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Abstract. X- and Q-band electron paramagnetic resonance studies have been carried out on a polycrystalline superconductor $YBa_{1.9}Na_{0.1}Cu_3O_{7-\delta}$ (Y–Ba–Na–Cu–O) over the temperature range 4.2–300 K. It is concluded that the monovalent Na^+ ions substitute for Ba^{2+} ions, and not for Cu^{2+} ions. The onset of the superconducting transition is determined to occur at 91 K, while the absorption of microwaves in low magnetic fields begins to occur below 100 K. The value of the upper critical field estimated here, as well as that of the specific heat coefficient, are lower than those reported for the pure $YBa_2Cu_3O_{7-\delta}$ ceramic. The local symmetry about the Cu^{2+} ion in the phase of the sample with increased oxygen vacancy content, responsible for the Cu^{2+} EPR signal, is deduced to be orthorhombic over the entire range of temperature investigated, as revealed by the Cu^{2+} principal values (g_z, g_x and g_y), which are, in turn, used to estimate the energy-level sequence for the Cu^{2+} ion. The covalency effect due to Cu–O bonding is found to be significant. The hyperfine splitting constant $|A_z|$, as estimated from the weak hyperfine structure at low magnetic fields, is estimated to be 8 mT at 4.2 K. The sample exhibits magnetic memory in the superconducting state.

1. Introduction

High-T_c superconducting materials based on $YBa_2Cu_3O_{7-\delta}$, with different modifications produced by the introduction of divalent, or trivalent, dopants partially replacing the Y, Ba or Cu ions, have been investigated by various experimental techniques. These modifications are made with a view to improving the superconducting properties, while retaining the mechanism responsible for high transition temperatures. The higher polarisability of divalent calcium group elements in high-T_c superconductors has significant influence on elevation of T_c (Ronay and Newns 1989).

The substituted monovalent Na^+ ions for divalent Ba^{2+} ions in $YBa_2Cu_3O_{7-\delta}$ are expected to introduce changes in the crystal structure and the density of states. The unit cell for the $YBa_{1.95}Na_{0.05}Cu_3O_{7-\delta}$ ceramic, which is close to the $YBa_{1.9}Na_{0.1}Cu_3O_{7-\delta}$ sample (Y–Ba–Na–Cu–O hereafter) investigated here, is orthorhombic (Ausloos *et al* 1988). The pure and doped $YBa_2Cu_3O_{7-\delta}$ samples display superconducting properties in the orthorhombic phase, in contrast to these samples in the tetragonal phase, in which no superconductivity is observed (Jorgensen *et al* 1987). The alkaline-group impurities

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introduced in $YBa_2Cu_3O_{7-\delta}$ cause lowering of the synthesis temperature, at which the sample is produced, by ~100 °C (see § 2 and Ausloos *et al* 1988). The energy levels of the Cu^{2+} ion in the phase of the sample that is responsible for the Cu^{2+} EPR signal, i.e. the phase with increased oxygen vacancy content in the present case, in the Y–Ba–Na–Cu–O sample can be deduced, using the experimentally determined principal values of the matrix **g**.

It is the purpose of the present paper to study in detail, using X- and Q-band electron paramagnetic resonance (EPR), the high-T_c material $YBa_{1.9}Na_{0.1}Cu_3O_{7-\delta}$. The X-band studies were made over the temperature range 4.2–300 K, while the Q-band studies were confined to room temperature.

2. Sample preparation

The Y–Ba–Na–Cu–O sample was prepared by the use of the conventional technique, by first mixing stoichiometric amounts of CuO, Y_2O_3 and $BaCO_3$ with an adequate proportion of $NaHCO_3$, and grinding the mixture in a ball mill. The mixture was then heated and calcinated at 800 °C for 12 h. The resulting product was reground, pressed into a pellet and sintered at 960 °C in oxygen gas for several hours. The product was finally cooled slowly to the room temperature.

