PHYSICAL REVIEW B VOLUME 52, NUMBER 10 1 SEPTEMBER 1995-II

EPR study of localized Cu^{2+} paramagnetic ions and Cu^{2+} pairs in the oxygen-deficient $PrBa_2Cu_3O_{6+x}$ and $Pr_{0.5}R_{0.5}Ba_2Cu_3O_{6+x}$ (R =Y,Er) compounds

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(Received 29 September 1994; revised manuscript received 21 March 1995)

Low-temperature EPR measurements are presented for the $PrBa_2Cu_3O_{6+x}$ and $Pr_{0.5}R_{0.5}Ba_2Cu_3O_{6+x}$ (R=Y,Er) compounds with oxygen deficiency (tetragonal phase). The nuclear hyperfine interaction of the Cu^{2+} ions has been observed in both compounds. The origin of the Cu^{2+} EPR spectra has been associated with localized divalent copper ions in the Cu(1) sites. A time-induced transformation of the Cu^{2+} local crystal-field symmetry from orthorhombic to tetragonal, related to the oxygen distribution in the Cu(1) plane, has been detected. The EPR spectra of pairs of weakly exchange-coupled divalent copper ions were also observed. These copper pairs are suggested to occur in the Cu(1) planes and to be magnetically isolated from the antiferromagnetic CuO_2 planes.

I. INTRODUCTION

One of the most intriguing problems encountered in the study of the $YBa_2Cu_3O_{6+x}$ materials, which in their oxygenated phase ($x \sim 1$), exhibit high-T_c (HTC) superconductivity, is the absence of an electron paramagnetic resonance (EPR) signal arising from the bulk copper ions with spin 1/2.[1] Possible reasons for this behavior may be the delocalization of the Cu^{2+} states contributing in the conduction band for the oxygenated, metallic-superconductive phase and the strong two-dimensional antiferromagnetic correlations in the Cu(2) planes, persistent even above $T_N \sim 400$ K for the oxygen-deficient semiconducting phase. These effects are suggested to induce very fast electron spin-relaxation rates in the corresponding phases,[2,3] that broaden beyond detection the EPR signal from the bulk divalent copper ions, an explanation requiring further investigation.[1]

However, EPR studies of oxygen-deficient $RBa_2Cu_3O_{6+x}$ (R123) compounds, where R is a rare-earth element other than Ce and Tb, have revealed the presence of weak axial Cu^{2+} EPR spectra, which cannot be associated with the presence of impurity phases,[4,5] while an intense, temperature-dependent EPR line attributed to exchange-coupled copper ions has been observed at low temperatures.[5-7] These EPR spectra can be related to localized Cu^{2+} centers induced by the presence of a small amount of excess oxygen in the oxygen-deficient Cu(1) planes, giving rise to a paramagnetic component in the magnetic susceptibility of the corresponding antiferromagnetic compounds.[7] Similar EPR spectra have been recently reported in oxygen-deficient polycrystalline samples and single crystals of R123 and were attributed to quasi-one-dimensional (1D) magnetic clusters in the CuO_2 plane[8] in accordance with the interpretation of the EPR signals observed in $LaCuO_{4+\delta}$ samples prepared by fast quenching from room temperature.[9] The latter signals were interpreted in terms of the presence of isolated spin-polarized ferromagnetic clusters induced by oxygen holes in the copper planes, which under slow cooling conditions diffuse to form percolative conducting, and below T_c, superconducting phases.[10] However, this interpretation should be considered with caution when applied to the R123 systems, since for the oxygen-deficient phase of the latter compounds any appreciable doping of holes in the antiferromagnetic Cu(2) planes in the oxygen concentration range of $0<x<0.25$ is not expected, in accordance with the small variation of T_N in the corresponding regime.[11,12] Therefore, until detailed EPR investigations in R123 samples with well-defined oxygen content are reported, the observation of the single EPR line at low temperatures in oxygen-deficient R123 samples[7] with low oxygen content of $x \sim 0.2$, indicate that its origin is most likely associated with the formation of linear Cu clusters in the oxygen-deficient Cu(1) planes. Moreover, the concept of localized paramagnetic Cu centers in the Cu(1) sites along with the results of a Y123 single-crystal EPR study,[13] was used to interpret the observed axial Cu^{2+} EPR spectra in the tetragonal $LaBaSrCu_3O_{6+x}$ compound, where a disordered oxygen distribution in the Cu(1) plane was suggested to cause the formation of EPR-active octahedrally coordinated Cu^{2+} ions in both the oxygenated and nonoxygenated phase.[14] On this basis, EPR turns out to be a sensitive method to trace the presence of localized magnetic moments in the 123 systems.

