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An electron paramagnetic resonance study of Y–Ba–Cu–O-type ceramics in superconducting and non-superconducting phases

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Abstract. Electron paramagnetic resonance (EPR) studies of high-temperature superconducting and non-superconducting Y–Ba–Cu–O compounds were performed. The effect of different oxygen treatments on the EPR spectra was analysed. Changes were found in the linewidth and in the signal intensity. The compound in the so-called 'green phase' gives rise to a very symmetric EPR line, in contrast with the highly asymmetric lineshape arising from the superconducting samples. The signal, with $g \simeq 2$, is attributed to Cu^{2+} ions in sites with axial and lower symmetry. A possible correlation with the Jahn–Teller effect is suggested. EPR spectra from iron-substituted samples provide further information about the local environment of Cu(I) sites.

1. Introduction

The discovery of high-T_c superconductors (Bednorz and Müller 1986, Wu *et al* 1987) has provoked great interest in characterising these new materials by using different techniques. A large number of papers have been published about the existence of several phases in the compound Y–Ba–Cu–O. Some of them are superconducting—in particular the orthorhombic 1–2–3 phase presents a T_c of 90 K; others are insulators—e.g. the 2–1–1 phase (green phase).

Some insight can be gained if samples with different superconducting behaviours are analysed by the same technique, under similar conditions. In this paper, results from electron paramagnetic resonance (EPR) studies are presented. These were performed on 1–2–3 samples having various T_c, samples doped with iron and samples of the green phase. Spectra were taken at several temperatures. The spectra taken from samples belonging to the same group were highly reproducible.

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2. Experiment

The samples used in this study are classified in table 1. They were prepared starting from high-purity powders of Y_2O_3, $BaCO_3$, CuO and Fe_2O_3. The mixtures were first ground, pressed and heated at 900 °C for 12–18 h. Then, they were sintered at 950 °C for 2 h. Subsequently the oxygen treatment and cooling differed from sample to sample. Type 1 samples were further oxygenated for 2 h at 450 °C, type 2 samples were quenched from 750 to 800 °C, and type 3 samples were oven cooled in air overnight. Further details can be found in the work by Escudero *et al* (1987) and Gómez *et al* (1987). All the samples were characterised by x-ray diffraction (table 1, last column) and resistivity measurements.

The resistance curves of the samples are shown in figure 1, where the initial temperature T_i is indicated by arrows. This temperature T_i gives an idea of the width of the transition. In type 2 samples this width varies according to the quenching temperature. T_c is defined as the point when the zero-resistivity state is fully attained.

The EPR spectra were obtained with a Varian E104 reflection-type spectrometer with a multi-purpose cavity and with a Brucker ESR200D. Both are reflection X-band (9.5 GHz) types of spectrometer. The EPR spectra at 77 K were obtained by using a home-made Dewar container. The g-values were determined using a Hewlett–Packard frequency counter and a proton nuclear magnetic resonance gaussmeter.

All 1–2–3 samples show essentially the same EPR spectrum at room temperature, consisting of a broad asymmetric line at around 3000 G; this will be called the central field signal (CFS) subsequently. Figure 2 shows the spectra for orthorhombic samples of $Y_1Ba_2Cu_3O_{7-\delta}$. This signal resembles that from a polycrystalline sample with a paramagnetic centre, with an effective spin of $\frac{1}{2}$ (Gharbage *et al* 1986). Applying the analysis by Reynolds *et al* (1972), one can distinguish a shoulder and a divergence indicated by arrows in the figure, which have close $g_\parallel$ and $g_\perp$ values. However, closer examination of these spectra reveals a change in the linewidth of the divergence (measured peak to peak). The observed change between type 2 and type 1 samples was a decrease of about 20 G as the transition temperature goes from low to higher T_c. Figure 2(*b*) shows the spectrum obtained from a type 2 sample. It can be seen that the lineshape is slightly more asymmetric than that obtained for a type 1 sample (figure 2(*a*)). The linewidth of these latter samples was 120 G, on average. A better picture is displayed by the second derivative of the spectra, also included in the same figure.

Although the asymmetry of the first derivative distorts the lineshape in the second-derivative spectrum, at least two main peaks can be resolved. Therefore, within the experimental error, the spectra can be considered to arise from a paramagnetic centre in axial symmetry. Under such circumstances, the measured values of $g_\parallel$ and $g_\perp$ are given in table 2. These values have a negligible dependence on temperature, down to 90 K.

Table 1. Characterisation of samples.