3. Experimental arrangement

A Varian V4502 X-band spectrometer with a 12-in electromagnet, powered by a Bruker power supply (type B-MN50/200) and driven by a Bruker field controller (B-H15), was used, together with a cryostat for low-temperature measurements. A Varian V4561 microwave bridge (35 GHz) and cylindrical cavity were used for Q-band measurements. The Y–Ba–Na–Cu–O sample used was in the form of a small black irregular pellet and was chosen to be sufficiently small to prevent overloading of the cavity; also, a suitably low microwave power level was used so as not to saturate the EPR signal. The modulation frequency was chosen to be 400 Hz.

4. The Cu^{2+} EPR spectrum and the transition temperature

As discussed later in this section, the Cu^{2+} EPR lines arise from the presence of a normal phase, i.e. the phase with increased oxygen vacancies, in the sample. They do not arise out of surfaces of superconducting regions; for in that case the EPR lines will be completely broadened out, due to inhomogeneous broadening caused by flux exclusion on the surfaces of superconducting regions. The Cu^{2+} EPR lines could be observed all the way through from room temperature to liquid-helium temperature (LHT) (figure 1). A weak EPR line appeared at temperatures below $\simeq$180 K at the magnetic field value $\simeq$268 mT; this line became more intense at LHT. Figure 2 exhibits the Q-band spectrum at room temperature. The components of the tensor **g**, as determined from the Q-band spectrum, which enables more accurate determination of the principal values of the matrix **g** than does the X-band spectrum, are, at room temperature, $g_z = 2.2275$, $g_x = 2.1180$ and $g_y = 2.0460$ (using the convention $g_z > g_x > g_y$), exhibiting, unequivocally,
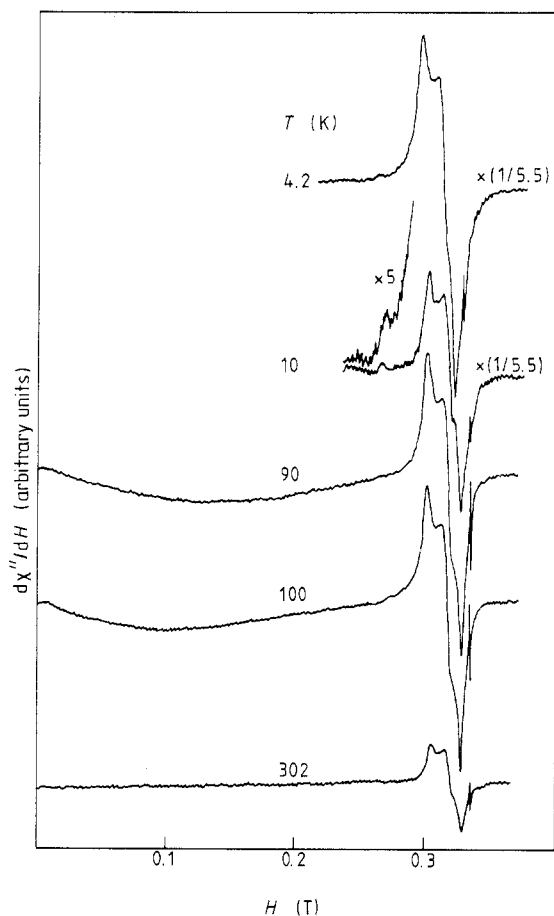
Figure 1. EPR spectra of the $YBa_{1.9}Na_{0.1}Cu_3O_{7-\delta}$ sample at various temperatures; there is a small peak at $\simeq 268$ mT at 10 K, as recorded using a larger gain.
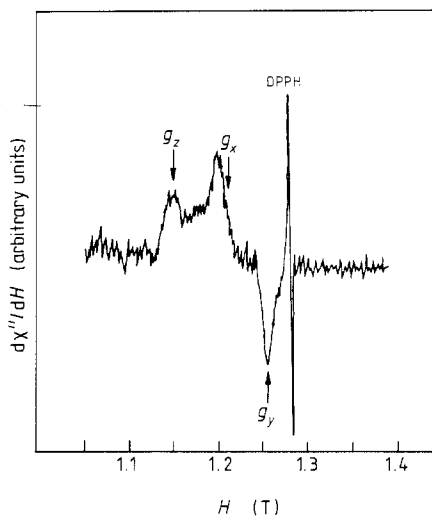
Figure 2. Room-temperature Q-band EPR spectrum of the $YBa_{1.9}Na_{0.1}Cu_3O_{7-\delta}$ sample, clearly exhibiting the Cu^{2+} lines, typical of orthorhombic symmetry.

orthorhombic local symmetry, around the Cu^{2+} ion; this is in accordance with the observation of Kobayashi *et al* (1988).

