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# Infrared and electron spin resonance for the high temperature superconductor $Y_1Ba_2Cu_3O_{9-x}$

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Samples of the high temperature superconductor Y–Ba–Cu–O were prepared to achieve the oxygen deficient perovskite structure $Y_1Ba_2Cu_3O_{9-x}$ with $x > 2$. The electrical resistance has been measured with the temperature in the range from 77 to 300 K, under the application of d.c. and a.c. with frequency 900 Hz. The d.c. produced a rather lower critical temperature $T_C$ with zero resistance at 77.1 K, but the a.c. gave a sharp drop in the resistance but zero resistance was reached at liquid nitrogen temperature. To elucidate this behaviour, an X-ray diffraction pattern was obtained. An infrared analysis was carried out for the sample and the starting materials to provide more information about the bonds. To complete the picture, electron spin resonance study is discussed. It is important to point out that this is the first time infrared measurements for superconductors have been carried out in Egypt.

## 1. Introduction

Since the recent discovery by Bednorz and Müller [1] of high temperature superconductors, a great deal of effort has been devoted to the study of the mechanisms that govern the superconductivity and charge transport of this new class of materials. Such a class covers a large number of the rare earths [2–4] and a great deal of the periodic table. One of the systems that has received great attention is the Y–Ba–Cu–O system which has zero resistance at critical temperature $T_c = 92$ K.

Infrared spectroscopy is one of the important techniques used to study the molecular structure of superconductors. There have already been several reports in which far infrared spectroscopy has been applied to the study of the superconducting energy gap in the $Y_1Ba_2Cu_3O_{9-x}$ compounds [5]. The spectra, however, are not simple to interpret and extracting a reliable value for the gap is not a straightforward process.

A study of the infrared reflection spectrum of the orthorhombic $Y_1Ba_2Cu_3O_{9-x}$ has been reported by Bonn *et al.* [5] and that of the tetragonal $Y_1Ba_2Cu_3O_{9-x}$ has been reported by Onari *et al.* [6].

Infrared spectra of the same compound for various oxygen concentrations have also been reported [7–11].

In the present work we will study the electrical resistance as a function of temperature of the system $Y_1Ba_2Cu_3O_{9-x}$ under d.c. and 900 Hz currents, ESR analysis and X-ray diffraction in addition to experimental determination of the infrared phonon spectrum of that compound.

## 2. Experimental work

### 2.1. Samples preparation

Samples with the composition $Y_1Ba_2Cu_3O_{9-x}$ were prepared using the method of solid state reaction, the details of preparation are given elsewhere [12, 13].

The starting materials were $Ba(NO_3)_2$ and CuO to give $Ba_2Cu_3O_5$ then $Y_2O_3$ was added to obtain the required compound.

### 2.2. Infrared measurements

The infrared transmission and the spectra were recorded at normal incidence of light in the range from 200 to 1000 $cm^{-1}$ with Pye Unicam SP3-300 Infrared double beam spectrophotometer.

The spectra were obtained for pressed pellets with normalized quantities of the compound $Y_1Ba_2Cu_3O_{9-x}$ and for the starting materials $Y_2O_3$ and $Ba_2Cu_3O_5$ for comparison, the results are given in Fig. 1.

### 2.3. Electrical resistance measurements

The electrical resistance was measured with the familiar four-probe method by applying 5 mA constant d.c. and also under 900 Hz, 100 mA current. The values of the d.c. and a.c. electrical resistances were measured



