Electron paramagnetic resonance of single-phase pellets of the high-T_c superconductor YBa$_2$Cu$_3$O$_{7-x}$

R. Bartucci, E. Colavita, and L. Sportelli

Dipartimento di Fisica, Università degli Studi della Calabria, 87036 Arcavacata di Rende, Cosenza, Italy

G. Balestrino and S. Barbanera

Istituto di Elettronica dello Stato Solido del Consiglio Nazionale delle Ricerche,
Via Cineto Romano 42, 00156 Roma, Italy

The Cu-local environment of the high-T_c superconductor YBa$_2$Cu$_3$O$_{7-x}$ has been investigated in the bulk form by the electron-spin-resonance technique. Two nonequivalent Cu^{2+} ion sites are singled out in this orthorhombic superconducting phase all over the experimental temperature range (77–298 K). The density of the magnetic moments drops under temperature increase from liquid nitrogen up to the superconductive transition temperature, therein it tails off almost linearly.

A wealth of techniques has been used by now to study the layered superconducting[1] YBa$_2$Cu$_3$O$_{7-x}$ and a lot of information on electronic, vibrational, and structural properties have become available.[2] The correlation of various results is also at hand and may be attempted.

We apply the electron-paramagnetic-resonance (EPR) technique[3] to investigate a single-phase- high-T_c pellet aiming at local properties around paramagnetic Cu ions. As it is well known the method is effective for those species having one or more unpaired electrons. The spectroscopic g-splitting factor of the Zeeman interaction term varies with the relative orientation of the crystal axes with respect to the magnetic field, unless metal ions are in regular octahedral crystal fields. Contrary to neutron and x-ray diffraction, local arrangements around Cu ions are probed and information about the environmental symmetry, electronegativity, as well as bondings with the nearest neighbors can be obtained.

We have evidence of two nonequivalent Cu^{2+} sites per unit cell, the first, Cu(1), having a square planar coordination and the second, Cu(2), a tetragonally distorted octahedral cage with a high delocalization of the unpaired electron in the $d_{x^2-y^2}$ cupric atom orbital. Moreover, the intensity of the EPR signal decreases sharply as temperature increases between 77 K and T_c and then tails off linearly up to room temperature. A localized magnetic moment description in terms of the Curie susceptibility law is very likely appropriate for all temperatures ranging from the superconductive transition temperature in the metal-like behavior of the sample.

Previous EPR measurements[4,5] have been taken on powdered Y-Ba-Cu-O superconductors and the finer details related to the two Cu ion sites are absent, although the intensity trend of the signal is roughly similar.

Polycrystalline YBa$_2$Cu$_3$O$_{7-x}$ samples were prepared and carefully characterized at Istituto di Elettronica dello Stato Solido del Consiglio Nazionale delle Ricerche. A mixture of Y$_2$O$_3$, BaCO$_3$, and CuO in the nominal molar ratio Y:2Ba:3Cu was ground and reacted for 12 h in an alumina crucible in flowing O$_2$ at 900 °C. A final heat treatment at 650 °C in oxygen atmosphere was given for 12 h.

X-ray diffraction spectra of the superconducting pellets were taken with a θ-2θ powder diffractometer using Co-$K\alpha$ radiation with a Fe filter. Figure 1 shows the x-ray diffraction pattern of one of our monophase polycrystalline samples. All the peaks in the pattern belong to the orthorhombic phase[6] YBa$_2$Cu$_3$O$_{7-x}$. Their Miller indeces are shown in the figure.

The dc resistance versus temperature was measured by the four-lead method. The superconductive transition temperature T_c was 92 ± 0.5 K (midpoint of the resistive transition) as shown in Fig. 2. Above T_c the behavior of the resistance was metal-like.

The EPR measurements were performed at the Physics Department of the University of Calabria using a Bruker Model ER-200D-SRC X-band spectrometer equipped with an ER4111VT temperature control unit (accuracy ± 0.3 K). The pellet was inserted in an EPR quartz tube which in turn was placed in a quartz Dewar centered in a TE$_{102}$ cavity. The microwave power was fixed well below the value causing signal saturation. The spectra were taken in the first-derivative mode with a modulation frequency of 100 kHz. 1,1'-diphenyl-2-picrylhydrazyl (DPPH, g = 2.0037) was used as a reference for the g value and the magnetic field calibration was done by a Magnon precision NMR gauss meter.

