PHYSICAL REVIEW B VOLUME 39, NUMBER 10 1 APRIL 1989

ESR experiments and spectra simulations in $YBa_2Cu_3O_{7-x}$, Y_2BaCuO_5, and $BaCuO_{2+x}$

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(Received 16 June 1988; revised manuscript received 26 September 1988)

Room-temperature *X*- and *Q*-band ESR spectra of the high-T_c superconductor $YBa_2Cu_3O_{7-x}$ and the semiconductors Y_2BaCuO_5 and $BaCuO_{2+x}$ are studied experimentally and theoretically by measuring, calculating, and fitting the powder spectra corresponding to an anisotropic Zeeman Hamiltonian for Cu^{2+} in orthorhombic and tetragonal local symmetries. ESR and x-ray studies in their corresponding oxygen-deficient stoichiometries, obtained by heat treatment under vacuum, were also done. Our results support those of Bowden *et al.* and Vier *et al.* in $RBa_2Cu_3O_{7-x}$ (R=Y, Eu), indicating that the Cu(1) and Cu(2) atoms in the pure $YBa_2Cu_3O_{7-x}$ phase are not ESR active and the small resonance observed in these compounds comes from other residual phases. The purest $YBa_2Cu_3O_{7-x}$ samples that we were able to prepare still have 0.1–0.5% mass fraction of other residual copper compounds which are responsible for the observed resonance.

INTRODUCTION

Since the pioneering work of Bednorz and Müller[1] on high-temperature ceramic superconductors a great amount of experimental work using different techniques has been done in $La_{2-x}Ba_xCuO_4$, $YBa_2Cu_3O_{7-x}$, and other isomorphous compounds. In particular, many reports on ESR, looking for the Cu^{2+} ($3d^9$) resonance in these compounds, have been published.[2-4] Although most of these results have shown, in general, the same features for the ESR spectra, the interpretations about the resonance observed at room temperature are not in agreement.[5-8] The main divergence comes from the fact that some authors attributed the observed resonance in these compounds to Cu^{2+} ions located in the superconducting compound and others to residual copper compounds which could still be present in the sample.

Therefore, this work aims to fit theoretical spectra simulations to the data obtained from systematic ESR experiments in several samples of the ceramic superconductor $YBa_2Cu_3O_{7-x}$ and in the semiconductors Y_2BaCuO_5 and $BaCuO_{2+x}$, as well as in their corresponding oxygen-deficient stoichiometry, in order to see if with these systematics we can help to clarify the problem of whether the observed ESR spectra can or cannot be attributed to Cu^{2+} ions in the superconducting ceramic. The conclusions of the present work are in agreement with those of Vier *et al.*[6] and Bowden *et al.*[7] in the sense that in the pure $YBa_2Cu_3O_{7-x}$ phase the Cu(1) and Cu(2) atoms are not ESR active, and that the resonance observed in these compounds is due to residual copper compounds. However, we show that they cannot be attributed to either Y_2BaCuO_4 or $BaCuO_{2+x}$.

EXPERIMENT

The samples were prepared according to the solid diffusion method which was reported previously.[5] The only difference was that for the present batch of samples the process of grinding and annealing during 20 h at 950 °C was repeated 3 to 6 times in order to get as much pure single-phase sample as possible. All the lines observed in the x-ray powder-diffraction pattern were indexed according to the reported data for the structures corresponding to $YBa_2Cu_3O_7$,[9] Y_2BaCuO_5,[10] and $BaCuO_{2+x}$.[11] Within the accuracy of the x-ray experiments no spurious phases were detected. Therefore, as far as the x-ray experiment is concerned our samples were at least 99% pure.

The deoxygenated samples were obtained after heating under a vacuum of 10^{-3} Torr during 20 h at various temperatures between 350 and 450 °C. The reoxygenated samples were obtained after a heat treatment at 450 °C during 12 h in an atmosphere of circulating oxygen, although only 3 h were enough to recover almost the same original oxygen concentration, except for the samples of Y_2BaCuO_5 (see below). The corresponding oxygen concentrations were calculated from the samples mass loss and gain after each heat treatment.[12]

The ESR experiments were carried out at room temperature in conventional ESR Varian *E*-line *X*- and *Q*-band spectrometers using a TE_{102} 100-kHz and TE_{011} 1-kHz cavities for *X* and *Q*-band, respectively. The samples were always run in the form of fine powder (10–30 μm) and were, in all cases, kept in a dry atmosphere.