As seen from figures 3(*a*) and 3(*b*), which exhibit the peak-to-peak line height (I_{PP}) and the linewidth (ΔH_{PP}), respectively, of the first derivative of the Cu^{2+} EPR line in Y–Ba–Na–Cu–O, both I_{PP} and ΔH_{PP} exhibit slight jumps around 91 K, implying that $T_c = 91$ K for the Y–Ba–Na–Cu–O sample. This is also the reported superconducting transition temperature of the pure $YBa_2Cu_3O_{7-\delta}$ ceramic (Bist *et al* 1988, Horn *et al* 1987, Stankowski *et al* 1987). As for I_{PP}, it shows a slight decrease below $\simeq 210$ K, which is, probably, due to the occurrence of a weak transition. This is in agreement with the ultrasonic measurements of Toulouse *et al* (1988), which indicated an instability due to the occurrence of a structural order–disorder transition in the $YBa_2Cu_3O_{7-\delta}$ ceramic, in the temperature range 210–230 K. Overall, the intensity variation is of T^{-1} form, typical of paramagnets. The linewidth, ΔH_{PP}, exhibits a slight increase below $\simeq 10$ K (figure 3(*b*)).
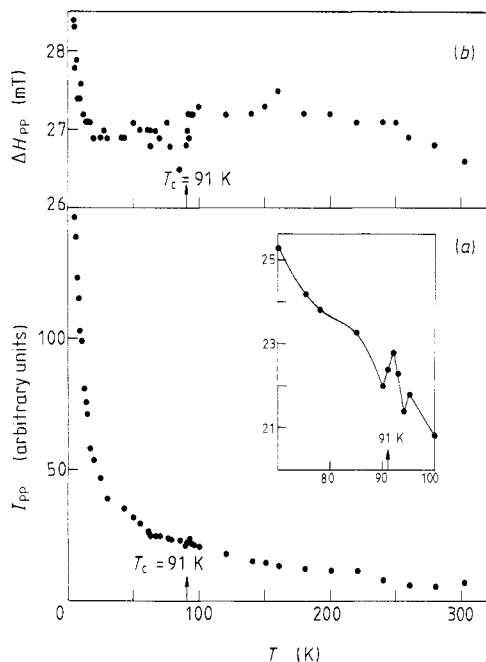
Figure 3. Plots of (a) the peak-to-peak height (I_{PP}) and (b) the EPR linewidth (ΔH_{PP}) of the first derivatives of the Cu^{2+} line in the Y–Ba–Na–Cu–O sample as functions of temperature.
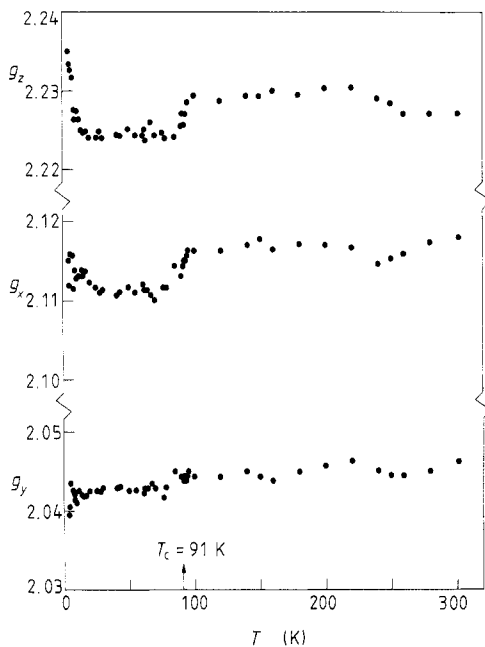
Figure 4. Plots of Cu^{2+} principal g-values (g_z, g_x, g_y) for the Y–Ba–Na–Cu–O sample as functions of temperature.