The Pr123 system is probably the most interesting compound in the R123 series, since it is the only nonsu-

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perconducting member of these isostructural compounds. This system is a semiconductor with antiferromagnetically ordered Cu moments in the CuO_2 planes even for the oxygenated phase, while antiferromagnetic ordering of the Pr moments occurs at 17 K, which is the highest T_N observed for the rare-earth sublattice.[15] Various models have been proposed to explain this behavior as the existence of a higher Pr valence state resulting in hole filling in the CuO_2 planes, a magnetic pair-breaking action of the Pr^{3+} ions, the most refined model of strong hybridization of the praseodymium $4f$ states with the oxygen p orbitals involving large p-f exchange interaction and leading to localization of holes in the CuO_2 planes,[16] while recently the idea of holes being present only in the Cu(1) chains has been suggested on a phenomenological basis in order to reconcile many experimental results.[17] Due to the d-electron localization, in principle, it is expected that there should be an EPR response of the Pr123 system. However, antiferromagnetic correlations that cause excessive broadening may suppress any bulk EPR signal from Cu(2) planes at ambient temperature. An indication for such a broad EPR signal which narrowed at room temperature, we obtained by preliminary EPR measurements on Pr123 samples,[18] however, a thorough study of such broad signals requires high microwave frequencies. On the other hand, one may expect Pr123 to favor the formation of EPR-active paramagnetic centers which may be studied by conventional X-band EPR. A recent EPR investigation of the (Pr,R)123 series in the oxygenated phase, where superconductivity develops for the second half of the series with the heavier lanthanide ions, revealed the EPR spectra of localized Cu^{2+} ions with different temperature behavior for the HTC and non-HTC samples and significant dependence on time exposition.[19] Based on these observations, we have carried out EPR experiments on the oxygen-deficient, tetragonal phase of the (Pr,R)123 series to trace the presence of localized Cu^{2+} centers in these compounds.

In the present work, low-temperature EPR spectra of the oxygen-deficient $PrBa_2Cu_3O_{6+x}$ and $Pr_{0.5}R_{0.5}Ba_2Cu_3O_{6+x}$ (R =Y,Er) compounds are presented, which revealed the existence of isolated Cu^{2+} ions with clearly resolved hyperfine structure as well as localized copper pairs.

II. EXPERIMENTAL RESULTS

The samples $PrBa_2Cu_3O_{6+x}$ and $Pr_{0.5}R_{0.5}Ba_2Cu_3O_{6+x}$ (R =Y,Er) were prepared by the solid-state reaction technique as described in Ref. 20. They were fully oxygenated under flowing oxygen at 450 °C for 24 h. Special care was taken in order to achieve the maximum degree of deoxygenation by fast cooling in a reducing atmosphere (helium) down to room temperature. According to thermogravimetric analysis measurements, the value of x is estimated to be approximately 0.2. Structure characterization was carried out using x-ray powder diffraction, which revealed a tetragonal unit cell ($P4/mm$ space group) for both samples, with lattice parameters being similar to those in Ref. 21 and verified that both samples were single phase.

The EPR spectra were recorded using an X-band Bruker ER 200D spectrometer with 100 KHz modulation of the steady magnetic field. An Oxford flow cryostat system was used for measurements at liquid-helium temperature. The samples were measured in the form of fine powder and were always kept in a dry atmosphere.

Figure 1 presents the EPR spectra of the oxygen-deficient $PrBa_2Cu_3O_{6+x}$ compound at low temperature, immediately after preparation [Fig. 1(a)] and after a period of one month [Fig. 1(b)], respectively. Within this time period, a radical change of the EPR spectra occurred. For the fresh sample, an intense anisotropic powder EPR spectrum of Cu^{2+} ions was observed [Fig. 1(a)], while for the aged one the nuclear hyperfine structure pattern of copper ions was clearly resolved [Fig. 1(b)]. Additionally, the EPR spectrum intensity for the latter sample was markedly reduced, approximately by a factor of 10, in comparison with the EPR spectrum intensity of the fresh sample. For the $Pr_{0.5}Er_{0.5}Ba_2Cu_3O_{6+x}$ compound a similar anisotropic Cu^{2+} EPR spectrum with resolved hyperfine structure was observed [Fig. 1(c)], which was still observable after storing the sample for one month, though not clearly resolved. Both kinds of EPR spectra can be described by the spin Hamiltonian of the form