The multiplicative factor shown on each spectra of various figures corresponds to the relative sensitivity necessary to observe the ESR spectra of the same mass of pure Y_2BaCuO_5. These factors already take into account the spectrometer gain, magnetic-field modulation amplitude, *Q* of the cavity, mass of the sample, etc. No corrections for skin depth were necessary because the size of the fine powder used in the experiments was always smaller than the skin depth corresponding to the conductivity of these materials (skin depth $\simeq 40\ \mu$m).

RESULTS

Y_2BaCuO_5

Figures 1(a)–1(d) show the X-band ESR spectra of Y_2BaCuO_5 after each deoxygenation and reoxygenation treatment. This figure shows that, except for small differences in the spectrometer set up conditions, no significant changes in the spectra could be observed. If $\alpha = \Delta m / m_0$ is defined as the fractional mass losses (see Fig. 1), then we observe that in spite of the small mass losses after each deoxygenation treatment, we could not attribute these losses to oxygen deficiencies because during the reoxygenation α was still increasing. Probably a small amount of barium carbonate was present in the original sample, therefore requiring more time to complete the full reaction.

X-ray-diffraction experiments in this series of samples did not reveal any other phases except Y_2BaCuO_5.

Figure 2 shows the ESR spectra of Y_2BaCuO_5 at X- and Q-band which were used to fit the theoretical powder spectra of Cu^{2+} (see below). The intensity of the observed resonance corresponds approximately to the total number of Cu^{2+} ions contained in the sample, in agreement with the reported data.[13,14]

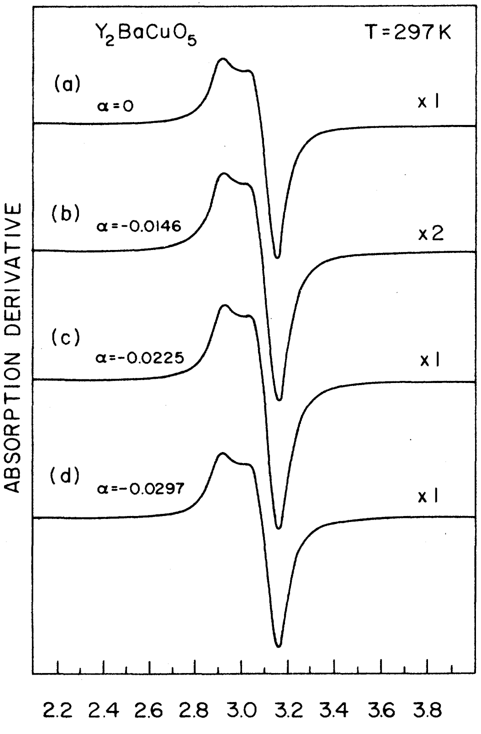

FIG. 1. X-band (9.08 GHz) ESR powder spectra of Y_2BaCuO_5 at $T = 297$ K after (a) freshly prepared, (b) and (c) deoxygenated during 20 h at 300 and 350 °C, respectively, (d) reoxygenated during 12 h at 450 °C. The parameter $\alpha = \Delta m / m_0$ indicates the fractional sample mass losses.

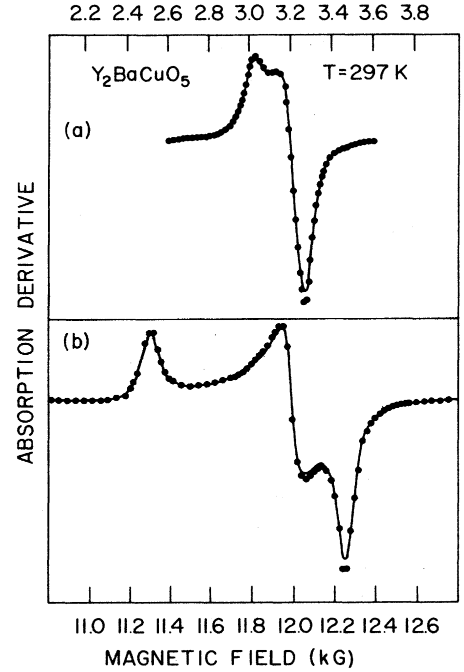

FIG. 2. ESR powder spectra of Y_2BaCuO_5 at $T = 297$ K. (a) X-band (9.50 GHz) and (b) Q-band (35.0 GHz). The theoretical fit gives $g_x = 2.08 \pm 0.01$, $g_y = 2.12 \pm 0.02$, $g_z = 2.25 \pm 0.01$; $\Delta H = (25 \pm 5)$ G and $\Delta H = (70 \pm 10)$ G for X and Q-band, respectively.