Small changes in the g_z and g_x principal values are also observed at $T_c = 91$ K, which may be due to the onset of superconductivity in the sample. A small increase in the value of each of the three principal g-values is observed at LHT (figure 4).

The transition temperature, T_c, is a measure of the density of states at the Fermi level according to the BCS theory (Kittel 1967). Since the value of T_c in the present Y–Ba–Na–Cu–O sample is the same as that in the pure YBa$_2$Cu$_3$O$_{7-\delta}$ ceramic, the monovalent Na$^+$ ions should substitute for the Ba^{2+} ions, because the number of carriers is not changed significantly. Had the Na$^+$ ions substituted for the Cu^{2+} ions the number of carriers would have been significantly decreased, causing a much lower T_c.

The present EPR signal indicates the presence of $\simeq 1.9 \times 10^{21}$ paramagnetic Cu^{2+} spins cm^{-3}, which represents $\simeq 11\%$ of total Cu concentration. (This is estimated by comparing the integrated intensity of this signal with that of the Cu^{2+} line in 2 mg of CuSO$_4 \cdot 5$H$_2$O sample.)

It is well known that there is no Cu^{2+} EPR signal that can be observed in the super-conducting phase of the ceramic. The Cu^{2+} EPR of such materials is usually due either to impurity phases, i.e. the green phase (Y$_2$BaCuO$_5$), or brown phase (YBa$_3$Cu$_2$O$_y$), as reported by Bowden *et al* (1987) and by McKinnon *et al* (1988), or to the ceramic with smaller oxygen content, as reported by Owens *et al* (1988), or the ceramic with increased oxygen vacancy content, as reported by Kobayashi *et al* (1988). Other possibilities are an Anderson lattice with an unusually high Kondo temperature (Mehran *et al* 1987a), a hole transferred from copper to oxygen (Benakki *et al* 1987) and Cu^{2+} ions in special coordination (Mehran *et al* 1987b). The reason for the EPR 'silence' of the pure

YBa$_2$Cu$_3$O$_{7-\delta}$ ceramic is not clear at present, as discussed by Mehran *et al* (1988a). The present Cu^{2+} signal is most definitely due to the presence in the sample of the phase with increased oxygen vacancy content, possessing a greater number of localised Cu^{2+} d electrons. For the present Cu^{2+} EPR signal is exactly like that reported for the phase with increased oxygen vacancy content by Kobayashi *et al* (1988) with exactly the same *g*-values. It is not due to the presence of the green phase, because the EPR spectrum of the Cu^{2+} in the green phase almost disappears below 15 K (McKinnon *et al* 1988). It is also not due to the brown phase, because the present Cu^{2+} EPR spectrum is significantly different from that reported for this phase by Bowden *et al* (1987) and by McKinnon *et al* (1988). The following discussion of the Cu^{2+} *g*-values, thus, applies to the phase with increased oxygen vacancy content.

The calculated R ($\equiv (g_x - g_y)/(g_z - g_x)$; $g_z > g_x > g_y$) values are found to be 0.66 and 0.59 at 302 and 4.2 K respectively. They indicate that the ground state of the Cu^{2+} ion is d$_{x^2-y^2}$, since $R < 1$. When $R > 1$, d$_{3z^2-r^2}$ is supposed to be the ground state (Dudley and Hathaway 1970).

The following expressions can be used to determine the energy level spacings:

$$g_z = g_e - 8\lambda\alpha_{11}/\Delta_1 \qquad g_x = g_e - 2\lambda\alpha_{22}/\Delta_2 \qquad g_y = g_e - 2\lambda\alpha_{33}/\Delta_3 \qquad (1)$$