Several spectra were taken from just below the transition temperature up to room temperature and no change of the line shape or its magnetic field position was ever recorded. A further test was performed dipping the sample in liquid nitrogen and the main EPR features were not only still observable but even clearer. The intensity of the resonant signal was certainly changing under temperature increases although at different rates.

Figure 3 shows EPR spectra of polycrystalline YBa$_2$Cu$_3$O$_{7-x}$ superconductive pellets at 77, 90, 107, 128, and 298 K. Four equally separated absorption bands can be figured out as it is expected when the unpaired electron of the Cu^{2+} ion interacts with the spin $I = \frac{3}{2}$ of
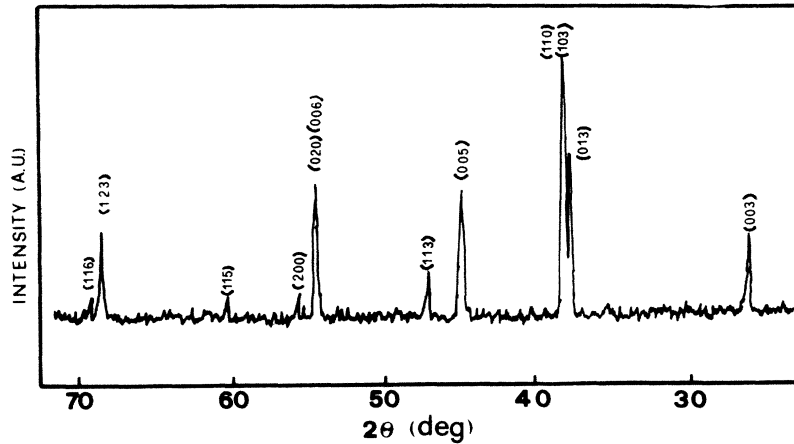
FIG. 1. X-ray diffraction pattern of the high-T_c superconductive $YBa_2Cu_3O_{7-x}$ pellet investigated by the electron spin resonance technique.

its own nucleus. Although a theoretical simulation would better clarify the experimental line shape, the dip at 3100 G may be interpreted as the superposition of two adjacent hyperfine features. The Cu^{2+} hole is in the $d_{x^2-y^2}$ orbital with lowest energy because of tetragonal distortions from octahedral symmetry. The spectrum at 77 K is by far the most intense and shows very clearly the shoulder at $g_\perp$ while the last two hyperfine features merge together.

Since the spectrum is the envelope of line shapes from all possible orientations of the z axis of the paramagnetic microcrystal with respect to the magnetic field, the orientation of the metal-ligand complex in the crystal cannot be determined. Only the mean g splitting and $|A|$ hyperfine factors with respect to the same crystal principal axes can be found. Nevertheless, a large number of bondings is expected to lie in the plane perpendicular to the z axis of the single cupric complex either for the pyramidal or square planar ligand environment and, actually a larger absorption is observed at higher magnetic fields. The corresponding $g_\perp$ value is about 2.069 which approaches fairly closely the free-electron g value of 2.0023 while the $g_\parallel$ value (2.194) is quite different being $g_\parallel > g_\perp$. No hyperfine structure can be resolved in the high magnetic field region while the $|A_\parallel|$ component can be estimated

to be 72 ± 2 G.

A careful inspection of our measurements shows that the intense negative wing is more symmetric at 77 K, the shoulder around $g_\perp$ is sharper, and moreover the last two hyperfine features merge together in one broad structure. These are, in our opinion, the presence signs of two different EPR signals and of a slight shift towards lower magnetic fields of one of the two distinct absorptions overlapping all over the experimental range. Actually, the comparison between present and previous[4,5] results forces us to claim for the evidence of these two contributions. Although powdered samples with different stoichiometry or phase do not show any EPR features in the high magnetic field region and the signal appears much broader than ours all over the acquisition range, nevertheless the EPR linewidth increases significantly below T_c.

