Proceed. Latin-American conference on high temperature Superconductivity
Rio de Janeiro, 1988

ESR STUDIES OF $YBa_2Cu_3O_{7-x}$, Y_2BaCuO_5 and $BaCuO_{2+w}$*

R.N.de Mesquita, J.H. Castilho, G.E. Barberis, C. Rettori
I. Torriani, O.F.de Lima, S. Gama and R. Jardim
Instituto de Física, Unicamp, 13081 Campinas (S.P.) Brasil

and

M.C. Terrile, H. Basso and O.R. Nascimento
Instituto de Física e Química, USP, 13560 São Carlos (S.P.) Brasil

Abstract

X and Q band ESR spectra of the high T_c superconductor $YBa_2Cu_3O_{7-x}$ and the related compounds Y_2BaCuO_5 and $BaCuO_{2+w}$ are reported. We study the room temperature spectra as a function of the oxygen concentrations x and w in the samples, and we fit the powder spectra with a model Hamiltonian for exchange narrowed coupled Cu^{2+} ions. We conclude that the Cu atoms in the superconductor are not ESR active, and that the observed resonances come from other residual phases with concentrations smaller than 5000 ppm, which cannot be observed by X-ray diffraction.

Several reports on $YBa_2Cu_3O_{7-x}$, Y_2BaCuO_5 and $BaCuO_{2+w}$ ESR spectra were published recently [1-6]. Although the general features of the different spectra reported are similar, the interpretations of the experiments disagree. The origin of the resonances in these compounds is understood by different authors in very different manner, some of them assuming that the resonances come from impurity phases. The main objective of this work is to clarify these divergencies, fitting a model for coupled Cu^{2+} ions to the experimental ESR data; we also study the ESR spectra as function of the oxygen concentration of the samples in order to better understand our results.

The samples were prepared according to the solid diffusion method which was reported previously [4]. The only difference was that for the present batch of samples the process of grinding and annealing during 20 hours at 950º C in an oxygen atmosphere were repeated 3 to 6

0000 1006

times in order to get as much as possible pure single phase samples.

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

The ESR experiments were carried out at room temperature in conventional ESR Varian E-Line X and Q-Band spectrometers. The samples were always run in form of fine powder (10 - 30 μm) and were in all cases kept in dry atmosphere.

The distances between Cu^{2+} ($3d^9$) ions in all these compounds is small enough to make their exchange (or superexchange) interaction important. Therefore, we assumed a system of coupled Cu^{2+}, with complete exchange narrowed hyperfine and Zeeman interactions as a model to fit the ESR resonances [7,8]. We fitted the corresponding Hamiltonian for S = 1/2 to the experimental spectra assuming also random orientation of the crystallites in the samples. More detailed analysis will be published elsewhere.

Table I - Fitting parameters for the ESR powder spectra

Sample	Microwave Band	g_x	g_y	g_z	ΔH(Gauss)
Y_2BaCuO_5	Q	2,08±0,01	2.12±0,02	2.25±0.01	70±10
	X	2,08±0,01	2.12±0.02	2.25±0.01	25±5
$BaCuO_{2.02}$(Fresh)	Q	2.055±0.005	2.055±0.005	2.24±0.01	100±10
	X	2.055±0.005	2.055±0.005	2.24±0.01	40±5
$BaCuO_{2.07}$(Old)	Q	2.05±0.02	2.12±0.02	2.22±0.02	202±20
	X	2.05±0.02	2.12±0.02	2.22±0.02	68±5
$YBa_2Cu_3O_7$	Q	2.05±0.02	2.09±0.03	2.24±0.02	188±20
	X	2.05±0.02	2.09±0.03	2.24±0.02	65±8

For 200% reduction to trim size 8½" x 6"

In the Y_2BaCuO_5 samples, no significant changes could be observed in the spectra after each deoxygenation and reoxygenation treatment. We could not attribute the mass losses of the samples to oxygen deficiencies because also during the reoxygenation the mass of the samples was still decreasing, probably due to the presence of small amounts of non-reacted carbonates. The spectra could be fitted with an orthorhombic Hamiltonian and the g-values obtained can be seen in Table I.