where λ is the spin–orbit coupling constant for the ^{2}D state of the free Cu^{2+} ion ($= -829$ cm^{-1}; Abragam and Bleaney 1970), α_{11}, α_{22}, α_{33} are the combined orbit and spin-orbit reduction parameters, g_e is the free-electron value ($= 2.0023$) and $\Delta_1 = \Delta E(d_{x^2-y^2} \leftrightarrow d_{xy})$, $\Delta_2 = \Delta E(d_{x^2-y^2} \leftrightarrow d_{xz})$, $\Delta_3 = \Delta E(d_{x^2-y^2} \leftrightarrow d_{yz})$. The approximate values at 302 K, thus found, are: $\Delta_1 = -35.59\lambda'$ ($= 15\,300$ cm^{-1}), $\Delta_2 = -17.27\lambda'$ ($= 7430$ cm^{-1}) and $\Delta_3 = -45.35\lambda'$ ($= 19\,500$ cm^{-1}), using the measured values of the *g*-components and assuming $\lambda\alpha_{11} \simeq \lambda\alpha_{22} \simeq \lambda\alpha_{33} = \lambda' = -430$ cm^{-1}, which is the value for the green phase (Y$_2$BaCuO$_5$), determined from electronic absorption measurements (Ong *et al* 1988). (The value for the green phase has been used here since no value for the phase with increased oxygen content has been reported.) The corresponding values at 4.2 K are: $\Delta_1 = -34.38\lambda'$ ($= 14\,780$ cm^{-1}), $\Delta_2 = -18.23\lambda'$ ($= 7840$ cm^{-1}) and $\Delta_3 = -53.76\lambda'$ ($= 23\,120$ cm^{-1}). The values of Δ_i ($i = 1, 2, 3$) at 302 and 4.2 K are slightly different from each other. Using (1), the following sequence of energy levels of the Cu^{2+} ion are obtained in Y–Ba–Na–Cu–O: $E_{x^2-y^2} < E_{3z^2-r^2} < E_{xz} < E_{xy} < E_{yz}$. The energy levels E_{xz} and E_{xy} for the phase with an increased oxygen vacancy content are in reverse sequence to those for the Cu^{2+} ion in some other crystals with orthorhombic symmetry (Lakshman and Jacob 1984), e.g. LiKSO$_4$ where $E_{x^2-y^2} < E_{3z^2-r^2} < E_{xy} < E_{xz} < E_{yz}$. The parameters, calculated from (1), for the phase with an increased oxygen vacancy content are (in cm): $\alpha_{11}/\Delta_1 = 3.4 \times 10^{-5}$, $\alpha_{22}/\Delta_2 = 7.0 \times 10^{-5}$ and $\alpha_{33}/\Delta_3 = 2.66 \times 10^{-5}$ at 302 K, whereas at 4.2 K these values are 3.5×10^{-5}, 6.6×10^{-5} and 2.2×10^{-5}, respectively. Using the reported values of $\Delta_1 = 11\,628$ cm^{-1} and $\Delta_3 = 18\,868$ cm^{-1} for the green phase (Ong *et al* 1988), the approximate values for α_{11} and α_{33} are found to be 0.34 and 0.50, respectively, at 302 K, and 0.41 and 0.42 respectively, at 4.2 K. (The value of α_{22} could not be estimated because the value of Δ_2 has not been reported in the literature). The relatively small values of these parameters reflect significant covalency effects due to Cu–O bonding in the phase with increased oxygen vacancy content. Precise values of the Cu^{2+} energy level spacings in YBa$_2$Cu$_3$O$_{7-\delta}$ are not available; the optical data for the pure ceramic YBa$_2$Cu$_3$O$_{7-\delta}$ (Kamarás *et al* 1987) indicate only a broad high-reflectance region, with a plasma edge, which gives a minimum at $\simeq 15\,000$ cm^{-1} and a second band at $\simeq 20\,000$ cm^{-1}. The values calculated here, $\Delta_1 = 15\,300$ cm^{-1} and
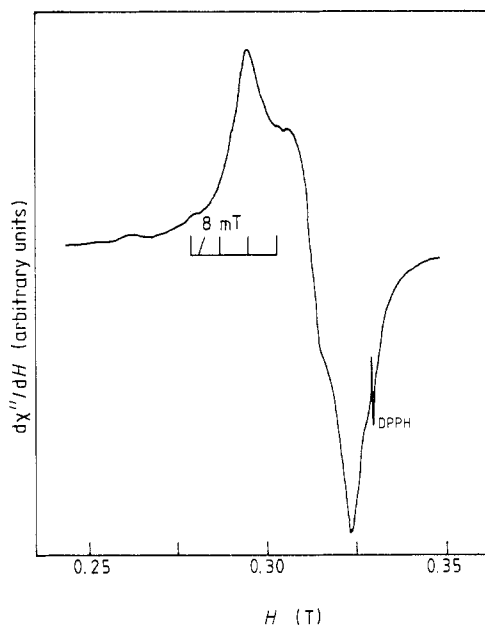
Figure 5. The X-band EPR spectrum of the polycrystalline Y–Ba–Na–Cu–O sample at 4.2 K. The weakly resolved hyperfine structure arises from overlapping spectra from the two nuclear isotopes ^{63}Cu and ^{65}Cu, with natural abundances 68.9% and 31.1% respectively, possessing the same nuclear spin $I = \frac{3}{2}$.

