*Rapid note*

# Cu-EPR in $YBa_2Cu_3O_{6+\delta}$ single crystals

**J. Sichelschmidt**[1], **B. Elschner**[1], **A. Loidl**[1], **K. Fischer**[2]

[1] Institut für Festkörperphysik, TH Darmstadt, D-64289 Darmstadt, Germany
[2] Institut für Physikalische Hochtechnologie e.V., D-07743 Jena, Germany

**Abstract.** We report on the observation of Cu-EPR signals in single crystalline material of $YBa_2Cu_3O_{6+\delta}$ in the narrow oxygen concentration range $0.7 < \delta < 0.9$ and for temperatures $80\,K < T < 200\,K$. We provide evidence that the signal results from $Cu^{2+}$ ions located in $\cdots Cu(1) \cdots O \cdots Cu(1) \cdots$ chain fragments.

**PACS:** 76.30.−V; 74.70.Vy

Soon after the discovery of high-$T_c$ superconductivity by Bednorz and Müller [1] the observation of electron paramagnetic resonance (EPR) signals due to the presence of $Cu^{2+}$ was reported in $YBa_2Cu_3O_7$ with a superconducting transition temperature $T_c$ close to 90 K [2]. However, later it became clear that these signals were due to impurity phases [3] or complex paramagnetic defects [4]. Subsequently, theoretical arguments have been put forward in order to explain why an intrinsic EPR signal of $Cu^{2+}$ may not be observed from the CuO planes in the cuprate superconductors [5, 6]. The situation is less clear in $YBa_2Cu_3O_{6+\delta}$ with $\delta < 1$. An EPR signal has been detected in a single crystal with $\delta = 0.5$ ($T_c \approx 40$ K) [7]. The $g$-factor was found to be almost isotropic and the line width of the EPR signal was independent of temperature. It has been concluded that the signal originates from $Cu^{2+}$ ions in a pseudo-cubic crystal field and has later on be ascribed to a defect state [4]. The most convincing experimental evidence for an intrinsic Cu-paramagnetic center has been provided by Shaltiel et al. [8] in a single crystal with an oxygen concentration close to $\delta = 0.4$. These experiments revealed an anisotropic $g$-factor of tetragonal symmetry with $g_\perp = 2.0418(5)$ and $g_\parallel = 2.2949(5)$ and were attributed to the existence of $Cu^{2+}$ in an octahedral oxygen coordination [8]. Qualitative arguments have been provided by Albino et al. [9] why EPR signals may be observable for $\delta < 0.8$.

In this Rapid Note we present results of a detailed EPR study of $YBa_2Cu_3O_{6+\delta}$ single crystals with oxygen concentrations ranging from 6 to 7. We observed an intrinsic EPR signal from unpaired $Cu^{2+}$ spins in a narrow concentration range $0.7 < \delta < 0.9$ and we will argue that these paramagnetic centers are located in the Cu(1) chains.

The EPR experiments were performed on single crystalline samples using a standard Varian $E$-line spectrometer at the X-band frequency (9.3 GHz) using a 100 kHz field modulation. The spectrometer is equipped with an Oxford Instruments helium flow cryostat and with an ITC-4 temperature controller. Almost 30 single crystals from three different crystallography laboratories (Shubnikov-Institut for Crystallography, Mocow [10]; Institut für Physikalische Hochtechnologie, Jena; and Institut für Physik der Universität, Frankfurt/M [11]) have been investigated. In some of the crystals small amounts of spurious phases have been detected. These samples were excluded from further investigation. In the single-phase material the oxygen content was varied by heat treatment in defined oxygen atmosphere or in vacuum. More than 50 temperature runs of samples with different oxygen concentrations have been performed. The oxygen content of each sample was checked via the crystal weight and via the superconducting phase transition temperatures. A typical crystal size was $1 \times 1 \times 0.1$ mm$^3$.