In order to understand the already published EPR results, we ground our polycrystalline pellet to powder and the EPR result of Mehran, Barnes, McGuire, and Callagher[5] was obtained at room temperature. We speculate that this finding may be related to the existence in the pellet of large crystallites with a preferential crystallographic orientation. This suggestion is supported by our preliminary results on single crystals of $YBa_2Cu_3O_{7-x}$ which give highly resolved EPR spectra. X-ray diffraction measurements further confirm the above hypothesis. In fact, the relative intensity of diffraction peaks does not follow the expected behavior for a completely randomly oriented specimen.[6] On the other hand, scanning electron micrographs of our pellet show the existence of a texture of rod-like crystallites.

The tripled perovskite structure of the orthorhombic superconducting phase is formed by one square-planar $Cu^{2+}(1)$ complex and two square-pyramidal $Cu^{2+}(2)$ ligand environments per unit cell.[7–11] Thus, we expect that the EPR signal from the $Cu^{2+}(2)$ unpaired electron is twice as intense as $Cu^{2+}(1)$ EPR. The low magnetic field region of the spectrum may display mainly the tetragonal distortion of the $Cu^{2+}(2)$ arrangement with the z axis along the elongated $Cu(2)-O$ bond. Accordingly $|A_\parallel|$ might be related to the absorption of the most
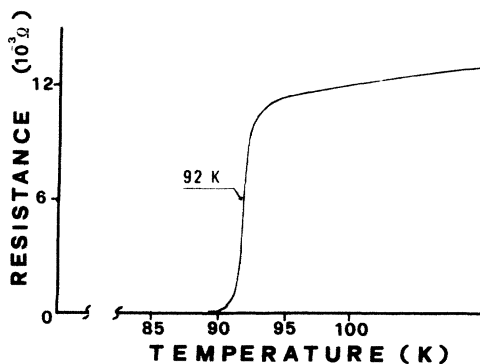

FIG. 2. dc resistance vs temperature of the investigated sample.
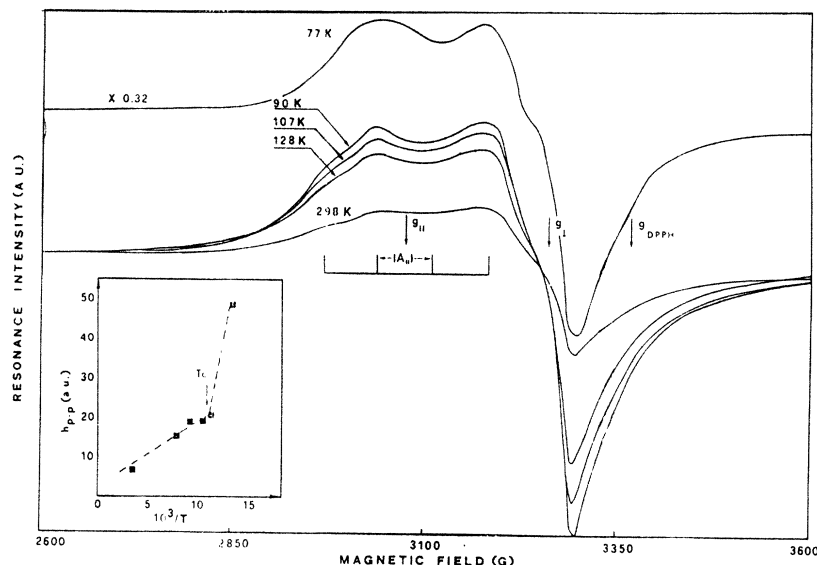
FIG. 3. Electron spin resonance spectra of the polycrystalline $YBa_2Cu_3O_{7-x}$ pellet. The inset shows the peak-to-peak intensity of the main derivative line shape vs $1/T$.

abundant cupric ion.

The EPR results suggest a high degree of overlap between the $3d_{x^2-y^2}$ metal-ion orbital and the orbitals of its surrounding ligands forming strong bonds along x and y axes and a weak bond along the tetragonal axis. A similar Cu environment is found, for example, in cupric acetate where the bridge of the two $Cu-O_4$ square-pyramidal complexes is due to carbon atoms instead of yttrium.[12]