Sample type	Composition	T_i (K)	T_c (K)	Structure
1	$YBa_2Cu_3O_{7-\delta}$	92	90	Orthorhombic
2	$YBa_2Cu_3O_{7-\delta}$	60	48	Orthorhombic
3	$YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ ($x = 0.0125$)	72	38	Orthorhombic
4	Y_2BaCuO_5	—	—	Green phase

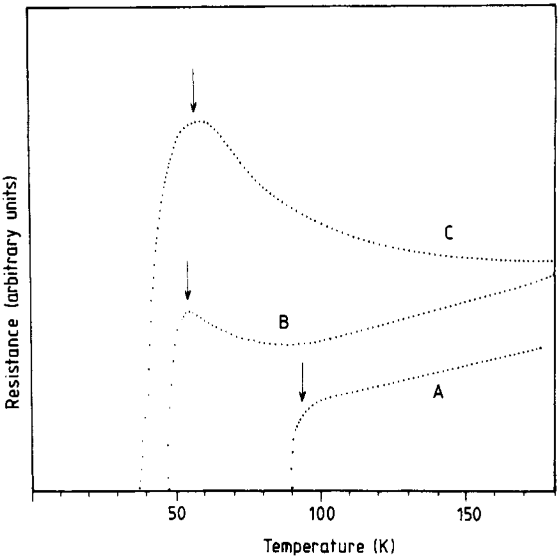

Figure 1. Curves of resistance against temperature for type 1 samples (curve A), type 2 samples (curve B) and type 3 samples (curve C). The temperature T_i is indicated by arrows.

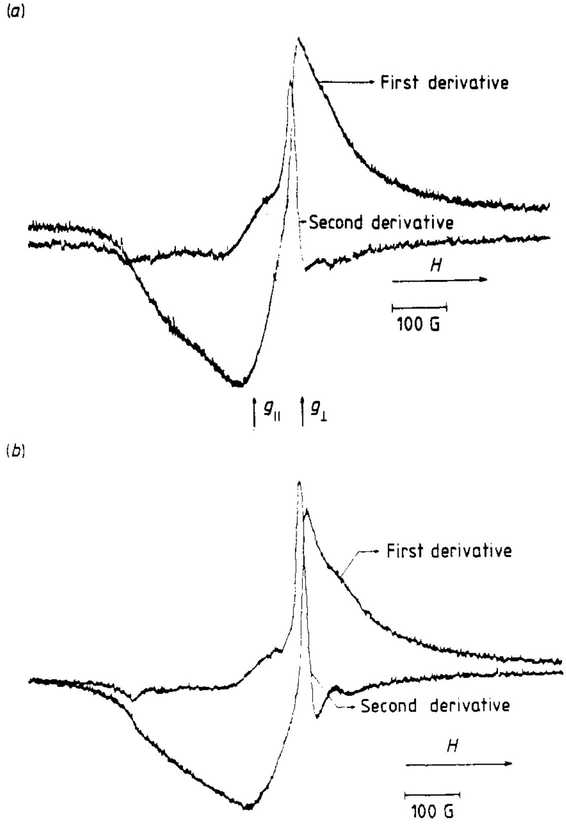

Figure 2. First and second derivatives of the CFS from (*a*) a type 1 sample and (*b*) a type 2 sample, taken at room temperature.

Table 2. g-values for different samples at room temperature.

Sample type	$g_\parallel$	$g_\perp$
1	2.109 ± 0.001	2.055 ± 0.001
2	2.120 ± 0.001	2.050 ± 0.001
4	$g = 2.100 \pm 0.001$	

The lowest temperature used in these experiments was 77 K. In samples with $T_i < 77$ K, it was possible to observe the CFS clearly. As the temperature was lowered, an increase in the intensity of the line was observed, together with a small decrease in the linewidth. In order to illustrate these effects, figure 3 shows the spectrum for a type 2 sample at 95 K.

The intensity of the CFS decreases as the oxygenation of the sample is increased and, consequently, T_c also increases towards 90 K. The intensity of the CFS in type 2 samples, without additional oxygen treatment, is almost twice that of type 1 samples, with full oxygen treatment. This is consistent with the resistivity measurements, since samples with a longer oxygen treatment show a more metallic-like behaviour.

Type 3 samples, with a small amount of iron, show the same sort of spectrum (i.e. a shoulder and a divergence) indicating, as before, the presence of a paramagnetic centre with an effective spin of $\frac{1}{2}$ in axial symmetry. The room-temperature spectrum is shown in figure 4. The intensity of the CFS is much weaker than that from samples without iron, and the distortion of the base line is due, in this case, to the lack of attenuation.