$BaCuO_{2+x}$

Figures 3(a)–3(d) show the X-band ESR spectra of $BaCuO_{2+x}$ for the same deoxygenation and reoxygenation treatment given to Y_2BaCuO_5. In this case a clear increase of the intensity and linewidth of the spectra is observed for the deoxygenated samples [Figs. 3(b) and 3(c)] and a subsequent decrease of the resonance intensity for the reoxygenated sample [Fig. 3(d)].

The samples corresponding to Figs. 3(b) and 3(c) showed clear mass losses during the deoxygenation treatment and that of Fig. 3(d), corresponding to the reoxygenation, showed an increase of the mass in exactly the same amount of the total losses during the deoxygenation treatment.[12] The oxygen concentrations shown in Fig. 3 were obtained after labeling the sample with the smallest concentration as being $BaCuO_2$.[15] The spectra corresponding to this sample was not shown because it gives similar spectra to that of Fig. 3(c).

Figure 4 shows the ESR spectra of $BaCuO_{2.02}$ at X- and Q-band which were used to fit the theoretical powder spectra of Cu^{2+} (see below).

X-ray-diffraction experiments in this series of samples show that the oxygen-rich $BaCuO_{2+x}$ samples do not present any structural changes as x is exchanged. The lattice parameter measured was in agreement with that found by Migeon *et al.*[15]

Figure 5 shows the time evolution of the X-band ESR spectra of $BaCuO_{2.07}$. The data were taken in a period of two months while the sample was kept in a dry atmo-

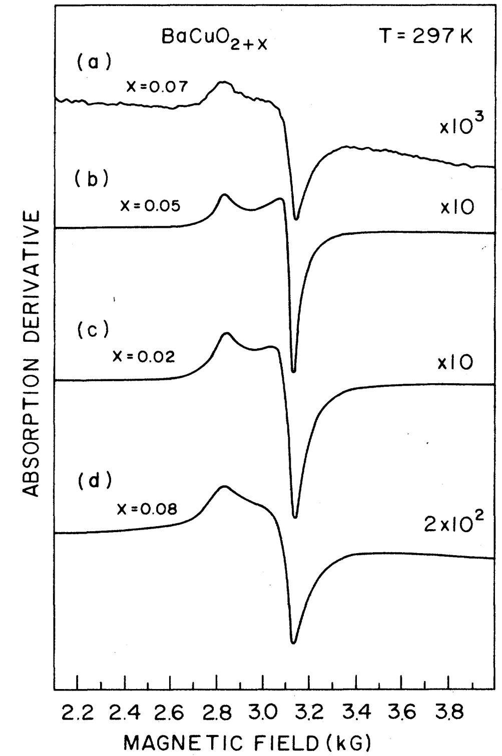

FIG. 3. X-band (9.08 GHz) ESR powder spectra of $BaCuO_{2+x}$ at $T=297$ K after (a) freshly prepared, (b) and (c) deoxygenated during 20 h at 300 and 350 °C, respectively, (d) reoxygenated during 12 h at 450 °C.

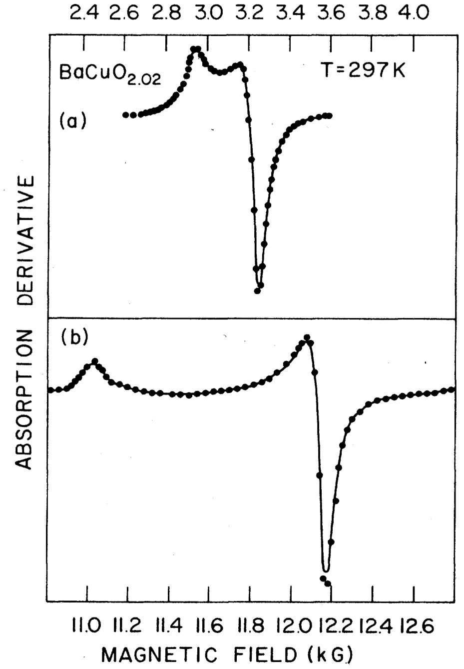

FIG. 4. ESR powder spectra of $BaCuO_{2.02}$ corresponding to the sample of Fig. 3(c) at $T=297$ K (a) X-band (9.50 GHz) and (b) Q-band (35.0 GHz). The theoretical fit gives $g_x=g_y=2.055\pm0.005$, $g_z=2.24\pm0.01$; $\Delta H=(40\pm5)$ G and $\Delta H=(100\pm10)$ G for X- and Q-band, respectively.

