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Comparison of the ESR spectra in ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ($1 > y > 0$) and related phases†

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Abstract. We report ESR measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ($0 < y < 1$), the 123 phase and related phases of the Y–Ba–Cu oxide system— Y_2BaCuO_5 (the green phase), $\text{Y}_2\text{Cu}_2\text{O}_5$ (the blue phase) and BaCuO_2 (the dark phase)—over a temperature range between 5 and 300 K. The ESR observed in the different phases are due to Cu ions. The temperature behaviour of the linewidths, ΔH , of the green and blue phases is in accordance with their magnetic phase transition. In the dark phase we observe a very large variation of the linewidth with temperature, $d(\Delta H)/dT = 25 \text{ G K}^{-1}$. The intensity of the 123 spectra varied by more than two orders of magnitude for different samples, indicating that its origin is due to impurity phases. Its lineshape, down to 80 K, resembles that of the green phase. On further cooling (below 60 K) the linewidth passes through a maximum at T_m , where T_m depends on y . Its signal intensity, as determined from the peak-to-peak intensity and linewidth, shows an exponential decrease with temperature. We show that the LT ESR line in the 123 samples originates from the interplay of the green and the dark impurity phases, and we present evidence of coupling between spins of these inclusions which is mediated by the conduction electrons of the 123 matrix. We also offer a qualitative explanation for the increase of the signal intensity of the LT line, and speculate about the rapid linear temperature dependence of the linewidth of the dark-phase ESR line.

1. Introduction

The mechanism of superconductivity in the new high-temperature superconductors (HTSC) is still unknown and any experimental evidence concerning their physical properties is potentially important. Most of the presently known HTSC compounds contain copper ions which (together with oxygen ions) seem to be an essential ingredient; so far all attempts to replace copper by other elements have been unsuccessful. It is therefore of greatest interest to obtain more experimental data about the structure and behaviour of these copper ions. ESR is a method of choice for the investigation of paramagnetic Cu ions. Hence it seemed worthwhile to carry out ESR measurements on the new HTSC, and, indeed, during the past year there have been a number of reports of ESR spectra from YBCO specimens which showed somewhat anomalous behaviour. However [1–9], it was soon demonstrated by a number of laboratories that the observed signals, at least in part, must be due to impurities or inclusions. Pure, single-phase 123 superconducting

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YBCO showed no ESR signal at room temperature [10, 11] (except for ESR in single crystals [8, 12] whose origin is attributed to Cu^{2+} centres [12]). Hence two questions can be raised.

- (i) Why Cu ions present in 123 compounds cannot be detected in ESR measurements.
- (ii) What is the source of the anomalous ESR spectra observed in multiphase 123 YBaCuO?

In an attempt to provide answers to these problems we carried out a number of experiments. We prepared samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ of varying oxygen content ($0 < y < 1$) using two different methods of preparation, and also samples of other phases of the CuO–BaO– Y_2O_3 phase system: phases which might be present as inclusions in multiphase samples of 123, and might be the origin of the ESR signals. We recorded their X-band ESR spectra over a wide range of temperatures.

2. Experimental procedure

The compounds investigated were $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ($0 < y < 0.9$) (the 123 – YBaCuO phase), and three other phases of the Y–Ba–Cu oxides system: Y_2BaCuO_5 (the 211 green phase), $\text{Y}_2\text{Cu}_2\text{O}_5$ (the 202 blue phase) and BaCuO_2 (the 011 dark phase).

The 123 compounds were prepared by two different methods.

(i) The arc-furnace method (referred to here as AM) where the oxides, mixed in appropriate proportions, were melted together in an arc furnace. The melted button was turned over and remelted several times in an atmosphere consisting of a mixture of argon and oxygen. The material in the arc furnace was then cast into a cylindrical mould using a vacuum technique. Finally, the samples were heat treated in oxygen at 950°C for 24 hours, and then slowly furnace cooled in oxygen. The cooling was interrupted for two hours at a time at 750, 500 and 350°C .

A number of homogeneous samples, in batches of about 50, were prepared using this method. In some of these samples the onset of the superconductive transition T_c (as measured by microwave absorption) was observed even above 100 K .