An insulating green phase sample (type 4) gives rise to a more symmetric line, as can be seen in figure 5. The intensity of this signal is about 40 times that of type 1 samples.

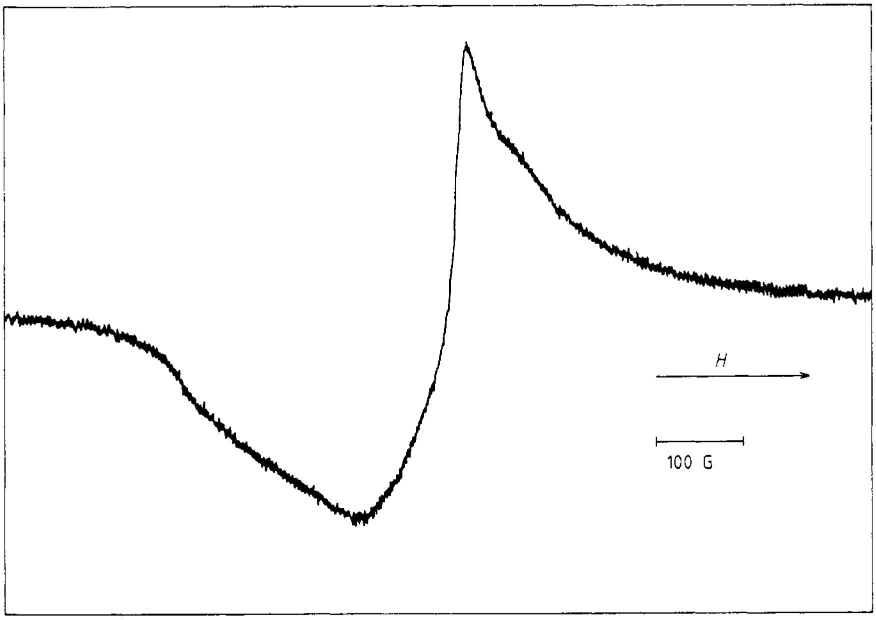

Figure 3. An EPR spectrum of a type 2 sample taken at 95 K. The vertical scale is 0.5 times that in figure 2.

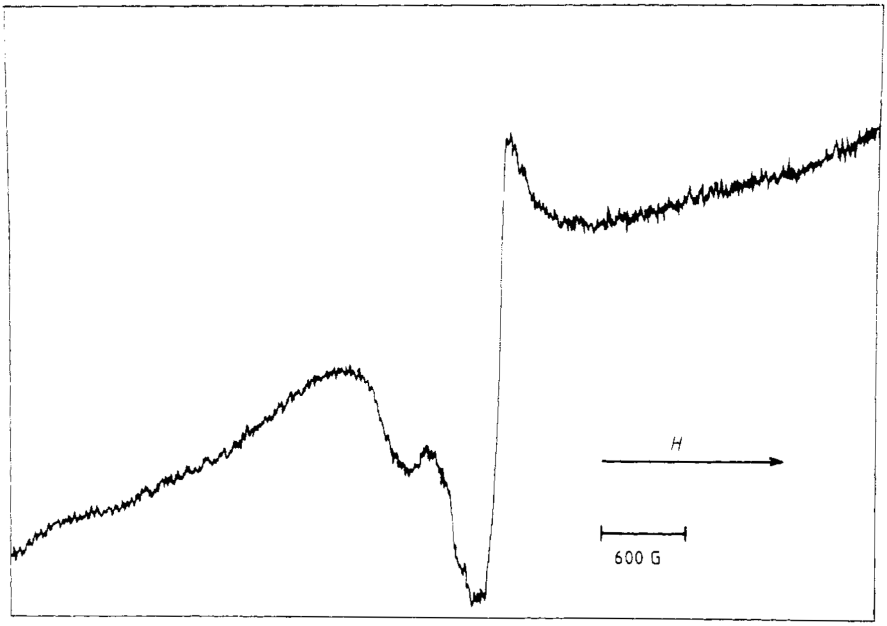

Figure 4. A spectrum from a type 3 sample (with iron) taken at room temperature.