$\Delta_3 = 19\,500\,\text{cm}^{-1}$, for the phase with an increased oxygen vacancy content in the Y–Ba–Na–Cu–O sample correspond closely to these values.

It is possible to resolve the weak hyperfine structure of the Cu^{2+} ion at 4.2 K as exhibited in figure 5; this structure occurs at magnetic fields just below that where the main Cu^{2+} line is found, yielding the estimate that $|A_z|$ is 8 mT. (No spectral simulation was attempted. The peaks were judged by visual examination as indicated in figure 5.) This value is comparable to those reported for the $YBa_2Cu_3O_{7-\delta}$ sample in the polycrystalline (Bartucci *et al* 1988) and single-crystal (Mehran *et al* 1988b) forms. The hyperfine structures due to A_x, A_y, which are expected to occur at higher magnetic fields, are not resolved, implying that A_x, A_y are too small to be estimated from the X-band EPR spectrum.

5. The effect of magnetic memory

The magnetic memory effect, i.e. the moving of the low-field microwave-absorption signal to higher fields after exposures to higher magnetic fields during the previous scans in the temperature range 95–93.5 K, as produced by flux trapping in the Y–Ba–Na–Cu–O sample, for repeated magnetic field scans with a fixed modulation amplitude of 400 Hz frequency, is exhibited in figure 6. It is to be noted from figure 6 that the peaks, as observed upon cooling and upon warming at the same temperature, do not occur at exactly the same value of the magnetic field. This is because in the previous scans the highest magnetic field values were different from each other. Khachaturyan *et al* (1987) observed a similar effect in $YBa_2Cu_3O_{7-\delta}$. The frozen magnetic flux within the superconducting ceramic $YBa_2Cu_3O_{7-\delta}$ was observed by Lippold *et al* (1988). They concluded that the ceramic contains non-superconducting regions forming paths through the sample.
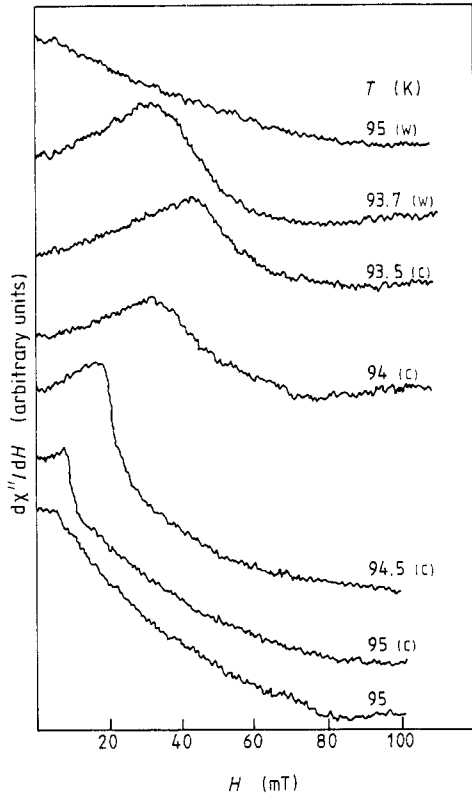
Figure 6. The magnetic-memory effect around 95 K, exhibiting irreversible properties of the Y-Ba–Na–Cu–O sample for several repeats of the sweeps of the external magnetic field with changes of temperature within the range of 1.5 K. The sample was exposed to magnetic fields up to anywhere from 300 to 400 mT during the previous scans. The letters c and w in brackets after temperatures indicate cooling and warming, respectively. The starting point was at 95 K, represented by the lowest plot.
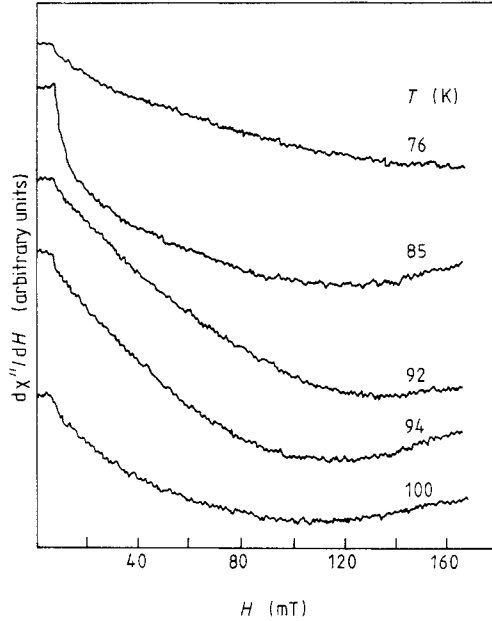
Figure 7. The low-field microwave absorption peaks in the Y–Ba–Na–Cu–O sample at various temperatures near T_c.