(ii) The well known sintering method (referred to here as SM).

We did not determine the oxygen content of the superconducting material after the oxygen anneal. However, by comparison of T_c with other reports, we estimated the oxygen content to be no less than 6.8; we will refer to these compounds as $\text{YBa}_2\text{Cu}_3\text{O}_7$ compounds. In order to prepare samples with lower oxygen content, oxygen was desorbed from the $\text{YBa}_2\text{Cu}_3\text{O}_7$ master compounds by heating in vacuum at temperatures between 350 and 450°C , for about 24 hours. The loss of oxygen was determined from the weight difference before and after heat treatment. In order to check the uniformity of oxygen content, a few heating runs were extended to 48 h and 72 h. No further weight changes were observed, thus confirming that the samples had reached the steady state.

The two samples with the maximum oxygen content (in the orthorhombic, superconducting phase), will be denoted as AM^+ and SM^+ respectively, while the two oxygen-deficient samples, in the tetragonal phase, will be denoted as AM^- ($y = 0.7$) and SM^- ($y = 0.9$).

All the other phases were prepared by the usual ceramic processes, using metal oxides as starting materials. The structure of all the materials was checked by x-ray

diffraction, which showed that the compounds had the proper structure. In some of the $YBa_2Cu_3O_7$ samples traces of $BaCuO_2$ were detected.

The ESR spectra were obtained using an X-band E-line Varian spectrometer, with a room-temperature sensitivity better than 10^{12} spins, for a linewidth of 1 G. The temperature was measured and controlled by an Oxford Instruments temperature controller type ESR 910. As the temperature sensor was close to, but not inside, the sample tube (which contained helium as exchange gas), the estimated temperature accuracy was ± 1 K. The samples were in powder form, with grain size less than $10 \mu\text{m}$. The powder was fixed with molten wax in the ESR quartz container.

3. Results

3.1. The 123 $YBaCuO$ compound

At room temperature the superconducting 123 $YBaCuO$ multiphase specimens showed a conventional ESR spectrum of powder samples, with an anisotropic g tensor that can be attributed to Cu^{2+} ions. The intensity of this 'high-temperature' line (HT line) varied widely from sample to sample and was usually of the order of 1–0.1% of that expected from the number of Cu ions present. On cooling, initially there was only a slight change in the lineshape, while the signal intensity I_t varied approximately as $1/T$, as expected in the case of a paramagnetic ion. The signal intensity here was calculated as $I_t = \Delta H^2 I_{pp}$ at constant modulation and RF power where ΔH is the linewidth and I_{pp} is the peak-to-peak intensity. The onset of T_c in the superconducting AM^+ and SM^+ samples was monitored by the non-resonant absorption of microwaves, as the magnetic field was swept from zero to about 6 kG, as seen in figure 3. The distinct slope of the base line (see figure 3, spectrum at 85 K) is characteristic of a superconductor close below its T_c and is attributed to losses. The slope of the base line decreases with decreasing temperature. The origin of these losses has been discussed by various authors [13, 14].

Below about 50 K this non-resonant absorption of the superconducting material in the cavity gives rise to an appreciable increase of the absolute noise level (see figure 3, spectrum at 40 K). On further cooling, as the noise decreases, the signal-to-noise ratio improves; therefore, this noise affected least our measurements at low temperatures, where the signals are also much stronger. Similar spectra, but without the effects due to superconductivity, were observed in oxygen-deficient semiconducting samples ($y > 0.6$).

Below about 60 K, the HT spectrum in all of our multiphase 123 samples is gradually replaced by a stronger, broader, approximately symmetric line, apparently of different origin. On further cooling, the signal intensity begins to increase rapidly and the linewidth reaches its maximum and then decreases.

Figures 1 and 2 show the temperature dependence of the linewidths of four $YBa_2Cu_3O_{7-y}$ samples prepared by both the AM and SM methods: two with $y = 0$, while the other two samples were from the same respective batches but with $y > 0.7$ and hence with the tetragonal (non-superconducting) structure.

