30 mg).

Figure 2 presents the EPR spectra at room temperature of the oxygenated samples $\text{Pr}_{0.5}\text{Nd}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Pr}_{0.5}\text{La}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. For all the samples the characteristic EPR spectrum of divalent copper ions in the orthorhombic local symmetry was observed. The values of the spin Hamiltonian parameters g are similar to those of the BaCuO_2 compound [12], but the intensities and lineshape are different. The intensity of the lines is much stronger at liquid-nitrogen temperature than at room temperature. It was suggested previously [13] that spin-phonon interaction [14] plays an important role for the 123 systems with Pr atoms, and thus the intensity of the lines is affected by temperature.

A wide line (Fig. 3) was detected for all the members of the series in the tetragonal phase at liquid-nitrogen temperature. It has a spin Hamiltonian parameter with $g = 2.05(1)$. The linewidths (ΔH) of the various compounds of the series with Dy, Eu, Tm,

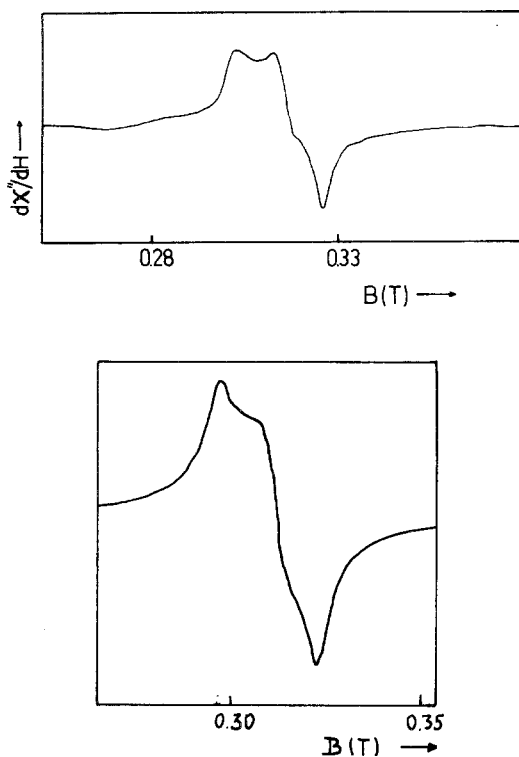


Fig. 2. EPR spectrum of (a) $\text{Pr}_{0.5}\text{La}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and (b) $\text{Pr}_{0.5}\text{Nd}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds in the orthorhombic phase at room temperature.

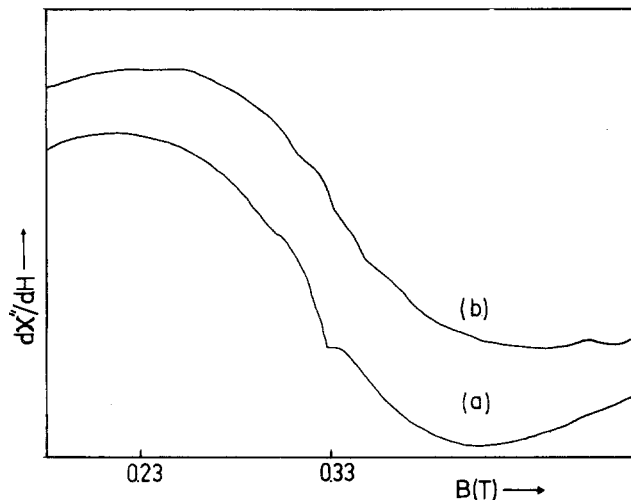


Fig. 3. EPR spectra of (a) $\text{Pr}_{0.5}\text{Dy}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and (b) $\text{PrTm}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds in the tetragonal phase at liquid-nitrogen temperature.

and Lu were found to be 0.200(5), 0.300(5), 0.200(5), and 0.220(5) T, respectively. For the samples with the rest of the Re ions, the line was much broader. We could ascribe this line to superexchange interaction between copper ions over oxygen (O_2^-) bridges [13].