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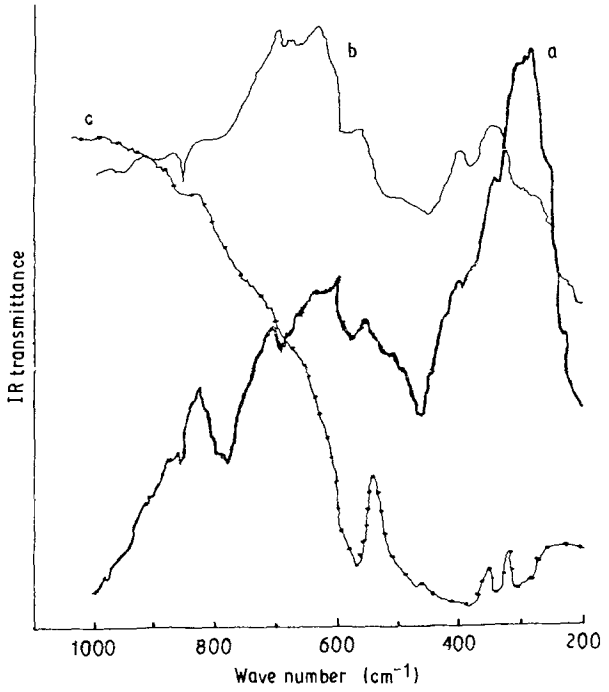


*Figure 1* Infrared transmittance of (a) $Y_1Ba_2Cu_3O_{9-x}$, (b) $Ba_2Cu_3O_5$ and (c) $Y_2O_3$.

with the temperature in the range between 77 and 300 K, and are shown in Fig. 2. The temperature was measured using a platinum resistance thermometer Pt 100, with accuracy $\pm$ 0.1 K.

## 2.4. X-ray diffraction

After the compound has been prepared it was necessary to check its superconducting quality, the widely

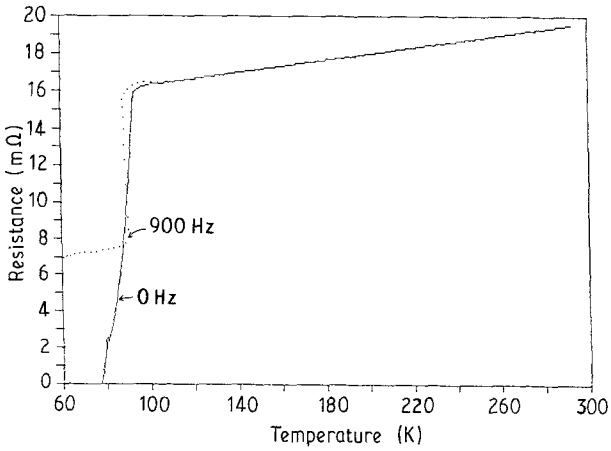


*Figure 2* Temperature dependence of resistance measured at (a) d.c. and (b) a.c. 900 Hz.

used quality control method is the X-ray diffraction which is useful for the determination of the structure of superconductors and also for determining the presence of non-superconducting residual phases left from processing.

X-ray powder diffraction data (2θ between 20° and 70° at 2° per minute) were taken for compound with copper-filtered $CuK_\alpha$ radiation.

Data analyses were performed using a computer program specially developed [14] for analysing X-ray powder data, a refinement pattern is shown in Fig. 4.

## 2.5. Electron spin resonance (ESR)

ESR spectrometer of the type JEOL-JES-FE/3X was used. The sample was finely granulated and inserted