3.1.1. Intensities. The signal intensities I_t increase relatively slowly from 300 K down to about 40 K, in the region where the linewidth (as seen in figure 1) does not change appreciably. Below 40 K (where there is a great increase in the linewidth) a sharp increase of the signal intensity is observed. The signal intensity increases eventually by

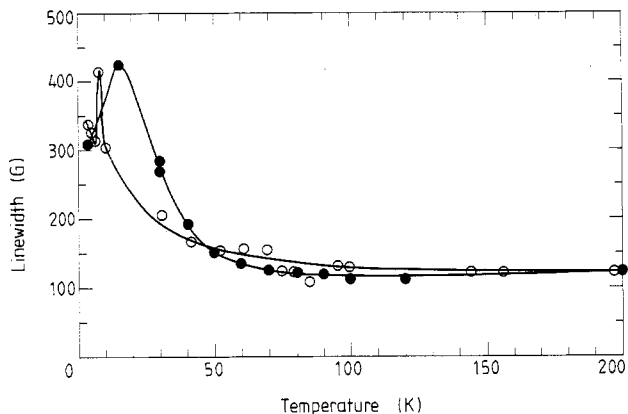


Figure 1. Linewidths of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (AM^+ , \circ) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-0.7}$ (AM^- , \bullet) as a function of temperature. Both samples were prepared from the same batch.

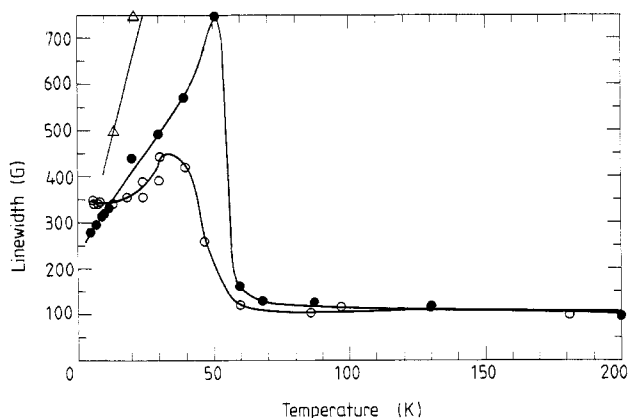


Figure 2. Linewidths of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (SM^+ , \circ) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-0.9}$ (SM^- , \bullet) as a function of temperature. Both samples were prepared from the same batch. At very low temperatures the temperature variation of the linewidth of SM^- shows some similarity to that of BaCuO_2 (Δ).

two or three orders of magnitude. Figures 4 and 5 show the signal intensity I_1 on a logarithmic scale as function of temperature for the superconducting and oxygen-deficient samples.

At low temperature the intensity dependence approximates closely, over more than two orders of magnitude, to an exponential function $I_1 = \alpha \exp(-T/T_0)$ where T_0 equals 15 K for the AM^+ and 12 K for the AM^- samples. For the SM^+ and SM^- samples $T_0 = 8.4$ K.

In the superconductivity SM^+ sample, the ESR line changes gradually from that of a Cu^{2+} , powdered, anisotropic g -value lineshape at RT into a symmetric line at low temperature. In contrast, after its oxygen content was reduced (i.e. in the oxygen-deficient SM^- sample), in the temperature region between 60 and 40 K the spectrum shows structure that could be resolved by graphical decomposition into two components. But this decomposition could not be resolved into a superposition of the HT and LT lines,

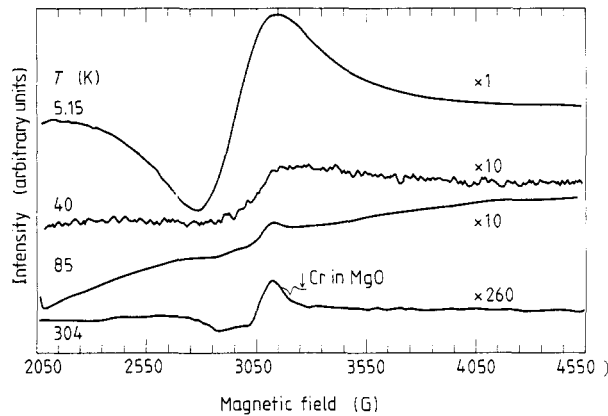


Figure 3. ESR spectra of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (SM^+) at different temperatures. Note the appearance of the base line slope at $T = 85$ K, just below T_c ($T_c = 91$ K), and the increase of noise at still lower temperature ($T = 40$ K).