Additional EPR signals were detected for (Pr, Yb) and (Pr, La) compounds arising from the paramagnetic rare earth ions. The EPR spectrum of $\text{Pr}_{0.5}\text{Yb}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound in the tetragonal phase, apart from the divalent copper signal, revealed an additional line with $g = 3.50(1)$ and linewidth $\Delta H \sim 0.02$ T at room temperature. This line exhibited also a hyperfine structure which was not well resolved (Fig. 4). However, the orthorhombic phase, a similar line was detected at liquid-nitrogen temperature, with

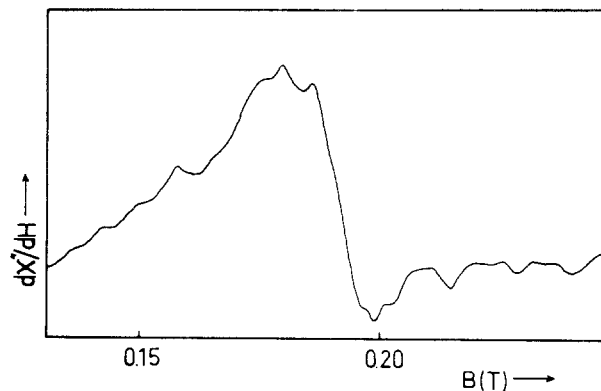


Fig. 4. Spectra of $\text{Pr}_{0.5}\text{Yb}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound in the tetragonal phase at room temperature.

approximately the same g -factor but greater linewidth and no hyperfine structure. The Yb^{3+} ion has $4f^{13}$ configuration on the open shell with ground state $^2F_{7/2}$, whose decomposition on a cubic crystal field is $J = \frac{7}{2} \rightarrow \Gamma_6 + \Gamma_7 + \Gamma_8$ [15]. The lowest level is a Γ_7 . The wavefunction describing the Γ_7 doublet for $J = \frac{7}{2}$ is $\frac{3}{2}|\mp \frac{5}{2}\rangle - \frac{1}{2}|\mp \frac{3}{2}\rangle$, which yields an isotropic g value of $24/7 = 3.429$. Interestingly, many authors [16,17] have reported g values very close to the theoretical one and also reported that this resonance is observable up to ~ 100 K, which implies a comparatively long spin-lattice relaxation time. An EPR investigation on polycrystalline samples of $\text{Y}_{0.99}\text{Yb}_{0.01}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ material has been presented previously [18,19]. The EPR spectrum of trivalent ytterbium ions with $g = 3.2(2)$ and linewidth $\Delta H \sim 0.05$ T has been observed. Consequently, the observed line of the $\text{Pr}_{0.5}\text{Yb}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound both in the tetragonal and orthorhombic phase could be attributed to the Yb^{3+} ions. In the orthorhombic phase, interaction with conduction electrons probably broadens the line [20] and prevents the detection of hyperfine structure.

Figure 5a presents the EPR spectrum of the $\text{Pr}_{0.5}\text{La}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound with large oxygen

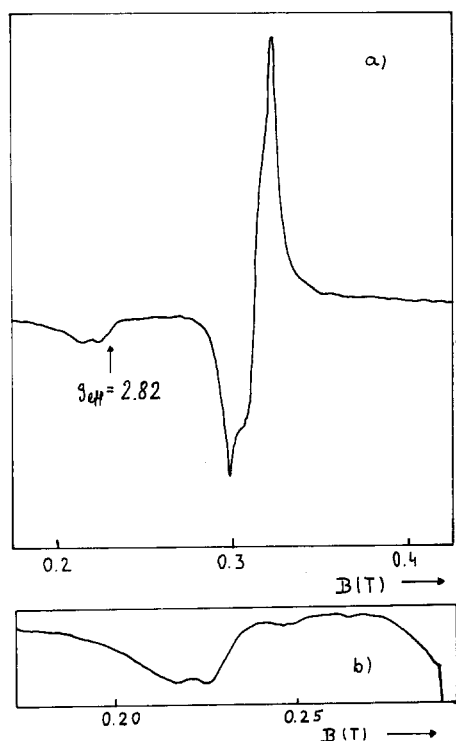


Fig. 5. EPR spectrum of the nonoxygenated sample $\text{Pr}_{0.5}\text{La}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ at room temperature (a) and in only a low magnetic field (b).