$$H=\mu_B S\cdot g\cdot B+S\cdot A\cdot I \ , \tag{1}$$

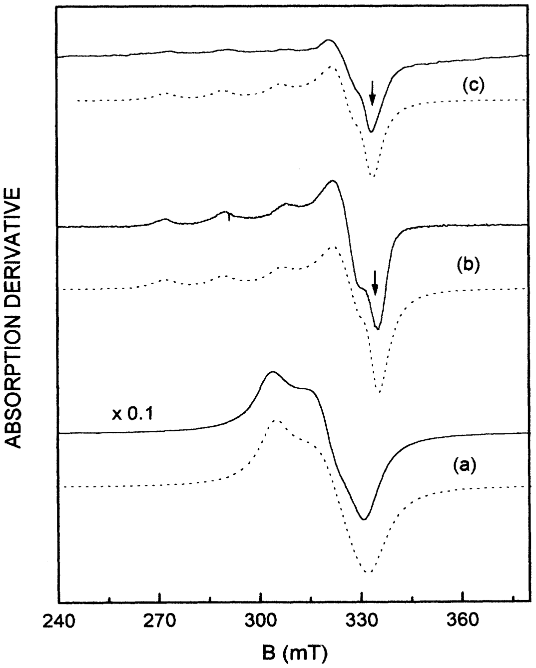

FIG. 1. The EPR spectra of Cu^{2+} ions at 4.4 K in (a) the $PrBa_2Cu_3O_{6+x}$ fresh sample, (b) the $PrBa_2Cu_3O_{6+x}$ aged sample and (c) the $Pr_{0.5}Er_{0.5}Ba_2Cu_3O_{6+x}$ fresh sample. The solid lines represent the experimental spectra, while the dashed lines represent the theoretical powder spectra obtained from simulation.

where $S=1/2$ and $I=3/2$ are the electron and nuclear spin of Cu^{2+} ions, while the symmetry of the g and A tensors is determined by the local crystal-field symmetry. The observed powder spectra were theoretically simulated according to the spin Hamiltonian (1), using the program QPOWA.[22] For the $PrBa_2Cu_3O_{6+x}$ fresh sample, where no hyperfine structure was observed, the theoretical powder spectrum [Fig. 1(a)] revealed orthorhombic crystal-field symmetry for the Cu^{2+} ions with the following principal values of the g tensor: $g_x=2.027(1)$, $g_y=2.088(1)$, and $g_z=2.212(1)$. These values are different than those reported for the green phase Y_2BaCuO_5 and $BaCuO_{2+x}$ compounds,[23] which are usually considered to be responsible for the observed Cu^{2+} EPR spectra in the Y123 compounds. For the $PrBa_2Cu_3O_{6+x}$ aged sample as well as the $Pr_{0.5}Er_{0.5}Ba_2Cu_3O_{6+x}$ one, the theoretical powder EPR spectra [Figs. 1(b) and 1(c)] revealed a transformation of the local crystal-field symmetry to the tetragonal one, with the following values of the spin-Hamiltonian parameters: $g_{\parallel}=2.263(1)$, $g_{\perp}=2.051(1)$, $A_{\parallel}=-177(3)\times 10^{-4}$ cm^{-1}, and $A_{\perp}=25(17)\times 10^{-4}$ cm^{-1} for the $PrBa_2Cu_3O_{6+x}$ sample, and $g_{\parallel}=2.265(1)$, $g_{\perp}=2.060(1)$, $A_{\parallel}=-166(3)\times 10^{-4}$ cm^{-1}, and $A_{\perp}=20(15)\times 10^{-4}$ cm^{-1} for the $Pr_{0.5}Er_{0.5}Ba_2Cu_3O_{6+x}$ one. In both cases, the observed EPR spectra cannot be simulated very accurately due to the contribution of another line [depicted by an arrow in Figs. 1(b) and 1(c)] arising from copper pairs as discussed below.

The observed EPR spectra cannot be related to any impurity phase except possibly for the $BaCuO_{2+x}$ one. Fresh samples of $BaCuO_{2+x}$ have been reported to produce an axial Cu^{2+} EPR spectrum at room temperature, which after a time period transformed into a rhombic one.[23] However, our EPR study of $BaCuO_{2+x}$ samples,[24] prepared under similar conditions with the present ones, did not confirm the observation of any axial Cu^{2+} EPR spectrum and most importantly it was found that the EPR spectrum of the $BaCuO_{2+x}$ compound at low temperature ($T<20$ K), especially in its oxygen-deficient phase, is dominated by the presence of an intense, single exchange narrowed EPR line, strongly temperature dependent and totally different from the present spectra. The latter observations as well as the presence of the nuclear hyperfine structure which has not been reported for any of the impurity phases, support the intrinsic character of the observed spectra.

The temperature dependence of the Cu^{2+} EPR spectrum in PR123 is presented in Fig. 2. The intensity of this spectrum follows closely the $1/T$ law expected for a simple paramagnetic center, indicating the isolated nature of the corresponding Cu^{2+} center which does seem to interact significantly with its environment.