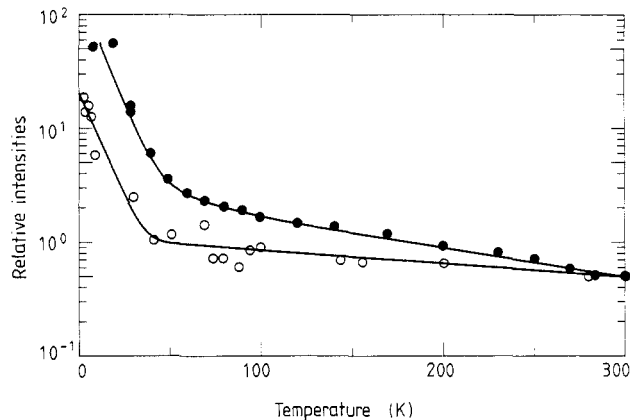


Figure 4. Signal intensity I_i (arbitrary units) of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (AM^+ , \circ) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-0.7}$ (AM^- , \bullet) as a function of temperature. Both samples were prepared from the same batch. At 300 K the intensities (per unit weight) of the two samples were the same.

taken with their weighting factor proportional to the temperature dependence of their corresponding intensity. This remark applies also to the spectra of AM^+ , AM^- and SM^+ samples, where a gradual transition from the HT to the LT lineshape was observed and it was not possible to resolve the spectra into two distinct lines.

3.1.2. g values. As mentioned above, the HT spectra are typical of a powder spectrum of a $S = \frac{1}{2}$ ion, with an anisotropic g tensor, characteristic of a Cu^{2+} ion on a site of low symmetry. A rough estimate for the powdered sample at room temperature gives $g_{xx} = 2.05$, $g_{yy} = 2.10$ and $g_{zz} = 2.20$, close to values reported in the literature (see below).

Below about 60 K the (symmetric) LT line shifts towards lower field (higher g values). As an example, figure 6 shows the g values of the AM^- sample ($\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$) as function of temperature (where an average g value was used for the anisotropic HT line). The

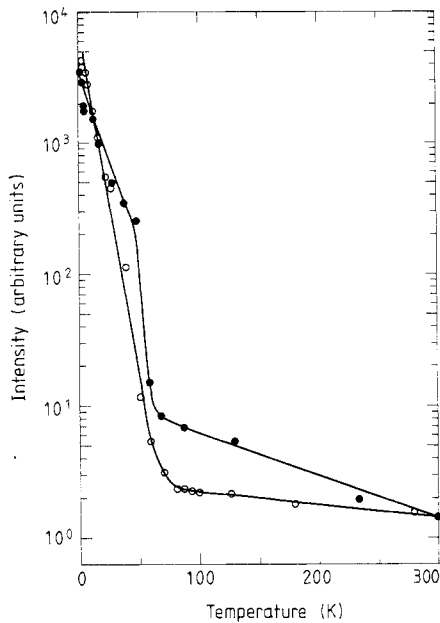


Figure 5. Signal intensity I_i (arbitrary units) of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (SM^+ , \circ) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-0.9}$ (SM^- , \bullet) as a function of temperature. Both samples were obtained from the same batch. At 300 K the intensities (per unit weight) of the two samples were the same.

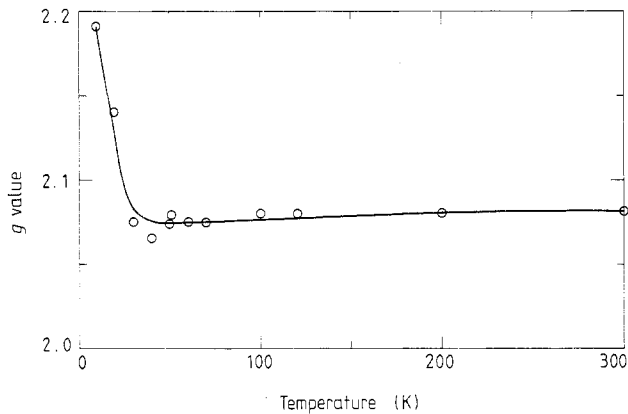


Figure 6. g value of $\text{YBa}_2\text{Cu}_3\text{O}_{7-0.7}$ (AM^-) as a function of temperature. From 300 to 40 K an average g value is given, as the spectra displayed powder structure with an anisotropic g tensor.

shift towards higher g values starts around the temperatures where the linewidth and the intensity start to increase (see figures 1, 2, 4 and 5).