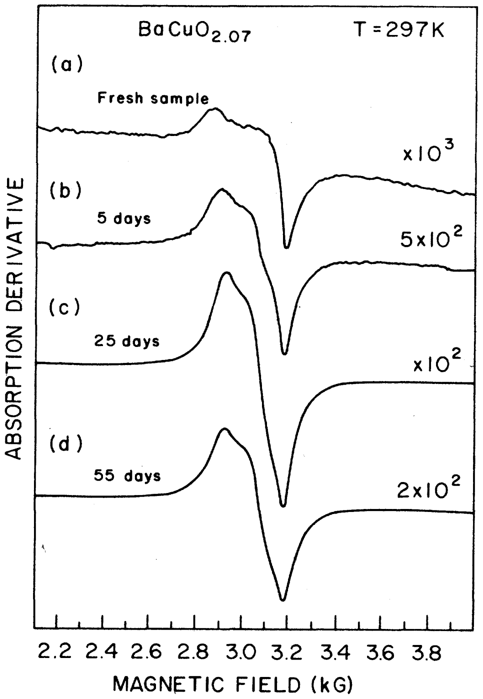

FIG. 5. Time evolution of the ESR powder spectra of $BaCuO_{2.07}$ after (a) freshly prepared, (b) 7 days, (c) 25 days, and (d) 60 days.

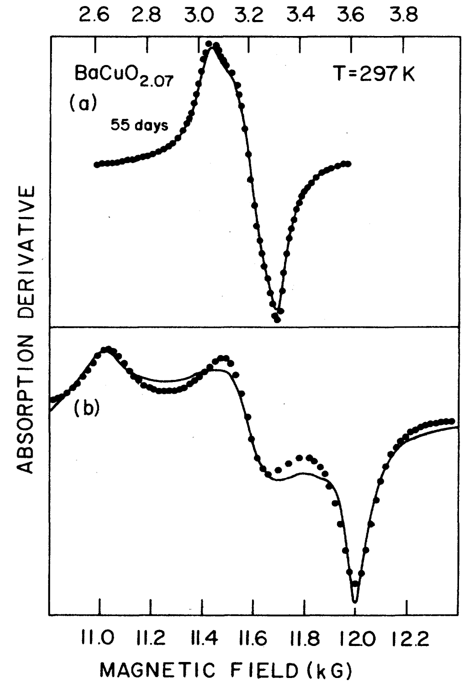

FIG. 6. ESR powder spectra of the $BaCuO_{2.07}$ corresponding to the sample of Fig. 5(d) at $T=297$ K. (a) X-band (9.50 GHz) and (b) Q-band (34.51 GHz). The theoretical fit gives $g_x=2.05\pm0.02$, $g_y=2.12\pm0.02$, $g_z=2.22\pm0.02$; $\Delta H=(68\pm5)$ G and $\Delta H=(202\pm20)$ G for X- and Q-band, respectively.

sphere of silica gel. The change in line shape and increase of the resonance intensity indicate that $BaCuO_{2.07}$ can easily react, probably to form some other compound whose spectra is clearly different from those of $BaCuO_{2+x}$ as shown in Fig. 3.

Figure 6 shows the ESR spectra of $BaCuO_{2.07}$ corresponding to Fig. 5(d) at *X*- and *Q*-band which were used to fit the theoretical powder spectra of Cu^{2+} (see below).

X-ray-diffraction experiments in this sample also show time evolution, revealing that other phases emerge after a few months.

$YBa_2Cu_3O_{7-x}$

Figures 7(a)–7(d) and 8(a)–8(d) show the *X*-band ESR spectra of two samples of $YBa_2Cu_3O_{7-x}$ for the same deoxygenation and reoxygenation treatment given to Y_2BaCuO_5 and $BaCuO_{2+x}$. The data show that no appreciable change is observed in the intensity of the resonance at various oxygen stages, but there is however a small change in the line shape of the resonance.