Freshly reacted $BaCuO_{2+w}$ samples present a tetragonal ESR spectrum (see Table I), whose intensity strongly depends on the samples oxygen concentration. This intensity decreases three orders of magnitude from the less (w = 0.0) to the most oxygenated (w = 0.07) sample. The ESR spectrum after one complete de and reoxygenation cycle completely reproduces the former spectrum, showing that oxygen comes out and enters in the samples in a reversible manner. We studied one of the $BaCuO_{2+w}$ samples ESR spectra as a function of time. We stored the more oxygenated of our samples in a dry atmosphere and we measured it in periods of one week during two months. We observed a strong change in the spectra, going from tetragonal to orthorhombic, with the g-values shown in Table I. This change was also observed by X-rays, presenting the appearance of unidentified spurious phases.

Two $YBa_2Cu_3O_{7-x}$ samples were studied by ESR as a function of oxygen concentration. One of them was grinded and annealed three times, and the other six times. The last one presents one order of magnitude smaller ESR intensity than the former. It is interesting to note that the resonances correspond to an orthorhombic phase with an increasing linewidth as the de and reoxygenation treatment proceeds. At the same time, X-ray analysis show that the change from orthorhombic to tetragonal phase occurs in the sample. The g-values of the fitting are comparable with those corresponding to the spurious phase in $BaCuO_{2+w}$ (see Table I).

Table II summarizes the relative intensities in our samples, which are related to the intensity of the same mass of the Y_2BaCuO_5 green phase in the same experimental conditions, which is stable. It can be observed that the more the thermal annealing, the smaller the

For 20% reduction to trim size 8½" x 6"

$YBa_2Cu_3O_{7-x}$ ESR signal.

Table II - ESR relative intensities

$YBa_2Cu_3O_{7-x}$ (1)		$YBa_2Cu_3O_{7-y}$ (2)		$BaCuO_{2+w}$	
X	Intensity	Y	Intensity	W	Intensity
0.0	$4x10^{-2}$	0.0	10^{-3}	0.07	10^{-3}
0.2	$4x10^{-2}$	0.1	10^{-3}	0.05	10^{-1}
0.3	$4x10^{-2}$	0.3	10^{-3}	0.02	10^{-1}
0.0*	$2x10^{-2}$	0.0*	10^{-3}	0.08*	$2x10^{-2}$

(1) annealed 60 hs.
(2) annealed 120 hs.
(*) reoxygenated

We conclude that: 1) The ESR signals observed in the superconducting $YBa_2Cu_3O_{7-x}$ come from some unidentified residual phase, that is reduced by the thermal treatments; 2) The g-values of Cu^{2+} in the Y_2BaCuO_5 (green phase) are different from those observed in the superconductor; 3) The "old" $BaCuO_{2+w}$ presents resonances coming from an unidentified phase, with g-values, within the error bars (see Table I), equal to the corresponding in the superconductor. More detailed analysis of this matter are in progress in our group and will be published elsewhere.

COMPLETE TEXT

REFERENCES

*Partially supported by FAPESP and CNPq, Brazil.

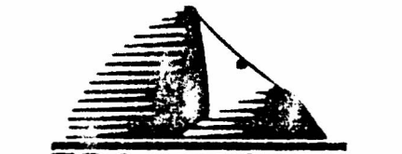
1. C. Rettori, D. Davidov, I. Belaish and J. Felner, Phys. Rev. B36, 4028 (1987)
2. D. Shaltiel, J. Genossar, A. Grayevsky, Z.H. Kalman, B. Fisher and N. Kaplan, Solid State Commun. 63, 987 (1987)
3. F. Mehran, S.E. Barnes, T.R. McGuire, W.J. Gallagher, R.L. Sundstrom, T.R. Dinger and D.A. Chance, Phys. Rev. B36, 740 (1987)
4. J.H. Castilho, P.A. Venegas, G.E. Barberis, C. Rettori, R.F. Jardim, S. Gama, D. Davidov and I. Felner, Solid State Commun. 64, 1043 (1987)
5. D.C. Vier, S.B. Oseroff, C.T. Salling, J.F. Smyth, S. Schultz, Y. Dalichaouch, B.W. Lee, M.B. Maple, Z. Fisk and J.D. Thompson, Phys. Rev. B36, 8888 (1987)
6. R. Bartucci, E. Colavita, L. Sporetelli, G. Balestrino and S. Barbanera, Phys. Rev. B37, 2313 (1988)
7. P.W. Anderson, Jour. of the Phys. Soc. Japan 9, 307 (1954)
8. R. Calvo and M.A. Masa, Phys. Rev. B28, 1244 (1983)
9. I.K. Schuller, D.G. Hinks, M.A. Beno, D.W. Capone II, L. Soderholm, J.P. Locquet, Y. Broynseraede, C.U. Segre and K. Zhang, Solid State Commun. 63, 385 (1987)