We have measured a number of different $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples. They show similar behaviour, namely the presence of the high-temperature and low-temperature lines. The intensity of the LT line decreases exponentially with increasing temperature. Comparison between different samples measured under similar conditions showed widely different absolute signal intensities of the low-temperature line. One particular sample, (J444) kindly provided by A Junod [15], with an onset of superconducting temperature of 100 K as measured by microwave absorption, showed a very low intensity of the LT line. Its

ESR signal intensity was at least one order of magnitude weaker than observed in other samples and its T_c (as measured by the microwave method) was higher by about 3 K.

We conclude from our ESR experimental results on $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ samples that both the fully oxidised (AM^+ and SM^+) and the oxygen-deficient (AM^- and SM^-) samples showed similar behaviour. However, there were important differences: namely, the temperature of the maximum linewidth, T_m , varies from sample to sample, increasing with the oxygen deficit y , and there are differences in the temperature dependence of linewidth, intensity etc. Thus, on cooling below T_m the linewidth in the oxygen-rich samples (AM^+ , SM^+) remained approximately constant, while in the oxygen-deficient samples (AM^- , SM^-) it decreased linearly from T_m down to 5 K. Also, there were differences between the samples in the magnitude of the linewidth and in the signal intensity. These results suggest that the ESR signals observed in 123 compounds are due to additional phases, not related directly to superconductivity in YBaCuO , and their presence depends on sample preparation.

3.2. Other phases in the $\text{CuO-BaO-Y}_2\text{O}_3$ system

3.2.1. The green phase. A number of laboratories have reported the ESR powder spectrum of the 211 green phase, Y_2BaCuO_5 [2, 16–18]. More recently, Kobayashi and co-workers [18] carried out ESR measurements on single-crystal specimens (down to 83 K) and obtained $g_{xx} = 2.050$, $g_{yy} = 2.094$ and $g_{zz} = 2.222$, very close to the values observed in the 123 compound mentioned above.

Our measurements of Y_2BaCuO_5 at room temperature showed that the measured signal intensities I_i agreed roughly with those expected (assuming that the ESR signal is due to all Cu^{2+} ions present). The shape and position of the powder line we obtained agree with those in the literature [19].

On cooling, the structure in the ESR line becomes less pronounced in the vicinity of 100 K. On further cooling, below about 40 K, the lineshape starts to change into a more symmetric one and its linewidth increases. At about 20 K a rapid increase of the linewidth is observed; at still lower temperature a structure appears, indicating some kind of phase transition. The linewidth as a function of temperature is shown in figure 7, where for comparison the linewidth of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$, obtained in figure 1, is also shown. Our ESR results are consistent with susceptibility measurements [15, 20, 21], where a magnetic moment of $\mu = 1.92$ is obtained from the Curie–Weiss behaviour in the paramagnetic state, as expected for a $S = \frac{1}{2} \text{Cu}^{2+}$ ion. The $1/\chi$ against T graph extrapolated from high temperature cuts the T axis at about -40 K. But on cooling down, it bends up and there is a maximum in $1/\chi$ at 14 K, thus apparently confirming that the 211 phase orders antiferromagnetically. However, the reported T_N (the maximum of $1/\chi$) ranges from 14 to 54 K. Also, Kanoda *et al* [22] found that the ESR line of the 211 green phase broadens and vanishes near 20 K, which they interpreted as due to a Néel transition at 14 K, as derived from their magnetic susceptibility measurements. Thus the reason for the spread in T_N deserves further investigation.

3.2.2. The blue phase $\text{Y}_2\text{Cu}_2\text{O}_5$. In $\text{Y}_2\text{Cu}_2\text{O}_5$ a symmetric line was observed at room temperature and the intensities measured agreed (roughly) with those expected (assuming that the ESR signal is due to all Cu^{2+} ions present). The linewidth (figure 7) is constant down to 120 K, where it increases appreciably, and at 20 K there is a further huge increase in the linewidth, indicating a phase transition.