The spectra of Figs. 7(a) and 8(a) correspond to samples which were milled three and six times and annealed at 950 °C in an oxygen atmosphere during a total of 60 and 120 h, respectively, in steps of 20 h. As we can see it is clear from these data that the longer the heat treatment the smaller the observed resonance. The relative intensity of the resonance for the sample of Fig. 8(a), to that of the green phase (Y_2BaCuO_5) of Fig. 1, allow us to estimate that there are still about 0.1% mass fraction of spurious phases in our purest $YBa_2Cu_3O_{7-x}$ samples. Indeed, very small regions of a secondary phase could be observed

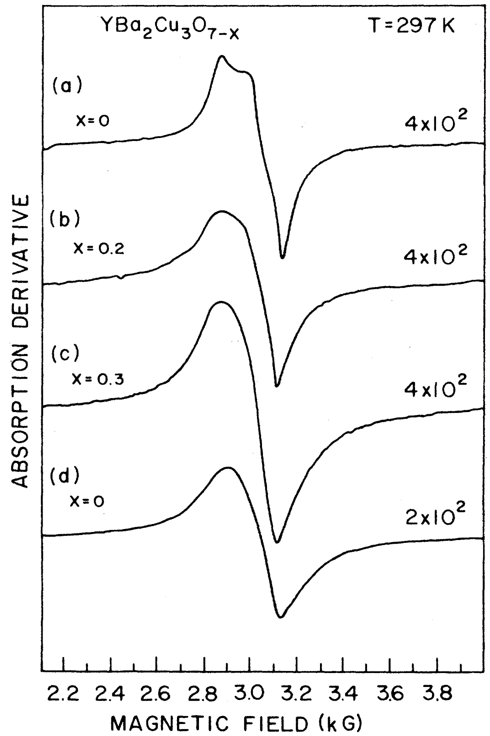

FIG. 7. *X*-band (9.08 GHz) ESR powder spectra of $YBa_2Cu_3O_{7-x}$ at $T=297$ K after (a) freshly prepared (milled three times and annealed at 950 °C during a total of 60 h in steps of 20 h), (b) and (c) deoxygenated during 20 h at 300 and 350 °C, respectively, (d) reoxygenated during 12 h at 450 °C.

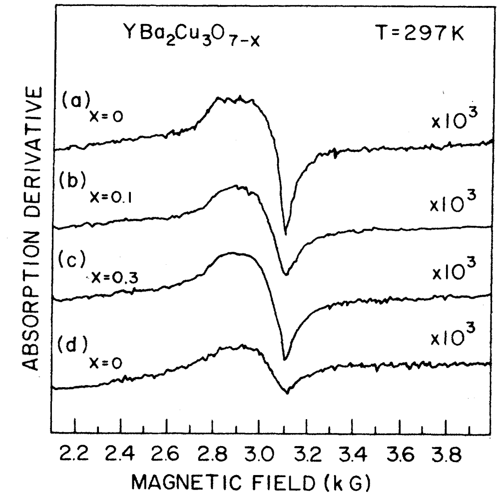

FIG. 8. *X*-band (9.08 GHz) ESR powder spectra of $YBa_2Cu_3O_{7-x}$ at $T=297$ K after (a) freshly prepared (milled six times and annealed at 950 °C during a total of 120 h in steps of 20 h), (b) and (c) deoxygenated during 20 h at 300 and 350 °C, respectively, (d) reoxygenated during 12 h at 450 °C.