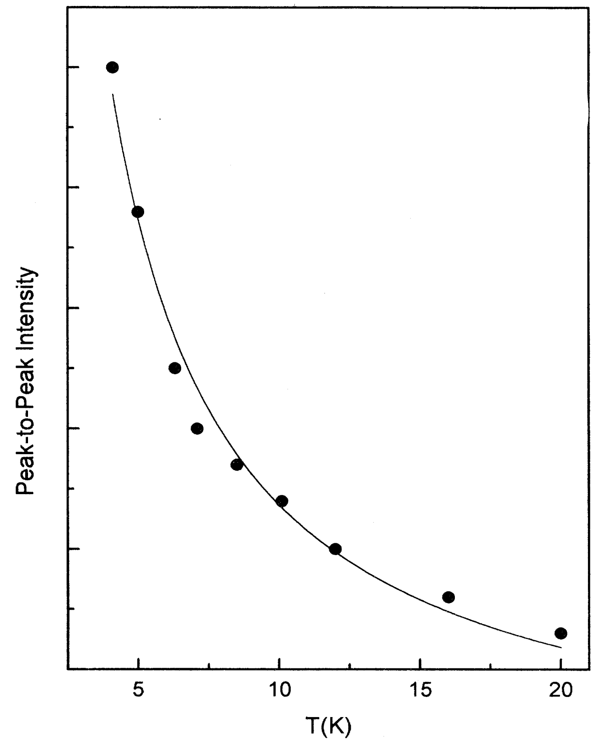

FIG. 2. Temperature dependence of the peak-to-peak intensity of the Cu^{2+} EPR spectrum in $PrBa_2Cu_3O_{6+x}$. The solid line corresponds to an $\sim 1/T$ law.

In order to obtain information on the ground state of these Cu^{2+} centers we employ the well-known formulas for the g values of copper ions in axial and rhombic local field symmetry. In the orthorhombic symmetry, observed for the fresh $PrBa_2Cu_3O_{6+x}$ sample, both the $d(x^2-y^2)$ and the $d(3z^2-r^2)$ orbitals belong to the same irreducible representation and the corresponding ground state Ψ_1 can be written in the crystal-field approximation as[25] $\Psi_1=ad(x^2-y^2)-bd(3z^2-r^2)$ with the normalization condition $a^2+b^2=1$. The corresponding g values are then given by $g_z=2.0023-8\lambda_0\kappa_1^2\alpha^2/E_{xy}$, $g_y=2.0023-2\lambda_0\kappa_2^2(a+\sqrt{3}b)^2/E_{xz}$, and $g_x=2.0023-2\lambda_0\kappa_3^2(a-\sqrt{3}b)^2/E_{yz}$, where λ_0 is the spin-orbit coupling constant equal to -828 cm^{-1} for the free Cu^{2+} ion, $\kappa_i(1,2,3)$ are the covalency reduction parameters and $E_{ij}(i,j=x,y,z)$ is the splitting energy of the d_{ij} level with respect to the ground one.

According to crystal-field theory, the relation $g_z>g_y>g_x$ between the principal values of the g tensor implies an essentially $d(x^2-y^2)$ ground state. The actual values of the splitting energies are not known. However, in order to obtain an estimate of the ground state, we make use of the $d\leftrightarrow d$ transitions identified in the optical spectra of nonsuperconducting, tetragonal thin films of Y123.[26] In that work, three transitions at ~ 0.5, 1.7, and 2.57 eV were detected, from which it is plausible to assume that $E_{xy}\sim 1.7$ eV and $E_{xz},E_{yz}\sim 2.57$ eV, while the first transition at ~ 0.5 eV is most probably associated with the excitation between the ground state and the corresponding excited one. Using the equations for the g values and further assuming $\kappa_2^2=\kappa_3^2=\kappa_\perp^2$ (Ref. 25), the following values of the relevant parameters were derived: $a=0.985$, $b=0.17$, and $\kappa_1^2=0.45$, $\kappa_\perp^2=0.65$. The small values of κ_i^2 reveal the presence of considerable covalent bonding, especially in the xy plane, indicating increased delocalization of the Cu^{2+} unpaired electron density to the ligand atoms, which may be further related to the suppression of the hyperfine structure in the corresponding spectrum.

In the tetragonal crystal-field symmetry, the observed relation $g_{\parallel} > g_{\perp}$ indicates a $d(x^2-y^2)$ ground state which can be approximated with the B_{1g} antibonding molecular orbital derived for the square planar Cu^{2+} complex:[27]

$$\Psi_{B1g} = ad(x^2-y^2) - a'(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})/2 ,$$

where $\sigma^{(i)} (i = 1,2,3,4)$ are the sp^2 hybridized orbitals of the four oxygen ligands in the xy plane. Then, a^2 can be approximated by

$$a^2 = -A_{\parallel}/P + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} + 2.0023) + 0.04 ,$$

where $P = g\mu_B g_N \mu_N \langle r^{-3} \rangle = 0.036$ for the free Cu^{2+} ion. Using this relation and the experimental values of $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$ we obtained the values of $a^2 = 0.82$ and $a^2 = 0.79$ for the Pr123 and (Pr,Er)123 compounds, respectively.