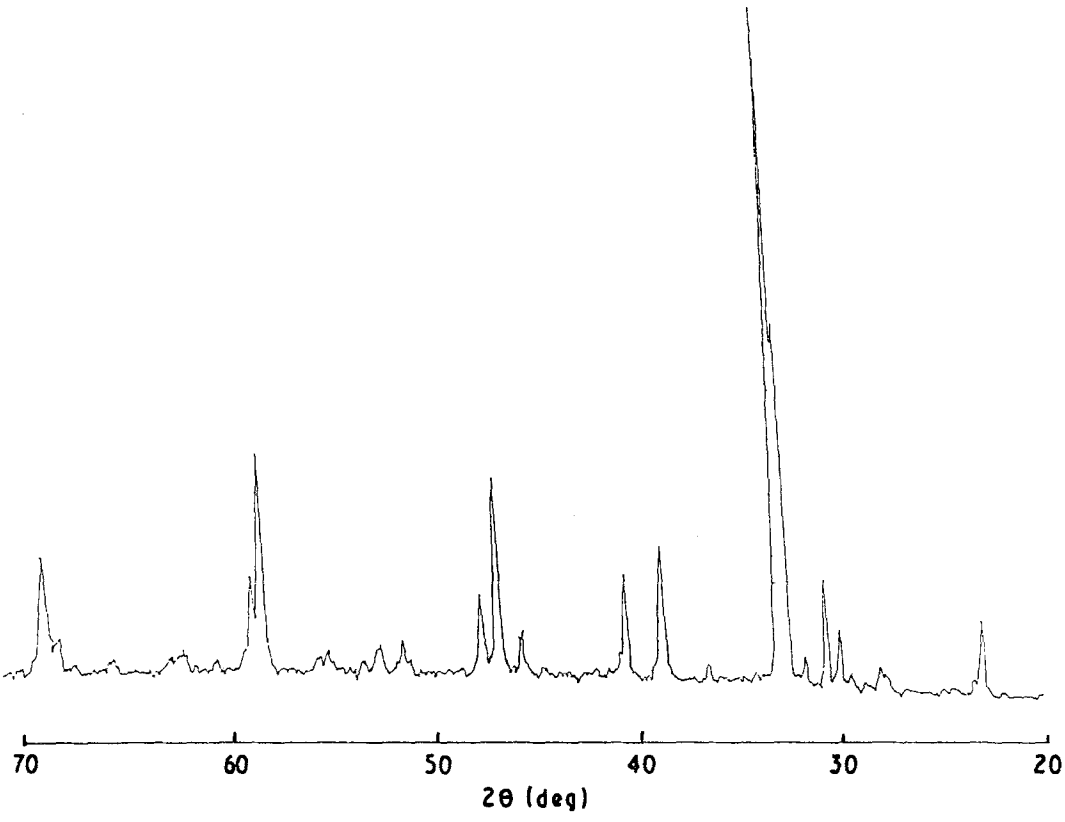


*Figure 3* X-ray diffraction pattern for $Y_1Ba_2Cu_3O_{9-x}$ (experimental).

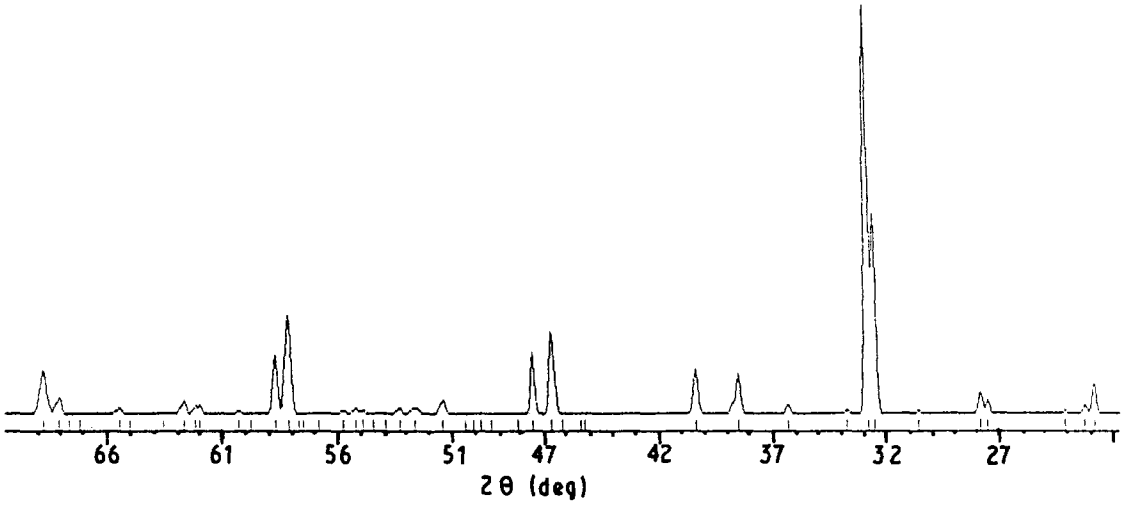


*Figure 4* X-ray diffraction pattern for $Y_1Ba_2Cu_3O_{9-x}$ (computer refined).