6. The lower critical field H_{c1}, the thermodynamic critical field H_c, the upper critical field H_{c2} and the electronic specific heat coefficient (γ)

As the temperature is lowered below 100 K, a broad (microwave) absorption peak begins to occur at low magnetic fields in the Y–Ba–Na–Cu–O sample; this is exhibited in figure 7. This temperature is higher, by about 10 K, than the superconducting transition temperature $T_c = 91$ K. This is due to the fact that parts of the sample become superconducting at 100 K and microwaves are sensitive to even small parts of the sample becoming superconducting. Furthermore, as a result of thermal fluctuations (Freitas *et al* 1987), there is a finite probability of formation of Cooper pairs in superconductors even above T_c, enhancing the conductivity and diamagnetism of the material. In high-T_c superconductors this effect is about 10 000 times greater than that in conventional

superconductors. This is in accordance with the observation of the reverse AC Josephson effect in Y–Ba–Cu–O material at 240 K, for which the superconducting transition occurs at 90 K, as reported by Chen *et al* (1987).

The value of the magnetic field at which the maximum of the microwave absorption peak occurs is designated the lower critical field, H_{c1} (Rettori *et al* 1987, Khachaturyan *et al* 1987, Blazey *et al* 1987). The lower critical field $H_{c1} \perp c$ (i.e. for the orientation of the magnetic field perpendicular to the c axis) for Y–Ba–Cu–O crystals is observed to be in the range from 0.5 mT (just below T_c) to 18 mT (at 0 K) (Krusin-Elbaum *et al* 1989); this is in agreement with the present data. The estimated value of H_{c1}, extrapolated to 0 K, is found to be 18 mT. Using this value, the thermodynamic critical field, H_c, and the upper critical field, H_{c2}, can be determined from the following relations (Orlando *et al* 1979, Narlikar and Ekbote 1983):

$$H_c = \sqrt{2}H_{c1}\kappa/\ln\kappa \qquad H_{c2} = \sqrt{2}\kappa H_c \qquad (2)$$

where κ is the ratio of the penetration depth, λ, to the coherence length, ξ ($\lambda/\xi \simeq 70$) (Rettori *et al* 1987, Orlando *et al* 1979). The estimated magnitudes, as extrapolated to $T = 0$, are $H_c(0) = 420$ mT and $H_{c2}(0) = 42$ T. This value of $H_{c2}(0)$ is smaller than the typical values ($\simeq 80$ T) determined for the $YBa_2Cu_3O_{7-\delta}$ ceramic (Orlando *et al* 1987), and is comparable in value to $H_{c2}^{\perp}(0) \simeq 30$ T, determined for the magnetic field orientation perpendicular to the ab plane of the $YBa_2Cu_3O_{7-\delta}$ crystal (Worthington *et al* 1987).