MARIA CRISTINA
TERRILE

ABSTRACTS

LATIN-AMERICAN CONFERENCE ON HIGH TEMPERATURE SUPERCONDUCTIVITY

MAY 4-6, 1988
HOTEL GLORIA



EBS/LACHTS
Rio de Janeiro, Brazil, 1988

1039

Campo	Dado
*****	Documento 1 de 1
No. Registro	002288832
Tipo de material	TRABALHO DE EVENTO - NACIONAL
Entrada Principal	Mesquita, R. N. (*) NAC
Título	ESR studies of Y'BA IND. 2''CU IND. 3''O IND.7-X','Y IND.2''BA''CU''O IND.5' and 'BA''CU''O IND.2+w'.
Imprenta	Rio de Janeiro, 1988.
Descrição	5 p..
Assunto	FÍSICA
Autor Secundário	Castilho, J. H. (*) NAC Universidade Estadual de Campinas - UNICAMP - Instituto de Física Gleb Wataghin - Campinas - SP
Autor Secundário	Barberis, G. E. (*) NAC Universidade Estadual de Campinas - UNICAMP - Instituto de Física Gleb Wataghin - Campinas - SP
Autor Secundário	Rettori, C. (*) NAC Universidade Estadual de Campinas - UNICAMP - Instituto de Física Gleb Wataghin - Campinas - SP
Autor Secundário	Torriani, I. (*) NAC Universidade Estadual de Campinas - UNICAMP - Instituto de Física Gleb Wataghin - Campinas - SP
Autor Secundário	Lima, O. F. (*) NAC Universidade Estadual de Campinas - UNICAMP - Instituto de Física Gleb Wataghin - Campinas - SP
Autor Secundário	Gama, S. (*) NAC Universidade Estadual de Campinas - UNICAMP - Instituto de Física Gleb Wataghin - Campinas - SP
Autor Secundário	Jardim, R. F. (*) NAC Universidade Estadual de Campinas - UNICAMP - Instituto de Física Gleb Wataghin - Campinas - SP
Autor Secundário	Terrile, Maria Cristina
Autor Secundário	Basso, Heitor Cury
Autor Secundário	Nascimento, Otaciro Rangel
Autor Secundário	Latin-American Cnference on High Temperature Superconductivity (1988 Rio de Janeiro)
Fonte	Proceedings, Rio de Janeiro : 1988
Localiz.Eletrônica	"Clicar" sobre o botão para acesso ao Currículo Lattes de Maria Cristina Terrile -- http://buscatextual.cnpq.br/buscatextual/visualizacv.do?id=K4787757E9
Localiz.Eletrônica	"Clicar" sobre o botão para acesso ao Currículo Lattes de Heitor Cury Basso -- http://buscatextual.cnpq.br/buscatextual/visualizacv.do?id=K4787065J3
Localiz.Eletrônica	"Clicar" sobre o botão para acesso ao Currículo Lattes de Otaciro Rangel Nascimento -- http://buscatextual.cnpq.br/buscatextual/visualizacv.do?id=K4787757U0
Unidade USP	IFQSC -- INST DE FÍSICA E QUÍMICA DE SÃO CARLOS
Unidade USP	IFQSC -- INST DE FÍSICA E QUÍMICA DE SÃO CARLOS
Unidade USP	IFQSC -- INST DE FÍSICA E QUÍMICA DE SÃO CARLOS
Localização	IFSC PROD001006