A well defined but weak EPR signal has been observed in crystals with oxygen concentrations $6.7 < 6 + \delta < 6.9$ and for temperatures $80\,K < T < 200\,K$. A typical example of an experimentally observed spectrum is shown in the upper panel of Fig. 1 for $YBa_2Cu_3O_{6.82}$ ($T_c = 65$ K) at 105 K (solid line). Here we show the field derivative of the absorption $I(B)$ vs the magnetic field $B$ for two different angles. Upon rotation of the $c$-axis from parallel ($\Theta = 0°$) to perpendicular ($\Theta = 90°$) with respect to the external magnetic field the resonance field $B_{res}$ is shifted by almost 40 mT. The absorption lines at all angles can be described by purely Lorentzian line shapes (dashed lines in the upper part of Fig. 1).

A summary of the angle dependent measurements for $\delta = 0.82$ and $T = 105$ K is shown in the lower panel of Fig. 1. The angular dependence of the resonance field for the rotating $c$-axis is well described by anisotropic

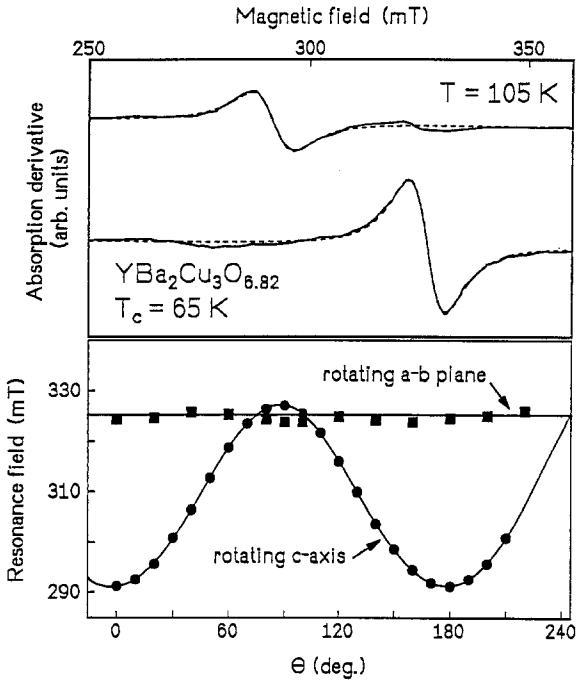


**Fig. 1.** upper frame: Absorption derivative $I(B)$ vs. magnetic field $B$ in $YBa_2Cu_3O_{6.82}$ at two different orientations at 105 K (solid lines). The fits with purely Lorentzian line shapes are indicated by dashed lines. lower frame: Angular dependence of the resonance field $B_{res}$ in $YBa_2Cu_3O_{6.82}$ for two different crystal orientations (solid symbols). The results of the fits as described in the text are indicated by solid lines

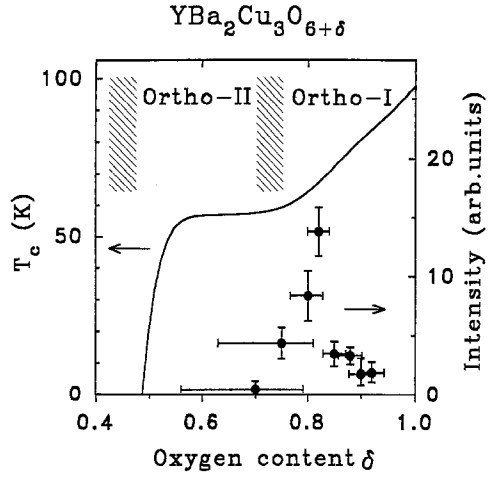


**Fig. 2.** Oxygen-concentration dependence of the integrated intensity of the EPR signal in $YBa_2Cu_3O_{6+\delta}$ (right scale). The concentration dependence of the superconducting phase transition temperature $T_c$ is also shown (left scale)