into a quartz capillary tube of 1 mm inner diameter and 30 mm length. A cylindrical microwave cavity was used in which a dewar flask, containing liquid nitrogen and the sample tube, was placed perpendicular to the external field. The experiment was carried out by linearly increasing and decreasing magnetic field.

In this work we confine ourselves for spectra recorded with small modulation amplitude ( $\simeq 0.05$ G) and relatively fast recording speed ( $\simeq 0.4$ G s$^{-1}$) [15].

## 3. Results and discussion

As shown in Fig. 2 the $T_c$ under the application of d.c. is 77.1 K which is very low compared with the usual $T_c = 92$ K expected for the orthorhombic phase $Y_1Ba_2Cu_3O_{9-2}$, which strongly suggests a presence of a non-superconducting phase such as the tetragonal phase or a low $T_c$ superconducting as the 2 1 1 phase in addition to the high temperature superconducting phase $Y_1Ba_2Cu_3O_{9-2}$. Moreover the resistance under 900 Hz current did not fall to zero although it showed a sharp decrease which also suggests a presence of multiphase compound or some sort of distortion to the superconducting state, this result has led us to do more physical investigations to study that behaviour.

Fig. 3 shows the X-ray diffraction pattern for our sample, the characteristic peaks of the 1 2 3 orthorhombic phase [16] are shown. Although this phase is the dominant one, but the pattern shows weak characteristic peaks related to the non-superconducting tetragonal phase [17] such as ($2\theta = 30°$, $2\theta = 45.6°$).

Comparing our infrared results measured at room temperature with other reported patterns [18] suggests that there is a difference in the microscopic properties of the material at the surface with respect to the bulk.

It is interesting to know that although there are 21 infrared active phonons in the material [18] only 11 of them namely (255, 295, 335, 395, 420, 470, 575, 625, 690, 780, 860 cm$^{-1}$) are obvious in the infrared spectrum. This can be understood as arising from strongly anisotropic screening which prevents phonon modes polarized along $a$ and $b$ crystal axes from interacting

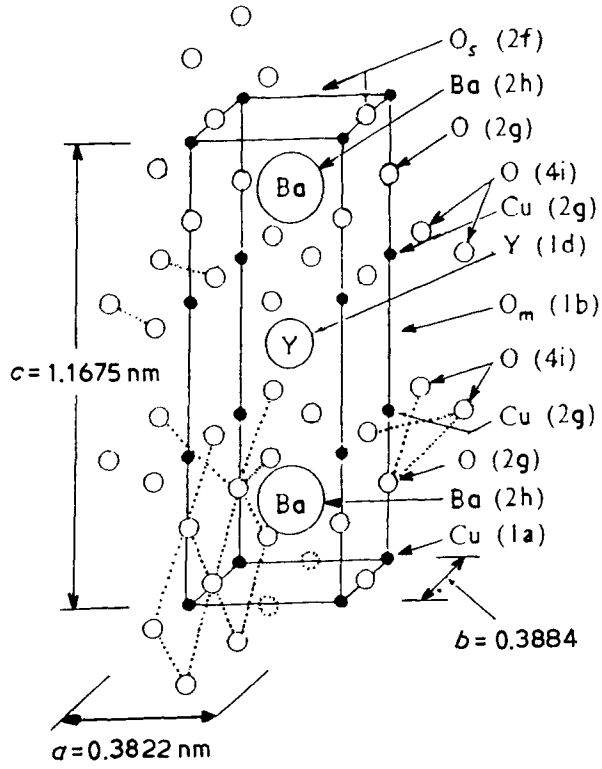


*Figure 5* Structure of $Y_1Ba_2Cu_3O_{9-x}$.