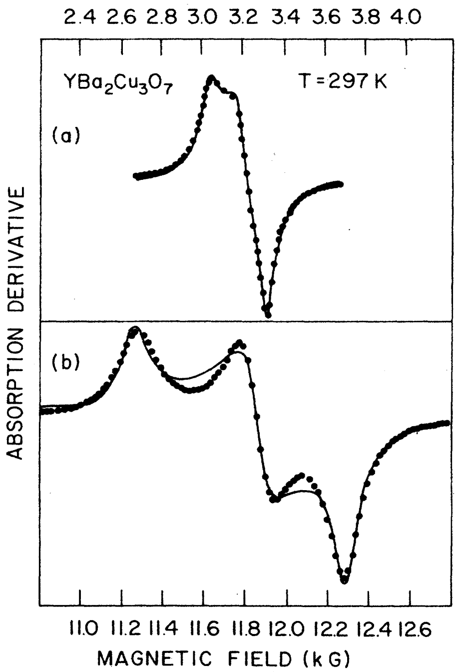

FIG. 9. ESR powder spectra of the $YBa_2Cu_3O_7$ corresponding to the sample of Fig. 7(a) at $T=297$ K. (a) *X*-band (9.50 GHz) and (b) *Q*-band (34.84 GHz). The theoretical fit gives $g_x=2.05\pm0.02$, $g_y=2.09\pm0.03$, $g_z=2.24\pm0.02$; $\Delta H=(65\pm8)$ G and $\Delta H=(188\pm20)$ G for *X*- and *Q*-band, respectively.

through optical microscopy on the $YBa_2Cu_3O_{7-x}$ polished samples. This proved to be a very useful and simple technique for secondary phase detection.

Within the accuracy of our x-ray-diffraction experiments no phase other than the orthorhombic $YBa_2Cu_3O_{7-x}$ phase could be detected in the samples of Figs. 7(a) and 8(a). But the well-known transformation from orthorhombic to tetragonal structure[16] was clearly in both series of samples as the oxygen deficiency was increased.

Figure 9 shows the ESR spectra of $YBa_2Cu_3O_{7-x}$ corresponding to the Fig. 7(a) at *X*- and *Q*-band which were used to fit the theoretical powder spectra of Cu^{2+} (see below).

ANALYSIS AND DISCUSSION

The structure of each compound studied in this work has at least two different Cu sites per unit cell. As the Cu^{2+} ($3d^9$) ions at different sites are close enough, it is expected that exchange (or superexchange) interaction will couple them. It is well known that, first, when the exchange energy between ions is big enough as compared with the hyperfine parameter, the whole hyperfine structure collapses to only one line; second, when the difference between the Zeeman energies for the two sites is less than the exchange, the two lines corresponding to the two sites also collapse to only one resonance. Taking this into consideration, we expect to have only one exchange-narrowed resonance for all the different interacting Cu^{2+} ions.[17-20]

Considering the Zeeman energy difference between two sites to be small, the *g*-matrix still transforms as a tensor

$$\overleftrightarrow{g}^2 = (\overleftrightarrow{g}_A^2 + \overleftrightarrow{g}_B^2)/2\,, \tag{1}$$

where *A* and *B* represent two Cu^{2+} sites.[17,19] These considerations can be extended for more than two sites and the energy of the system can be written as

$$\hat{H} = \mu_B \mathbf{H} \overleftrightarrow{g} \mathbf{S} \tag{2}$$

for an effective spin $\frac{1}{2}$.

Since the line shape $P(H, \theta, \phi)$ in the presence of exchange is nearly Lorentzian,[20] we assume a Lorentzian line shape to calculate the spectra. Furthermore, we need a few more assumptions to calculate the spectra. These are (i) three orthogonal axes *x*, *y*, and *z* are chosen to coincide with the principal axes of the *g*-tensor; (ii) the linewidth is isotropic; (iii) the crystallites in the powder are randomly oriented; and (iv) the absorption coefficient *K* is proportional to[21,22]

$$K \sim [(g_x g_z/g)^2 + g_y^2]\,. \tag{3}$$

Then, the line shape for our resonance will be given by

$$I(H) = \gamma \int_0^{\pi/2} K P(H,\theta,\phi) \sin\theta \, d\theta\,. \tag{4}$$

We calculated $I(H)$ in Eq. (4) as a function of four parameters, the three principal *g*-factors g_x, g_y, and g_z and ΔH, which is the linewidth at half height of the Lorentzian line. The scaling factor γ, is just necessary to fit the height of the experimental spectra. The field derivative of Eq. (4) was fitted by the least-squares method to the experimental spectrum. The results of these fittings are shown by closed circles superposed to the experimental spectra in Figs. 2, 4, 6, and 9. In the caption of the same figures the obtained parameters are given. Small differences in the fits of Figs. 6 and 9 could be minimized including an angle-dependent linewidth $\Delta H(\theta,\phi)$ but this was not done, because the number of parameters and computing time increases without improving the understanding of the problem. The linewidth ΔH necessary to fit the experimental spectra at the *Q*-band is larger than that at the *X*-band, indicating that the linewidth is inhomogeneously broadened. This inhomogeneity may be due to a *g*-value distribution caused by crystal-field inhomogeneities at the Cu^{2+} sites.