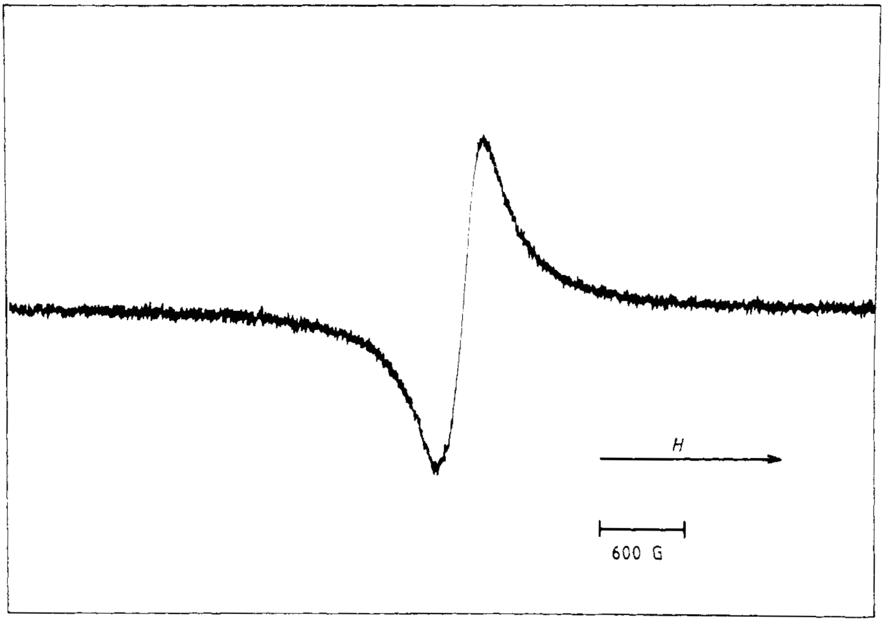

Figure 5. An EPR spectrum of a green phase sample taken at room temperature.

At 77 K, this spectrum showed only an increase in intensity and a small narrowing of the linewidth.

In all superconducting samples a strong signal at around 0 G (zero-field signal) was detected at temperatures less than 90 K. The intensity of this signal increases when the temperature is decreased and also it is more conspicuous in samples with a higher T_c. This signal has been attributed to flux trapping (Blazey *et al* 1987) although at present it is not yet clear whether this is fully correct. The nature and behaviour of this signal are currently being studied and will be the topic of a future publication.

The observations below T_c were difficult, not only because of the interference of the very strong zero-field signal but also owing to the partial Meissner shielding. Nevertheless, it is possible to overcome these problems and to observe the spectrum below T_c, as reported by Durny *et al* (1987).

3. Discussion

Copper is commonly found in 1+, 2+ and 3+ oxidation states. Of these, Cu^+ does not produce an EPR signal, while Cu^{3+} can only be detected at very low temperatures (Blumberg *et al* 1963). Therefore, in EPR, one expects to detect only Cu^{2+} ions.

The simplest of the spectra presented in § 2 is that due to the green phase (figure 5). In this structure, all copper sites are equivalent and are almost in the geometrical centre of a square pyramid of oxygen ions. The nominal oxidation of copper ions is 2+ for all of them. The immediate environment of all Cu^{2+} is highly symmetrical and therefore, as is usual in this case, there is a possibility of a dynamic Jahn–Teller (JT) effect (Reynolds *et al* 1974). This could explain the width of this signal (300 G). A broadening of the signal is usually attributed to dipole–dipole interactions; however, these interactions would not explain such a large broadening, since the distance between copper ions is large in the green phase (Hazen *et al* 1987).

An argument in favour of a dynamic JT effect arises if one calculates an average $\bar{g} = (g_\parallel + 2g_\perp)/3$ using the values in table 2. The result $\bar{g} = 2.073$ is in close agreement with the g-value from the green phase. It should be mentioned that the spectrum of the green phase is quite symmetric at all temperatures, reflecting the high symmetry of the copper sites; however, the shape of the line could be asymmetric for certain values of the JT coupling coefficient (Reynolds *et al* 1974).

In the 1–2–3 phase, there are two different sites for copper (Le Page *et al* 1987). Cu(I) sites are disposed in chains having fourfold coordination, although the actual coordination and nominal valence depend on the oxygen content in the orthorhombic phase. One expects some Cu^{2+} in these sites. In contrast, Cu(II) sites are surrounded by five oxygen ions, in a rather similar environment to the green phase, although Cu(II) sites are in a less symmetrical situation than in the green phase (Hazen *et al* 1987). The valence of Cu(II) ions is expected to be 2+.

The CFS in the 1–2–3 phase can be understood as a superposition of two different lines: the first is a narrow split line attributed to Cu^{2+} ions in Cu(I) sites. The other is a broad asymmetric signal due to Cu(II) sites. This last assignment is based on the similarity of the CFS of the green phase, except for the asymmetry. This change could be due to the lowering of the symmetry of the copper surroundings in the pyramids of the 1–2–3 compounds, in comparison with the pyramids in the green phase.