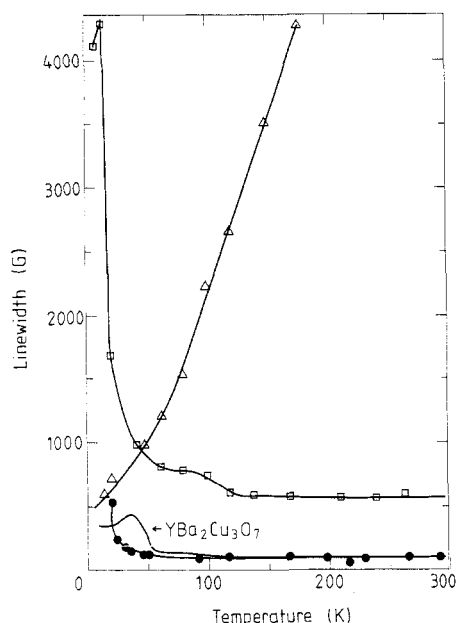


Figure 7. The linewidth of Y_2BaCuO_5 (\bullet), $\text{Y}_2\text{Cu}_2\text{O}_5$ (\square) and BaCuO_2 (Δ) as a function of temperature. For comparison the linewidth of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (AM^+ and SM^-) is also shown.

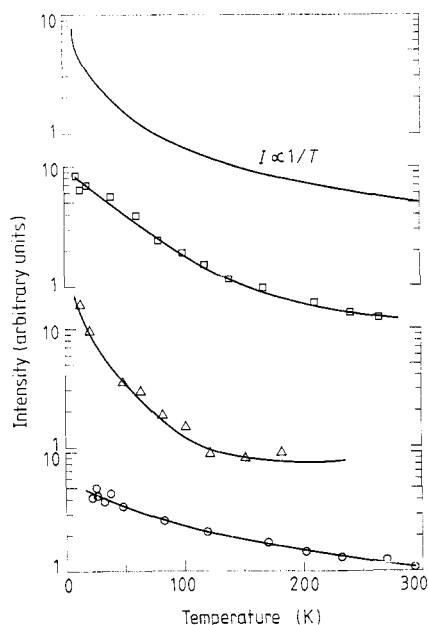


Figure 8. Signal intensity (in arbitrary units) of Y_3BaCuO_5 (\circ), $\text{Y}_2\text{Cu}_2\text{O}_5$ (\square) BaCuO_2 (Δ). At 300 K they show approximately the same intensity per Cu ion. For comparison the curve for $1/T$ is also shown.

Susceptibility measurements by Troc *et al* [22] confirm the ESR results, indicating that there is an antiferromagnetic transition at 13 K.

3.2.3. The 011 dark phase BaCuO_2 . At room temperature our BaCuO_2 showed a typical ESR powder spectrum with anisotropic g ; the intensity of the (narrow) room-temperature BaCuO_2 line corresponding to roughly only 0.5% of the expected intensity and we conclude that it originates from some impurity phases. Similar room-temperature spectra were reported by other investigators [1, 2]. On cooling, a broad line, about 4000 G, appears below 180 K; it narrows rapidly with decreasing temperature and reaches less than 600 G at 14 K (figure 7).

The signal intensity I_i of this broad line agrees roughly with that calculated for the Cu ions in BaCuO_2 . The narrow RT line of BaCuO_2 was clearly detected down to the lowest temperatures employed (5 K), superimposed on the broad LT line, indicating that the magnetic moments associated with these two lines are distinct and do not interact, in contrast to the resonance lines observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$.

The magnetic susceptibility of BaCuO_2 shows no magnetic phase transitions down to 4 K. But there are appreciable discrepancies between the results reported from different laboratories [23, 24]. Specific heat measurements [25] show a distinct peak at 14 K.

The variation of the logarithm of the signal intensities I_i in these three compounds, namely the green, blue and dark phases, as function of temperature is shown in figure 8; a curve proportional to $1/T$ is also included for comparison. Though none of the three compounds follows a $1/T$ function exactly, the deviation from $1/T$ is rather small. For

BaCuO_2 in the temperature range 10–50 K a $1/(T - T_0)$ curve, with $T_0 \approx 8$ K gives a better fit.