$g$-factors in a system with uniaxial symmetry, namely $g=(g_\perp^2\cdot\cos^2\Theta+g_\parallel^2\cdot\sin^2\Theta)^{1/2}$ with $g_\parallel=2.28(1)$ and $g_\perp=2.03(1)$. When the $a/b$-plane is rotated the resonance field is constant for all angles. This observation can be understood by the fact that our specimen were twinned single crystals of pseudo-orthorhombic symmetry in that concentration range. Very similar results were obtained for a number of single crystals in the concentration regime $0.7<\delta<0.9$. These crystals revealed similar resonance fields and similar line widths of the order of 20 mT. However, the intensity of the signal strongly depended on the oxygen concentration. Figure 2 shows the integrated intensity of the absorption line vs the oxygen concentration $\delta$. The strongest signals were detected close to $\delta=0.8$ and no signals could be detected for $\delta<0.7$ and $\delta>0.9$. Figure 2 also indicates the concentration dependence of the superconducting phase transition temperature [12]. It seems important to note that the maximum EPR absorption can be observed in the vicinity of the upper end of the $T_c=60$ K plateau.

The line width of the EPR signal follows a rather unusual temperature dependence (not shown here). With decreasing temperature the line width decreases, passes through a minimum close to 100 K and strongly increases on further cooling until the signal is lost below 80 K. A similar temperature dependence of the line width has been reported by Shaltiel et al. [8] and has been explained by the onset of local superconductivity. We assume that the $T$ dependence of the line width reflects the spin fluctuation rates in the Cu(2)O-planes and at present we analyze the results along these lines. Finally, we want to mention that the temperature dependence of the intensity of the EPR signal as observed in the present investigation is almost temperature independent. This result closely resembles the behavior of the static magnetic susceptibility in impurity-free $YBa_2Cu_3O_{6+\delta}$ material [13], but is not readily understood on the basis of present theoretical models.

Our results concerning the $T$-dependence of the line width and the anisotropy of the $g$-values agree with the results of Shaltiel et al. [8] for an as-grown crystal with $\delta=0.4$. Their crystal exhibited a superconducting phase transition temperature $T_c=30$ K and long-range antiferromagnetic order. The principal and most relevant difference to their work is that we observe a Cu-EPR signal cose to $\delta\approx0.8$, in samples which are definitely non-magnetic and reveal superconductivity below $T\approx70$ K. In addition, our results were reversible concerning annealing procedures, i.e. we were able to suppress the EPR signal by changing the oxygen concentration and to recover it when the previous oxygen content was fixed again.

We strongly suggest that we have observed the EPR signal of paramagnetic chain fragments along the $b$-axis. Arguments in favour of this suggestion can be derived from the structural details revealed by the phase diagram of $YBa_2Cu_3O_{6+\delta}$ which can be subdivided into three regimes [14]: For $\delta<0.4$ the O(1) sites, which are empty at $\delta=0$, are partially occupied. In this tetragonal phase the compound is insulating and antiferromagnetic. For $\delta>0.4$ a redistribution of the oxygen ions takes place with the effect that only the O(1) sites along the $b$-axis become occupied. This is accompanied by a slight orthorhombic distortion of the tetragonal unit cell. For $0.4<\delta<0.7$ superstructure reflections reveal the presence of regular arrays of empty and filled chains along $b$. In this so-called orthorhombic II (Ortho II) structure $YBa_2Cu_3O_{6+\delta}$ is metallic and magnetic long-range order is suppressed. Finally, for $\delta>0.7$ the remaining empty chains along $b$ are filled (orthorhombic I (Ortho I) phase).

It is generally believed that no signal can be observed from $Cu^{2+}$ ions in the Cu(2)O-planes for all oxygen concentrations. This fact is due to the strong antiferromagnetic exchange interaction [6]. For $\delta = 0$ Cu(1) is in a monovalent state. The additional oxygen ions redistribute the charge within the chains transforming $Cu^{+}$ partially into a bivalent state. However, in the tetragonal phase, Cu seems to be in a predominantly monovalent state [15]. In addition, the influence of long range magnetic order may broaden the signal from the Cu(1) ions which are in a divalent state. One is led to conclude that no EPR signal should be observed in the tetragonal phase. $Cu^{2+}$ ions in completely filled Cu(1) chains, characteristic for the Ortho II structure, as well as for $\delta = 1$, are coupled to pairs with a non-magnetic ground state yielding no EPR signal for $\delta < 0.7$ and for $\delta = 1$, respectively. For $\delta > 0.7$ empty chains are filled with no evidence for oxygen vacancy ordering. Hence, only in a narrow regime above the threshold value between the Ortho II to the Ortho I phase paramagnetically active chain fragments are created which can be detected via EPR techniques.