To our knowledge, there has not been any report on the hyperfine structure of the Cu^{2+} EPR spectrum in the R123 materials, except for the case of CuO thin films annealed at high temperatures ($\theta > 600$ °C), where the dilution of the CuO molecules into the glass substrate gave rise to magnetically isolated Cu^{2+} paramagnetic centers.[28] The observation of the axial hyperfine structured Cu^{2+} EPR spectra for the Pr-based samples, indicates the presence of isolated divalent copper centers with significantly lower relaxation rate than for the other R123 compounds and considerable degree of localization of the Cu^{2+} ions, as evidenced from the relatively high value of the a^2 parameter.

For the $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_{6+x}$ sample a more complicated EPR spectrum was detected (Fig. 3), comprising, besides the Cu^{2+} pattern (note the hyperfine line at ~275 mT), additional lines at the center of the spectrum and at lower and higher field (lines 1 to 6 in Fig. 3) arising from pairs of exchange-coupled copper ions. In a preliminary account of this work,[29] this EPR spectrum was described, assuming for simplicity isotropic g and A tensors, by the following spin Hamiltonian in the Zeeman representation:[30]

$$H = g\mu_B B(S_{1z} + S_{2z}) + A(S_1 \cdot I_1 + S_2 \cdot I_2) + \sum_{p,q=x,y,z} D_{pq} S_{1z} S_{2z} - J S_1 \cdot S_2 , \qquad (2)$$

where S_1, S_2 are the spin operators of the two copper electrons, I_1 and I_2 are the corresponding nuclear spins, D_{pq} are the dipolar tensor components in the Zeeman representation, and J is the exchange parameter. In the weak exchange limit $J < h\nu$, there are four $\Delta M = \pm 1$ transitions and one $\Delta M = \pm 2$. The first-order transitions fields are[30]

$$B_i = B_0 + [\pm(D_{zz} - J) - A(M_{I1} + M_{I2})]/2g\mu_B \pm \varphi/g\mu_B \qquad (3a)$$

for the four $\Delta M = \pm 1$ transitions, and

$$B = B_0/2 - A(M_{I1} + M_{I2})/2g\mu_B \qquad (3b)$$

for the $\Delta M = \pm 2$ transition, with

$$\varphi = \{[1/2(D_{xx} + D_{yy}) - J]^2 + A^2(M_{I1} - M_{I2})^2\}^{1/2}/2 ,$$

and $B_0 = h\nu/g\mu_B$.

When the anisotropic interactions become vanishingly small $D_{pq} \ll J$, the φ term tends to a value of $[J + A(M_{I1} + M_{I2})]/2$ so that two of the $\Delta M = \pm 1$ transitions merge to a single one at the center of the spectrum, while the other two occur at resonance fields $B_0 \pm J/g\mu_B$. The latter transitions are usually referred to as the singlet-triplet ($S \leftrightarrow T$) transitions and in the case of negligible anisotropic interactions becomes allowed through the nuclear hyperfine interaction. The two lines (3) and (4) [Fig. 3(b)] at higher (~580 mT) and lower field (~90 mT) can be identified as the $S \leftrightarrow T$ transitions, while the other two more intense and sharper lines overlapping with the Cu^{2+} spectrum, depicted with (1) and (2) in Fig. 3(a), can be identified as the transitions between the $S = 1$ states of the copper pair. From their positions a value of the exchange parameter $J = 0.22$ cm^{-1} and a small value of the zero-field splitting parameter $D \sim 0.013$ cm^{-1} can be derived. However, this interpretation does not explain the broad feature, line (5) in Fig. 3(b), observed at ~760 mT and requires the presence of additional copper pairs with larger exchange parameter.

Another possible explanation is to consider the spectrum as a result of the superposition of two different pair spectra. The first one can be identified as a triplet ($S = 1$) spectrum with large zero-field splitting.[31] Using the reported formulas for the powder $S = 1$ spectrum,[31] the most pronounced lines at ~90 mT ($z1$ transition), ~580 mT ($y2$ transition), and 760 mT ($z2$ transition) can be described by an $S = 1$ state with axial zero-field splitting constant of $D \sim 0.4$ cm^{-1} and a small rhombic component. Additional lines of weak intensity are expected to occur at ~200 mT (double quantum transition) and ~450 mT ($\times 2$ transition), which probably are present in the spectrum but due to their small intensity are in the