The splitting of the Cu(I) signal into $g_\parallel$ and $g_\perp$ is very small, but typical of some Cu^{2+} compounds. One way of explaining this splitting is through crystal-field theory.

Assuming this theory to be valid, it is well known that

$$g_{\parallel} = 2(1 - 4\lambda K_{\parallel}^2/\Delta_1)$$
$$g_{\perp} = 2(1 - \lambda K_{\perp}^2/\Delta_2)$$

where λ is the spin–orbit coupling constant ($-829\ \mathrm{cm}^{-1}$), Δ_1 and Δ_2 are the crystal-field splittings between the ground state and the excited states, and $K_{\parallel}$ and $K_{\perp}$ are correction factors due to covalency. Now, common copper complexes show Δ_1 values of the order $13\,500\ \mathrm{cm}^{-1}$ and $\Delta_2 \simeq 18\,500\ \mathrm{cm}^{-1}$ (Dudley and Hathaway 1970). Using these values and those obtained for $g_{\parallel}$ and $g_{\perp}$, one can obtain $K_{\parallel} = 0.5$ and $K_{\perp} = 0.7$, while the usual values found for copper complexes are about 0.7 for both $K_{\parallel}$ and $K_{\perp}$. Apparently, there is no special reason why there should be a strong directional covalent bonding in the high-T_c materials; therefore, one should look for other explanations.

Recently, it has been mentioned in the literature that a mechanism involving the interaction of conduction electrons with a distortion field and phonon modes, leading to a JT polaron, could be related to the high-T_c phenomena (Jagadish and Sinha 1987). Furthermore, Hock *et al* (1983) have studied the JT polaron problem for a tetragonal symmetry complex, concluding that, for sufficiently strong coupling, the electron may become trapped in the field of the lattice distortion. Some researchers (Reynolds *et al* 1974) have studied the EPR lineshape of Cu^{2+} in MgO and CaO as a function of the JT strength coupling, showing that, as the coupling increases, the EPR line becomes more asymmetric. These facts then might be correlated with the observed asymmetry in the EPR absorption line of the $YBa_2Cu_3O_{7-\delta}$ compounds.

In view of these ideas, it is clear that the splitting of the signal could be an indication of the presence of a JT distortion. In order to investigate this possibility a theory developed by Ham (1968) could be used. This theory considers JT ions with a ^2E_g ground state in octahedral coordination and, since this condition is not strictly fulfilled in the 1–2–3 phases, there are obvious limitations. Using the values for $g_{\parallel}$ and $g_{\perp}$ and the $10Dq$ splitting, one can obtain an estimation of the JT coupling strength q. Some copper complexes may have a very large $10Dq$ splitting, with extreme values around $32\,000\ \mathrm{cm}^{-1}$ (Arakawa and Hirose 1987, Carrington and McLachlan 1967). If one takes this value, q-values as high as 0.45 are obtained. This range for q points towards a static JT distortion (Ham 1968).

The spectra of the sample containing iron also showed a shoulder and a divergence, as shown in figure 4, and the striking fact is that the intensity of the spectrum is much lower than that of any sample without iron. Mössbauer studies (Gómez *et al* 1987) performed on the same samples showed that the iron ions enter substitutionally at Cu(I) sites and that strong local electric fields produce a low-spin configuration for iron. These ions can be in a divalent or trivalent ionic state. As Fe^{2+} in a low-spin configuration has a zero total spin, no EPR signals are expected. In contrast, the linewidth of the iron-doped sample is about 40 G wider than that of a $YBa_2Cu_3O_{7-\delta}$ sample. This might be due to the presence of Fe^{3+} in a low-spin configuration with an effective spin of $\frac{1}{2}$ contributing to the absorption around $g \simeq 2$. However, as mentioned before, the intensity of the signal is very small.

These features cannot be explained in a simple way, since they are surely related to the defect Cu^{2+} states which arise from the deviation from oxygen stoichiometry. The fact that there are higher oxidation states for iron must certainly influence the mixed-valence state of copper compounds. Experiments are being carried out at present in order to verify the validity of these assumptions.

In summary, our results suggest the following.

(i) The oxygen treatment in $YBa_2Cu_3O_{7-\delta}$ compounds influences the lineshape, linewidth and intensity of the EPR spectra.

(ii) The origin of this signal can be attributed to the superposition of paramagnetic centres with $S = \frac{1}{2}$ in different symmetry sites.

(iii) A possible correlation with the JT effect could be proposed.

(iv) Doping with iron influences the mixed-valence equilibrium of the copper ions.

However, as the oxygen content increases, the intensity of this signal decreases, probably due to the metallic-like behaviour of the sample compared with the insulating green phase.

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