with the infrared electric field, but allows those modes with dipoles oscillating parallel to the $c$ axis to appear [19]. It is important to notice that the two peaks around 420 and 470 cm$^{-1}$ are concerning with the vibrations of the Cu–O basal planes of the pyramids [20], see Fig. 5. This mode is probably assigned to the O–Cu–O stretching related mode for the copper in the mid plane and the adjacent oxygen at the top of the pyramid, since this Cu–O bond length is the shortest in the Cu–O bonds of the unit cell. This linear O–Cu–O chain is characteristic only for the tetragonal structure [5–11, 18, 19], therefore this is also a confirmation for the presence of the non-superconducting tetragonal phase which explains the low $T_c$ of the d.c. measurements, and may be the reason for the absence of $T_c$ for the a.c. measurements.

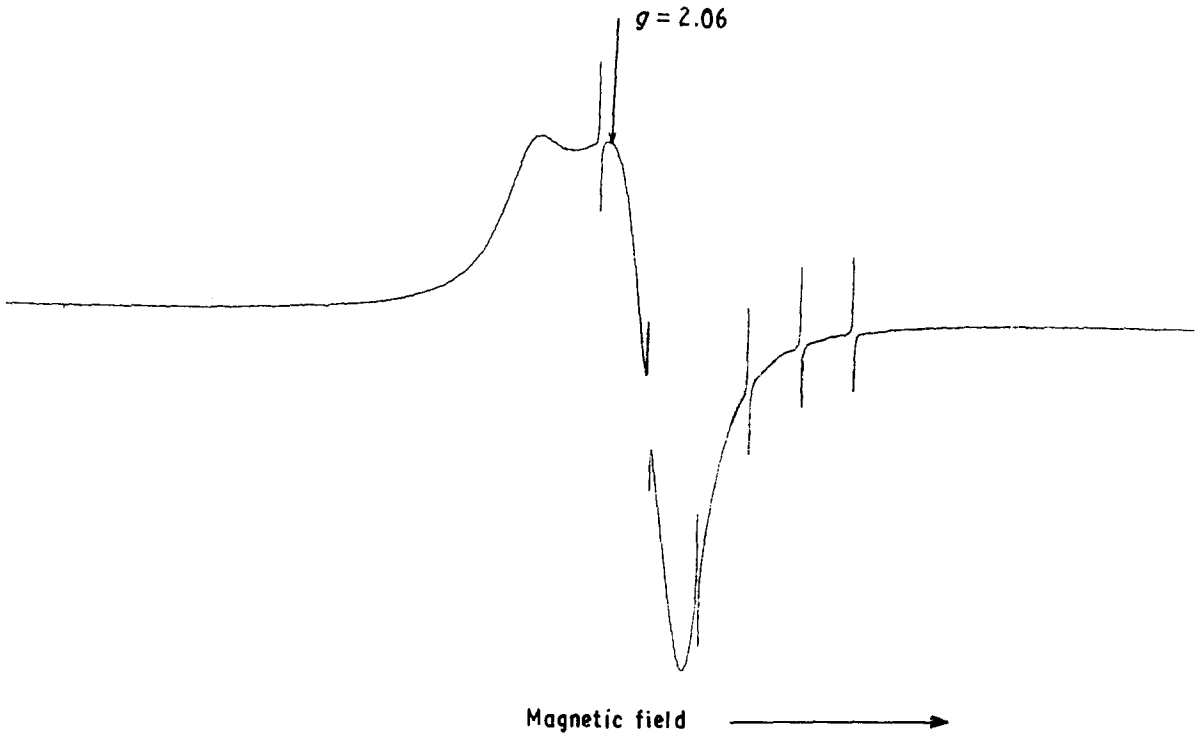


*Figure 6* ESR absorption signal of $Cu^{2+}$.