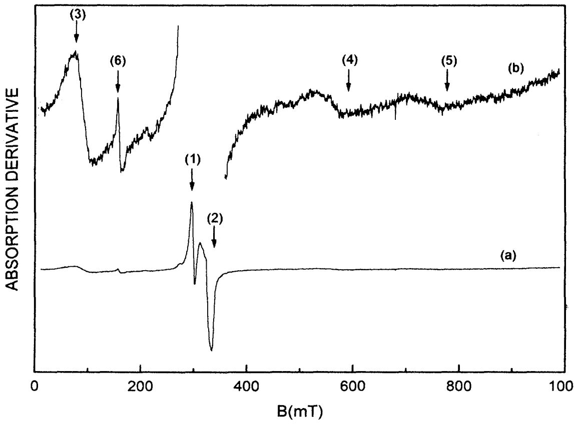

FIG. 3. The EPR spectrum of the fresh $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_{6+x}$ sample at 4.4 K at (a) low and (b) high spectrometer gain. The arrows indicate the transition fields of the pair EPR spectra.

limit of noise [Fig. 3(b)]. The second pair spectrum will be responsible for the sharp lines (1) and (2) and can be identified as a typical powder spectrum of copper pairs with small zero-field splitting, frequently occurring for dipolar coupled copper dimers.[32] The line (6) centered at $g=4.19(1)$ can be identified as the half-field $\Delta M=\pm 2$ transition of the latter spectrum. However, its shape and position is very similar to the spikelike line arising from Fe^{3+} ions in rhombic symmetry and may arise from traces of iron impurity in the sample or in the resonant cavity, and thus for the present time we consider the origin of this line ambiguous.

The temperature dependence of the intensity of the first type of pair spectrum follows closely the $1/T$ law indicating that the $S=1$ state is either the ground state of the copper pair (ferromagnetic exchange interaction) or that the antiferromagnetic exchange interaction is rather small ($J<4$ K), so that at the studied temperature range the excited triplet is well populated according to the Boltzmann statistics. For the second type of pair spectrum [sharp lines 1 and 2 in Fig. 3(a)], the intensity is rather difficult to be traced due to its superposition with the monomer Cu^{2+} EPR spectrum. However, the amplitude of line (1) decreases with increasing temperature from 4 K, indicating a small exchange interaction.

The EPR spectrum of (Pr,Y)123 after a time period of 1 month is presented in Fig. 4. As can be seen, the main features of the first type pair spectrum (large D) remained the same, while the lines at the center merged into a single spectrum which can be simulated with an orthorhombic g tensor with principal values close to those obtained for the corresponding Cu^{2+} spectrum in the Pr123 sample. Additionally, the intensity of the $g\sim 4.2$ line decreased considerably following the decrease of the intensity of the central pair spectrum and thus indicating that this line may belong to the pair spectrum with the small D value. It is also worth noting that a similar line with $g\sim 4.2$ has been previously detected in the nonoxygenated phase of the $LaBaSrCu_3O_{6+x}$ compound but not in the corresponding oxygenated sample implying that its origin cannot be easily related with iron traces in the samples.

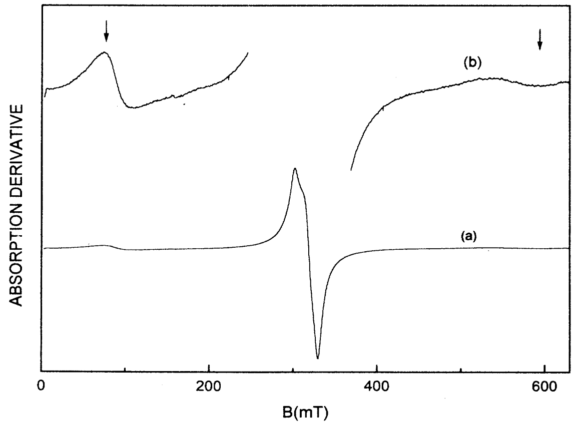

FIG. 4. The EPR spectrum of the aged $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_{6+x}$ sample at 4.4 K at (a) low and (b) high spectrometer gain. The arrows indicate the transition fields of the pair EPR spectrum with the large D value.

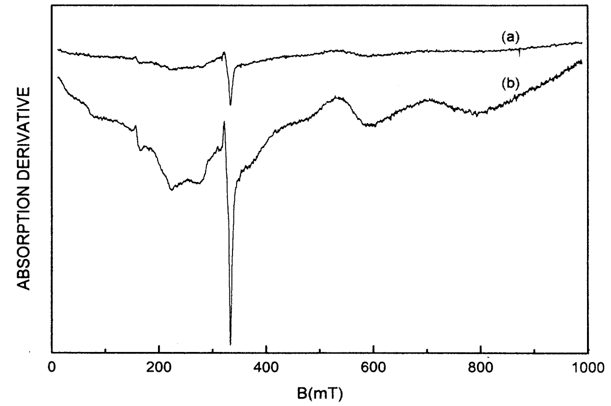

FIG. 5. The EPR spectrum of the fresh sample $Pr_{0.5}Er_{0.5}Ba_2Cu_3O_{6+x}$ recorded at (a) 1 mW and (b) 31 mW microwave power. The spectra were taken at 10 K.