4. Discussion

Our ESR measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ show that the ESR spectrum is not an intrinsic property of the multiphase material as it varies from sample to sample. However, all the 123 polyphase samples have a common feature: namely, a high-temperature (HT) signal with a structure that can be attributed to a Cu^{2+} doublet with an anisotropic g tensor, presumably originating from inclusions of 211 green phase (of the order of 1–0.1% or even less), in agreement with the lineshape, g value and the temperature variation of its intensity. The HT line disappears at temperatures not related to T_c and is replaced by an approximately symmetric low-temperature (LT) line. The intensity of the LT line increases very rapidly with decreasing temperature, accompanied by a shift of the line towards lower field (higher g values) and changes in linewidth. There are appreciable differences between the LT spectra of the different samples, depending on the oxygen content of the material, the method and details of preparation. Though the general features of the ESR spectra of samples from the same batch but with different oxygen content are similar, marked differences are observed, such as the shift of the maximum of the LT linewidth towards higher temperatures (from about 20 K for $y = 0$ to 40 K for $y \sim 0.7$) and also differences in lineshape, in width and in intensity as a function of temperature, as shown in figures 1–5.

The YBaCuO ESR spectrum seems to be due to two distinct sources. The HT asymmetric line, both in the oxygen-rich and oxygen-deficient samples, is no doubt due to inclusions of Y_2BaCuO_5 , the 211 green phase. This has been already suggested by a number of investigators [26].

The LT line, which overwhelms the HT line below about 60 K, is very unusual. Traces of BaCuO_2 (of the order of 1%) could perhaps account for the presence of a strong, broad line. This can be deduced from the linear temperature variation of its width below T_m : $d\Delta H/dT = 10 \text{ G K}^{-1}$ in AM^- and in SM^- , which shows a similar tendency as in BaCuO_2 (where $d\Delta H/dT = 24 \text{ G K}^{-1}$) but with smaller slope. However, the LT lines in AM^+ and SM^+ do not show a similar linewidth variation.

From the considerations of the linewidth and signal intensity at low temperature of the green and blue phases, it seems that inclusions of these two phases cannot account for the observed LT line in our multiphase 123 samples.

The most appealing suggestion as to the origin of the LT line, and suggested also by other authors [23, 25], is that it is due to BaCuO_2 inclusions. As we attribute the HT line of our samples to green-phase inclusions, one would expect that a simple superposition of the spectra of the two phases would reproduce the experimentally observed ESR lines of the 123 phase and their temperature variation. We therefore prepared mixtures, in different proportions, of the 211 green and 011 dark phases (in ratios from 1 : 6 to 1 : 200) and recorded their ESR spectra over a range of temperatures (figure 9). In agreement with expectations, from RT to about 100 K the spectra show the characteristic line of the green phase with an anisotropic g tensor. At low temperature, the broad line of the dark BaCuO_2 phase clearly overwhelms the green-phase line. However, this is not what we observed in the multiphase 123 samples; instead, a gradual transition from the HT line to the LT line takes place, and the linewidth passes through a maximum. This seems to indicate strong interactions between the two paramagnetic centres in the 123 phases:

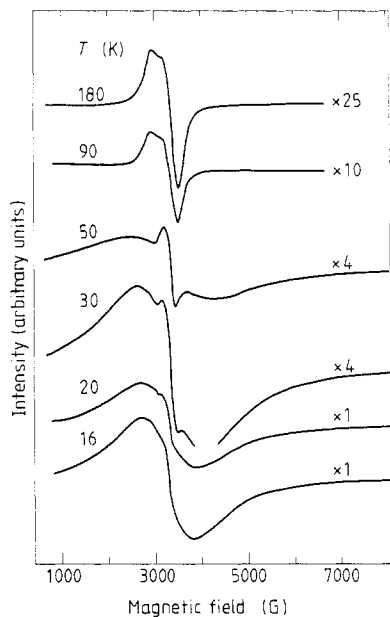


Figure 9. ESR spectra of a mixture of Y_2BaCuO_5 and BaCuO_2 (weight ratio 1:30) at various temperatures. Note that in the 16 K spectrum the narrow Y_2BaCuO_5 line is still visible.