deficiency. The spectrum is the superposition of a line coming from Cu^{2+} ions and another line centered at $g_{\text{eff}} = 2.82(1)$ with hyperfine structure (Fig. 5b) where the hyperfine constant was $A \sim 0.02 \text{ cm}^{-1}$. In a crystal field of symmetry C_{3v} , the 3H_4 ground state of Pr^{3+} ion ($4f^2$) splits into three singlets and three doublets. The lowest doublet consists of two states each of which could be described as a mixture of only three eigenstates of the total angular momentum J_z . These states are given by [21]

$$Y_{(-/+)} = a|J_z, \mp 4\rangle + b|J_z, \mp 1\rangle + c|J_z, \mp 2\rangle \quad (1)$$

where the two signs $(-/+)$ correspond to different levels. Since this doublet is not a Kramers doublet, no resonance absorption is expected. However, a local distortion in the mixed compound due to the complicated structural state [8] can further split the two levels [21]. The additional line in lower magnetic fields in $\text{Pr}_{0.5}\text{La}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ could be attributed to trivalent praseodymium ions. The fact that a similar signal was not observed in the other members of the series indicates the special behavior of La atoms. The role of the La atoms is currently under investigation.

A very significant aspect in the 123 superconductors is the microwave absorption in low magnetic fields. This absorption has been the subject of many studies [22]. It has been suggested that a strong signal near zero magnetic field in EPR measurements of high- T_c superconductors is made up of predominant nonresonant "reflection" of microwaves below T_c [22]. The phenomenon was interpreted in terms of Josephson weak links between the superconducting grains. Our EPR investigations at liquid-nitrogen temperature revealed the presence of zero-field absorption signals for the oxygenated samples (Pr, La), (Pr, Ho), and nonoxygenated samples (Pr, Lu), (Pr, Er). However, magnetic measurements did not reveal any phase transition to the superconducting state for these materials. Similar phenomena were reported previously for the oxygenated $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound ($T_c = 28$ K) and the $\text{La}_{0.5}\text{Sm}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound in the tetragonal phase [9]. In our case, some dynamic fluctuations in the EPR spectrum at liquid-nitrogen temperature were detected, which were interpreted as indications of the existence of very small superconducting regions in the sample. This seems to be true for the previously mentioned four Pr compounds. Consequently, microwave low-field absorption proves to be a very sensitive way of checking even small quantities of the superconducting phase, which cannot be detected by magnetic measurements.

Finally, we wish to comment on the EPR observations of other workers on Pr 123 compounds. Collin *et al.* [3] report that EPR experiments on PrBa₂Cu₃O_{7-δ} single crystals did not reveal any resonance peak from 6 to 300 K. From our experience on EPR measurements of the high-*T_c* 123 superconductors with Pr ions, assuming samples of good quality, a possible reason which could prevent the detection of EPR signals could be the decrease of the volume of the sample that is penetrated by the microwave radiation due to the skin effect [24]. Moreover, as mentioned previously [14], spin-phonon interactions may have an essential influence on the intensity of the EPR signals. Remarkably, neutron inelastic scattering spectra has shown that the phonon feature becomes dominant in the spectra of PrBa₂Cu₃O_{7-δ} compounds [25].

3. CONCLUSION

We conclude that superconductivity in the Pr_{0.5}Re_{0.5}Ba₂Cu₃O_{7-δ} systems appears only for compounds with the Re ionic radius smaller than that of the Gd ion (Table I). The EPR signals coming from trivalent rare earth ions were detected. Significantly enough, to the best of our knowledge the observation of Pr³⁺ ions is reported for the first time in these materials.

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