For the (Pr,Er)123 sample, at higher microwave power, a similar but more complicated EPR spectrum appeared (Fig. 5). The complexity of the spectrum is mainly due to the presence of a broad background line arising from the resonance of the Er^{3+} ions, which cannot be simulated very accurately and subtracted from the spectrum. An analysis of the Er^{3+} EPR resonance in the Er123 matrix on the basis of the crystal-field interaction will be given in a forthcoming paper. For the present case, we note that dipolar interactions among the Er ions, for Er-concentration reduced by 50% as in the studied sample, may give resonance lines with peak-to-peak width, for the Gaussian line shape, of at least 300 mT, while additional broadening may occur at low temperatures due to ordering effects of the rare-earth sublattice. However, from Fig. 5 the absorptionlike lines of the triplet $S=1$ spectrum can be seen at ~ 600 and ~ 800 mT, while the $z1$ transition at ~ 90 mT can also be traced, though relatively obscured by the Er resonance. The feature at ~ 200 mT may be related with the double quantum transition of the triplet spectrum and its relatively strong intensity complies with the increased microwave power needed to detect this line.[31] The shift of the $y2(\sim 600$ mT) and $z2(\sim 800$ mT) transitions to higher field in comparison with the corresponding (Pr,Y)123 spectrum indicate a slightly larger D parameter. Additional lines are observed in the center of the spectrum which, however, cannot be resolved. Finally, we note that for the Pr123 sample similar features at ~ 90 and ~ 600 mT were also observed but with very weak intensity in comparison with the Cu^{2+} spectrum.

III. DISCUSSION

The assignment of the "isolated" Cu^{2+} ions to any special copper site in the crystal lattice is rather difficult with the present powder EPR data. However, their origin can possibly be traced on a small fraction of the $Cu^{2+}(1)$ ions induced by the incorporation of the excess oxygen ($x \sim 0.2$) in the oxygen-deficient Cu(1) planes, rather than the Cu(2) ones where the strong in-plane antiferromagnetic correlations are expected to suppress the EPR resonance. Additionally, the presence of any oxygen vacancies leading to the stabilization of the Cu^{2+} resonance is most likely to occur in the Cu(1) plane rather than the Cu(2) one where all oxygen sites are expected to be fully occupied.

A previous EPR study on an oxygen-deficient Y123 single crystal of tetragonal structure revealed the presence of a weak tetragonal Cu^{2+} EPR spectrum with g values relatively close to the present ones.[13] That EPR spectrum was attributed to $Cu^{2+}(1)$ ions in a pseudo-octahedral coordination, suffering an elongation along the c axis due to the action of a pseudo-Jahn-Teller effect. The same model was used to allow for the tetragonal Cu^{2+} EPR spectra observed in the $LaBaSrCu_3O_{6+x}$ compound, where the presence of the structurally frustrating La and Sr atoms causes a disordered oxygen distribution in the Cu(1) plane, resulting in an averaging of the crystal structure to tetragonal, independently on the oxygen content.[14] The sixfold coordination around Cu(1) was assumed in order to comply with the single-crystal EPR data[13] which defined $g_{\parallel}$ to be along the crystallographic c axis, with the resultant $d(x^2-y^2)$ ground state in the ab plane.[14] Evidence for an elongation of the octahedral coordination along the c axis is provided by extended x-ray-absorption fine-structure experiments on Y123 materials, which revealed a double-site configuration of the apical oxygen atom O(4), with the two corresponding Cu(1)-O(4) bond lengths differing considerably by ~ 0.13 Å.[33,24] The double-site O(4) configuration has been related to the motion of the O(4) atom in an anharmonic double-well potential.[33] However, the EPR observation of this effect, i.e., the O(4) atom at the longest distance from the Cu(1) atom, would not be possible, since the estimated tunneling frequency between the two sites is about 10^{13} Hz. A more likely explanation emerges within the picture of a static model proposed in Ref. 35, where the double-site O(4) configuration has been interpreted in terms of vacancy-induced local static distortions. In this case, the elongation of the Cu(1)-O(4) bond may be stabilized by the presence of next-nearest-neighbor oxygen vacancies in the Cu(1) plane.