The intensity trend of present EPR signals versus temperature is shown in the inset of Fig. 3. Although we focus mainly on the temperature region above T_c, nevertheless the signal amplitude variation below and above T_c may deserve theoretical attention because of its possible relation to a change of the sample spin density. No change of the Cu oxidation state in the orthorhombic cell is observed since there occurs not even the slightest modification of the EPR line shape other than its attenuation. At 77 K, however, the EPR signal is twice as intense as the one at 90 K. At higher temperatures, above T_c, that is, in the metallic state, the quasi-two-dimensional motion of superconductive pairs within $Cu(1)-O_2$ planes[13] is damped and the EPR response due to localized magnetic moments on Cu^{2+} ions may change because of a more delocalized metal-like paramagnetism. All that should give rise to a net attenuation of the total spin density value according to the observed scaling of the EPR signal. Similar findings have been already published and tentatively interpreted.[4,5] Whatever the proper theoretical explanation is, the parallel behavior of the EPR response and of the electrical conductivity versus temperature is suggestive and very likely indicative of a related mecha-nism between the two.

The present interpretation is supported by infrared,[14] neutron,[8-10] and x-ray diffraction[7,11] measurements. They also suggest the presence of two symmetrically non-equivalent microenvironments of Cu ions. We can moreover exclude that copper ions are present in oxidation states other than Cu^{2+} in agreement with photoemission results.[15]

In conclusion, we observe hyperfine structures in EPR spectra of superconductive $YBa_2Cu_3O_{7-x}$ pellets. Most probably the good quality and the presence of large crystallites in the samples are responsible for the highly resolved spectra. The main contribution to the EPR spectra comes from the square-pyramidal Cu^{2+} ligand environment. The intensity trend of the EPR amplitude versus temperature suggest a big variation of the spin density amount on going from below to above T_c, but no change in the Cu oxidation state.

Measurements on $YBa_2Cu_3O_{7-x}$ single crystals are in progress and preliminary results show well-resolved hyperfine structures belonging to the two cupric species.

[1]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[2]For an extensive review of articles in the field, see A. Khurana, Phys. Today **40** (No. 9), 17 (1987), and references therein; Physical Review listing on Phys. Rev. Lett. **58**, 2155 (1987) and Phys. Rev. Lett. **59**, 1 (1987).

[3]G. E. Pake and T. L. Estle, *The Principles of Electron Paramagnetic Resonance* (Benjamin, London, 1987).

[4]D. Shaltiel, J. Genossar, A. Grayevsky, Z. H. Kolman, B. Fisher, and N. Kaplan, Solid State Commun. **63**, 987 (1987).

[5]F. Mehran, S. E. Barnes, T. R. McGuire, and W. J. Gallagher, Phys. Rev. B **36**, 740 (1987).

[6]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, and E. A. Rietman, S. Zohurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[7]T. Siegrist, S. Sunshine, D. W. Murphy, R. J. Cava, and S. N. Zahurak, Phys. Rev. B **35**, 7137 (1987).

[8]J. E. Gredan, A. H. O'Reilly, and C. V. Stager, Phys. Rev. B **35**, 8780 (1987).

[9]F. Beech, S. Miraglia, A. Santoro, and R. S. Roth, Phys. Rev. B **35**, 8778 (1987).

[10]K. Kamaràs, C. D. Porter, M. G. Doss, S. L. Herr, D. B. Tanner, D. A. Bonn, J. E. Greedan, A. H. O'Reilly, C. V. Stager, and T. Timusk, Phys. Rev. Lett. **59**, 919 (1987).

[11]Y. Le Page, W. R. McKinnon, J. M. Tarascon, L. H. Green, G. W. Hull, and D. M. Hwang, Phys. Rev. B **35**, 7245 (1987).

[12]B. A. Gordman and J. B. Raynor, *Electron Spin Resonance of Transition Metal Complexes,* Advances in Inorganic Chemistry and Radiochemistry, Vol. 13 (Academic, New York, London, 1970).

[13]V. Z. Kresin, Phys. Rev. B **35**, 8716 (1987).

[14]M. Stavola, D. M. Krol, W. Weber, S. A. Sunshine, A. Jajyaraman, G. A. Kourouklis, R. J. Cava, and E. A. Rietman, Phys. Rev. B **36**, 850 (1987).

[15]M. Onellion, Y. Chang, D. W. Niles, R. Joynt, G. Margaritondo, N. G. Stoffel, and J. M. Tarascon, Phys. Rev. B **36**, 819 (1987).