These conclusions are corroborated by further experimental and theoretical informations. It has been demonstrated by near-edge X-ray absorption spectroscopy that at the phase boundary from Ortho II to Ortho I, the fraction of monovalent $Cu^{+}$ substantially decreases with increasing $\delta$ and that simultaneously the fraction of $Cu^{2+}/Cu^{3+}$ is increased [15]. Recent numerical calculations [16] have shown that exactly at this phase boundary neutral chain fragments are no longer stable and holes are transferred into the Cu(2) planes. Within modified lattice gas models it has also been calculated that the maximum number of paramagnetically active chain fragments is found for oxygen concentrations $0.75 < \delta < 0.85$ [15]. This theoretical prediction is in accord with our experimental results. Hence, we conclude that we observe an intrinsic $Cu^{2+}$ EPR signal in $YBa_2Cu_3O_{6+\delta}$ from $\cdots Cu(1)\cdots O\cdots Cu(1)\cdots$ chain fragments.

This research was partly supported by the Sonderforschungsbereich 252 (Darmstadt/Frankfurt/Mainz/Stuttgart). It is a pleasure to thank W. Aßmus and L.E. Svistov for providing us with high-quality single crystalline samples.

## References

1. Bednorz, J.G., Müller, K.A.: Z. Phys. **B64**, 189 (1986)
2. see e.g. Mehran, F. et al.: Phys. Rev. **B36**, 740 (1987); Shaltiel, D. et al.: Solid State Commun. **63**, 987 (1987)
3. see e.g. Bowden, G.J. et al.: J. Phys. C**20**, L545 (1987); Vier, D.C. et al.: Phys. Rev. **B36**, 8888 (1987); Genossar, J. et al.: J. Phys. Condens. Matter **I**, 9471 (1989); Deville, A. et al.: J. Phys. (France) 50, 2357 (1989); Barham, R.J., Doetschman, D.C.: J. Mater. Res. **7**, 565 (1992)
4. Stankowski, J. et al.: Solid State Commun. **77**, 125 (1991)
5. Mehran, F., Anderson, P.W.: Solid State Commun. **71**, 29 (1988)
6. Chakravarty, S., Orbach, R.: Phys. Rev. Lett. **64**, 224 (1990)
7. Mehran, F. et al.: Solid State Commun. **66**, 299 (1988)
8. Shaltiel, D. et al.: Physica C**158**, 424 (1989)
9. Albino, J. et al.: J. Phys. C**21**, L237 (1988)
10. Bykov, A.B. et al.: J. Crystal Growth **91**, 302 (1988)
11. Kowalewski, J.: PhD Thesis, University Frankfurt/M, 1992
12. Aleksandrov, I.V. et al.: JETP Lett. **49**, 327 (1989)
13. Triscone, G. et al.: J. Alloys Comp. 195, 351 (1993)
14. for reviews on structural properties see e.g.: Hazen, R.: In Physical properties of high temperature superconductors II, p. 121; Ginsberg, D.M. (ed.). Singapore: World Scientific 1990; Greene, L.H., Bagley, B.G.: ibid., p. 509; Rossat-Mignod, J. et al.: In: Frontiers in solid state sciences, Vol. I, p. 265; Gupta, L.C., Multani, M.S. (eds.). Singapore: World Scientific 1993
15. Oyanagi, H. et al.: Jpn. J. Appl. Phys. **26**, L1516 (1987)
16. Uimin, G., Rossat-Mignod, J.: Physica C**199**, 251 (1992); Uimin, G., Stepanov, V.: Ann. Phys. **2**, 284 (1993)