In the present case, sixfold-coordinated Cu(1) ions are not very likely to occur, though not impossible. On the other hand, the axial local symmetry observed for the Cu^{2+} resonance at a certain time period is relatively high and implies that the corresponding centers should not have a very distorted oxygen coordination. Moreover, the observation of the hyperfine structure and the normal temperature behavior of their intensity imply that these centers are magnetically isolated from the antiferromagnetic copper planes. If these Cu centers were to occur in magnetically unassociated regions from the main lattice, they should be observable in Y123 and other R123 compounds as well. However, there has not been any reports of such signals in these compounds. In this respect, it seems that praseodymium plays an important role in the localization of these copper centers. The presence of the Pr ions, besides the immediate effect on its neighboring Cu(2) planes, e.g., the shortening of the distance among Pr and the oxygen atoms in the Cu(2) planes,[36] is expected to affect the more distant oxygen environment of the Cu(1) layer, e.g., the apical oxygen O(4), as well. Such an effect becomes evident if we consider the idea of holes being present in the Cu(1) chains only,[17] which inevitably requires a significant distortion of the apical oxygen which controls the charge transfer from the Cu(1) chains to the Cu(2) planes. In this case, it can be suggested that paramagnetic Cu(1) centers may effectively become "isolated" from the antiferromagnetic Cu(2) planes giving rise to the observed EPR spectra.

In this context, it is also worth noting the results of a recent spin-polarized MSXa calculation of the electronic structure of the square planar CuO_4^{6-} cluster.[37] They indicated the stabilization of the A_{1g} molecular orbital, which is nonmagnetic due to a dominant contribution of the oxygen $3s$ orbitals, as the ground state for short Cu-O distances (1.90 Å), while it was found that the stabilization of the B_{1g} magnetic ground state is favored by an increased Cu-O distance, e.g., 1.96 Å, or any other distortions, e.g., pseudotetrahedral distortion, that effectively increase the oxygen's separation. In the Pr case, one can speculate that the presence of subtle local structural distortions in the Cu(1) environment may be effective in the formation of localized Cu^{2+} centers. Furthermore, the observed time evolution of the EPR spectrum, which revealed a lowering of the local axial symmetry of Cu^{2+} ions to orthorhombic, can be related to any slight mobility of oxygen in the basal Cu(1) plane when stored at room temperature.

Based on similar arguments as for the Cu^{2+} monomers, the origin of the observed EPR pair spectra may be traced on a small number of Cu(1)-O-Cu(1) superexchange coupled pairs in the ab plane. The formation of copper pairs in the Cu(1) plane has been suggested from a superstructure investigation of an oxygen-deficient $YBa_2Cu_3O_{6+x}$ single crystal with $x=0.35$, by x-ray diffraction.[38] The derived superstructure cell consisted of well-separated, linear Cu-O-Cu dimers on every fourth site on the a and b axes, with the Cu(1) atoms shifted perpendicular to their dimer axis due to the effect of local strain. It was also found that only a small percentage (12%) of the oxygen atoms in the ab plane contributed to that superstructure, indicating a small number of such dimers. Additionally, theoretical calculations of oxygen superstructures in the oxygen-deficient $RBa_2Cu_3O_{6+x}$ compounds,[39] predict for low oxygen content ($x=1/8$) the appearance of superstructures in the Cu(1) plane comprising spatially isolated copper dimers. However, the question that naturally arises is why such copper dimers are not observed in Y123 materials but only in the Pr-based compounds. It seems that in the latter compounds these copper centers do not interact significantly with the antiferromagnetic CuO_2 planes and that the superexchange interaction, most probably antiferromagnetic, among them is effectively reduced.

In summary, we have presented the EPR spectra of localized Cu^{2+} ions in the oxygen-deficient $PrBa_2Cu_3O_{6+x}$ and $Pr_{0.5}R_{0.5}Ba_2Cu_3O_{6+x}$ (R =Y,Er) compounds. The observation of the copper hyperfine structure along with the derived g values allowed an estimate of the copper's ground state indicating a considerable degree of localization for the corresponding Cu^{2+} ions. The Cu^{2+} EPR spectra exhibited a significant time evolution deduced by the transformation of the local crystal-field symmetry from orthorhombic to tetragonal. These Cu^{2+} centers were ascribed to divalent copper ions in the Cu(1) sites, subjected to the action of Pr-induced local structural distortions. The observed time evolution of the EPR spectra was related to the time-dependent oxygen distribution in the basal Cu(1). Additionally, the EPR spectra of two kinds of pairs of copper ions were detected with large ($D \sim 0.4$ cm^{-1}) and small zero-field splitting constants and weak exchange interaction. These copper pairs were suggested to arise from a small fraction of magnetically isolated superexchange coupled Cu^{2+}(1) ions.

ACKNOWLEDGMENT

This work was partially supported by the General Secretariat for Research and Technology, Greece, under Grant No. 91 EΔ 312.

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