the HT centre (the green phase) and the LT centre (presumably the BaCuO_2 phase). One can interpret this behaviour by assuming that the spins in the small inclusions of the green and dark phases are interacting via the conduction electron of the 123 compound in which these inclusions are embedded. Because of these interactions we have, in the multiphase 123 compounds, not two independent resonances but one combined resonance. This speculation is supported by the temperature dependence of the linewidth of the SM^+ and SM^- compounds (see figure 2). Indeed, in SM^- , where the electric conductivity is low, the interaction is expected to be weak and at low temperature the temperature dependence of the linewidth is similar to that of the dark phase. In the SM^+ compound we observe a smaller linewidth at the maximum and subsequently saturation of the linewidth at lower temperatures. The temperature of the linewidth maximum, T_m , differs from sample to sample and increases with the oxygen deficit. This may be due either to changes (with the oxygen treatment) in the paramagnetic centres themselves or to changes in the surrounding $\text{YBa}_2\text{Cu}_3\text{O}_x$ matrix.

Another puzzling question is why the BaCuO_2 linewidth changes so rapidly with temperature. If one tries to attribute the LT signal in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ samples to BaCuO_2 inclusions, then it is difficult to account for the appreciably narrower linewidth and a much slower rate of change of linewidth with temperature for $y > 0.7$ than in BaCuO_2 .

We also cannot account for the apparently exponential decrease of ESR signal intensity with increasing temperature in the 123 samples. This was not observed in any other phase. We would like to note that this exponential decrease is based on the assumption that the intensity is proportional to $\Delta H^2 I_t$, assuming a Lorentzian lineshape in the essential region. But, due to the very large linewidth of the ESR line of the dark 011 phase inclusions at $T \geq 40$ K (see figures 1 and 7), most of the integral intensity of the line is not included in the calculation of I_t .

Also, the HT narrow line in BaCuO_2 is probably not intrinsic to this phase, but is due to some impurity phase. The very broad LT line in BaCuO_2 is also unusual for the

linewidth increases very rapidly with temperature: $d\Delta H/dT = 24 \text{ G K}^{-1}$. This cannot be due to a Korringa-like interaction as the material is an insulator (resistivity at room temperature $\sim 3 \times 10^5 \Omega \text{ cm}^{-1}$). We speculate that the dark phase may be in the state of a spin liquid with large spin fluctuations. If the liquid droplets are large enough and the effective dimension is two, then one may expect a linear temperature dependence just from the number of bosonic excitations with a quadratic dispersion dependence. It would be interesting to investigate this compound by neutron diffraction.

5. Conclusions

We have measured the ESR spectra of a large number of $YBa_2Cu_3O_{7-y}$ compounds with different oxygen content as function of temperature. The results, from room temperature down to about 60 K, show a spectrum characteristic of powder samples containing ions with anisotropic g tensors which can be related to the resonance of Cu^{2+} ions on low symmetry sites. This resonance resembles, though it is not identical to, the ESR spectrum of Y_2BaCuO_5 in its lineshape and width, as well as in its intensity. Thus inclusions of the green phase are present, in varying concentration, in most of the $YBa_2Cu_3O_x$ samples. Below a temperature somewhere between 60 and 40 K, far below T_c , the ESR spectrum changes into a symmetric line. The origin of this line is linked to $BaCuO_2$ impurities but its temperature behaviour is different. Its width increases and passes through a maximum at still lower temperatures. T_m , the temperature of the maximum linewidth, varies with the oxygen content, and it also differs slightly from sample to sample. In all these compounds there is an exponential variation of the LT signal intensity with temperature. We observe a marked difference between the spectra of the superconducting compound and those of the same samples after suppressing superconductivity by removal of oxygen. Neither the origin of the LT line nor the reason for its unusual temperature variation is clear at this stage. In spite of the origin of many details of the reported spectra still being unknown, we provide some qualitative information regarding the nature of the low-temperature resonance line and the growth of the apparent integral intensity at low temperatures.

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