The fitting parameters obtained for the three components of the *g*-tensor for Y_2BaCuO_5 and $BaCuO_{2+x}$ clearly indicate that the Cu^{2+} ions are located at a site of orthorhombic and tetragonal symmetry, respectively. Although the parameters obtained from Figs. 6 and 9, still show orthorhombic symmetry for the three components of the *g*-tensor, they do not correspond to those found for Y_2BaCuO_5. The proximity between the parameters obtained for the resonance of Figs. 6 and 9 suggest that the ESR signal observed in most of the $YBa_2Cu_3O_{7-x}$ samples may come from other copper compounds originated probably in $BaCuO_{2+x}$. It is clear that any other spurious copper compound with an orthorhombic local symmetry for the copper atoms which may be still present in a mass fraction of the order of 0.1–0.5%, according to our estimations from the relative ESR intensities, could also be responsible for the observed resonance.

Our powder spectra calculation can also reproduce easily the resonance with no structure, such as that shown in Fig. 7(c), by just increasing the residual linewidth.

CONCLUSION

In summary, supporting the conclusions of Bowden *et al.*[7] for the Y-based and Vier *et al.*[6] for the Eu-based 1:2:3 compounds our results indicate that in the pure phase of the high critical temperature superconductor $YBa_2Cu_3O_{7-x}$ and also in its oxygen-deficient tetragonal phase the resonance due to copper ions is not observable. The resonances which were attributed to Cu^{2+} ($3d^9$) in these compounds are only due to other spurious phases which could still be present in a mass fraction of the order of 0.1–0.5%. The *g*-values obtained for these room-temperature resonances show that these spurious phases cannot be associated to either residual Y_2BaCuO_5 or $BaCuO_{2+x}$ phases as suggested in Ref. 6. These small concentrations of spurious phases are hardly observed in x-ray-diffraction experiments, but they could be enough for the observed resonances and the small moment measured for Cu^{2+} in susceptibility experiments.[23]

Since all our samples were kept in a dry atmosphere, and time evolution in both the ESR spectra and x-ray-diffraction pattern were observed for $BaCuO_{2+x}$, we conclude that this compound is very unstable. No such instability was observed in Y_2BaCuO_5 and $YBa_2Cu_3O_{7-x}$ compounds.

It is interesting to note that the intensity of the resonance for the freshly prepared $BaCuO_{2.07}$ sample is also very small when compared with that of the green phase. So, similarly to $YBa_2Cu_3O_{7-x}$, it seems that for the oxygen-saturated $BaCuO_{2+x}$ the copper ions do not give rise to an ESR line either. Furthermore, the respective increase and decrease of the relative resonance intensity for the deoxygenated and reoxygenated samples of $BaCuO_{2+x}$ [see Figs. 3(b) and 3(d)], suggest that there may be Cu atom sites in the lattice structure with nearest-neighbor oxygen atoms weakly bounded to the Cu atoms which could easily produce an oxygen vacancy at these Cu atom sites, leading to the observation of the $Cu^{2+}(3d^9)$ resonance at these sites. Susceptibility experiments are obviously needed to clarify this point.

The fact that in the oxygen-deficient $YBa_2Cu_3O_{7-x}$ samples the intensity of the resonance did not increase with the oxygen losses (see Figs. 7 and 8) indicates that in this case the oxygen vacancies do not give rise to such a Cu atom site, like in $BaCuO_{2+x}$, where oxygen vacancies could lead to observations of the resonance of $Cu^{2+}(3d^9)$ ions in this compound.

Therefore, we suggest that, in general, when oxygen atoms occupy lattice positions close enough to Cu atoms in metallic or semiconducting compounds, Cu $(3d)$–O (p) orbitals can admix,[24] causing delocalization of the Cu $3d$ electrons. In addition, spin-orbit coupling could lead to fast spin-lattice relaxation and a large g-value distribution, which may be responsible for the absence of resonance in these compounds.[25]

ACKNOWLEDGMENTS

Partially supported by Fundação de Amparo a Pesquisa do Estado de São Paulo and Conselho Nacional de Desenvolvimento Cientifico e Tecnológico, Brazil.

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