The electronic specific heat coefficient (γ), or the Sommerfeld constant, in the normal state of a type-II superconductor, can be expressed in terms of its parameters in the superconducting state (Parks 1969) as follows:

$$\gamma \simeq (1/\mu_0)H_c^2(0)/T_c^2 \qquad (3)$$

where $\mu_0 = 4\pi \times 10^{-7}$ Wb A^{-1} m^{-1}, $H_c(0) = 420$ mT and $T_c = 91$ K for the Y–Ba–Na–Cu–O sample. The estimated value of γ is $\simeq 2.2$ mJ mol^{-1} K^{-2} for the Y–Ba–Na–Cu–O ceramic, using the number of formula units = 655 and density = 5 g cm^{-3} (taking into account the porous nature of the material). This value of γ is close to the lower limit of the values reported in the literature (Nevitt *et al* 1987) for high-T_c superconducting ceramics.

7. Concluding remarks

The present X- and Q-band EPR studies of the Y–Ba–Na–Cu–O sample, over the temperature range 4.2–300 K, reveal the following important aspects of this high-T_c superconductor.

(i) The sample exhibits a superconducting nature at $T_c = 91$ K.

(ii) The values, extrapolated to $T = 0$ K, of the lower critical field $H_{c1}(0) = 18$ mT, the thermodynamic critical field $H_c(0) = 420$ mT, and the upper critical field $H_{c2}(0) = 42$ T.

(iii) The memory effect, as observed at liquid-helium temperature, is due to flux trapping in the sample.

(iv) Cu^{2+} EPR lines are observed throughout the entire temperature range of measurement. This is due to the presence of the phase with increased oxygen vacancy content, characterised by an increased number of localised electrons of the Cu^{2+} ion. The principal

g-values exhibiting orthorhombic symmetry have been exploited to deduce the sequence of Cu^{2+} energy levels in this phase of the sample.

(v) The transition temperature $T_c = 91$ K, determined here, is the same as that determined for the YBa$_{0.95}$Na$_{0.05}$Cu$_3$O$_{7-\delta}$ ceramic by Ausloos *et al* (1988), implying that the Na$^+$ ions do indeed substitute for the Ba^{2+} ions.

(vi) Ordering of oxygen ions about the Cu^{2+} ions plays an important role in the structural changes of the Y–Ba–Na–Cu–O superconductor. This, together with oxygen content changes, i.e. changes in the value of δ, can alter the superconducting transition temperature significantly (Herman *et al* 1987). However, no significant change in T_c in the YBa$_{1.9}$Na$_{0.1}$Cu$_3$O$_{7-\delta}$ sample investigated here ($T_c = 91$ K) is observed, implying that δ is small.

(vii) The low-field microwave absorption peak is either due to Josephson currents in junctions between grains (Stankowski *et al* 1987), and/or due to deviation of the magnetic susceptibility from linear behaviour with respect to the magnetic field at the lower critical field (H_{c1}) (Obradors *et al* 1988, Ebner and Stroud 1985), since the EPR signal is proportional to the imaginary part of the susceptibility.

(viii) Upon comparison with the Y$_{0.9}$Er$_{0.1}$Ba$_{1.9}$Sr$_{0.1}$Cu$_3$O$_{7-\delta}$ sample, in which no EPR signal is observed (Misra and Misiak 1989), it appears that the introduction of alkali metal (Na$^+$) in YBa$_2$Cu$_3$O$_{7-\delta}$ enhances the formation of the phase with increased oxygen vacancy content, responsible for the Cu^{2+} EPR signal.

It is hoped that the present study will be helpful in understanding further the high-T_c superconductors fabricated by doping the YBa$_2$Cu$_3$O$_{7-\delta}$ ceramic, leading to more desirable high-T_c superconductors.

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