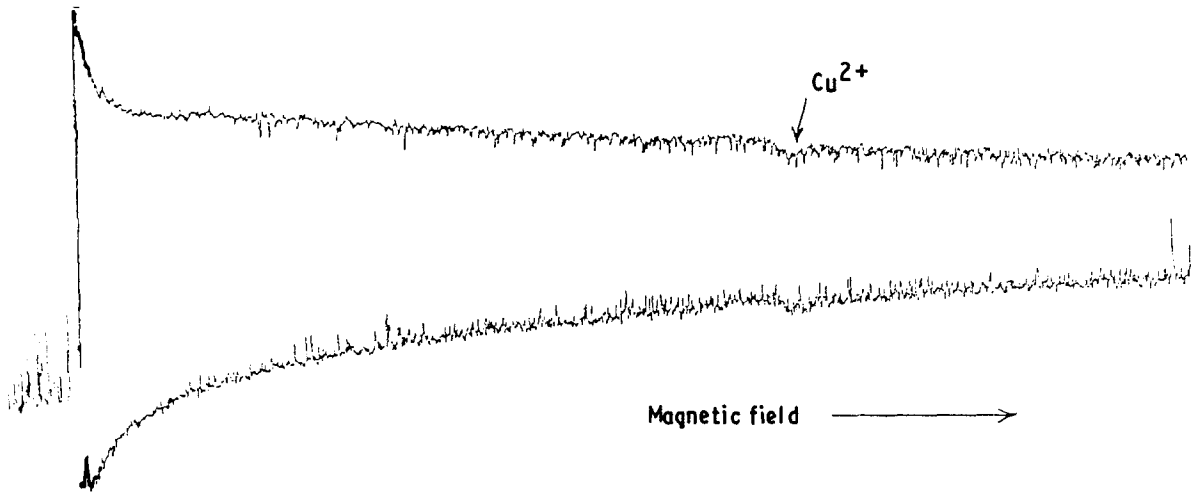


*Figure 7* ESR signal with increasing and decreasing magnetic field.

The ESR absorption spectrum of the compound $Y_1Ba_2Cu_3O_{9-x}$ at room temperature is shown in Fig. 6. The signal is a typical spectrum of the uniaxial system which reflects the importance of $Cu^{3+}$ to $Cu^{2+}$ ratio in the superconducting phenomena, where in the absence of the $Cu^{2+}$ signal, the spectrum was assumed to be symmetric. The resulting spectrum as shown in Fig. 6 indicates the existence of ESR $Cu^{2+}$ signal ($g \simeq 2.06$).

The typical ESR recording of oxide type superconductor can be seen in Fig. 7. There are three dominant features: the non-resonant low field line, the paramagnetic absorption of $Cu^{2+}$ ions around 3200 G and the upper and lower baseline for the increasing and decreasing field sweeps.

The magnetic prehistory of our sample also influences the amplitude, shape and position of low-field signal.

The paramagnetic signal has been investigated in detail by many people [21]. In the present work we point out that the appearance of the paramagnetic signal is always related to the presence of a non-superconducting phase around "3200 G". When the superconducting domain exists, the antiferromagnetic couplings between $Cu^{2+}$ ions prevent the detection of paramagnetic signal very well. This conclusion is again in good agreement with the results obtained above through the study of the d.c. and a.c. resistance, X-ray diffraction pattern and infrared analysis. Moreover the separation of hysteresis baselines as a function of external field reduces monotonously, and the rate of its change is slow which indicates the presence

of a non-superconducting phase when compared with the pure orthorhombic superconducting phase dashed line [22].

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The samples were prepared in the Faculty of Electronic Engineering, Monofia University.

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