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EPR study of deoxygenated high-temperature superconductors

R J SINGH[1,*], P K SHARMA[1] and SHAKEEL KHAN[2]
[1]Physics Department, Aligarh Muslim University, Aligarh 202 002, India
[2]Applied Physics Department, Z H College of Engineering and Technology, Aligarh Muslim University, Aligarh 202 002, India
*Email: ranajsingh@yahoo.com

Abstract. High-T_c superconductors are EPR silent but on a little deoxygenation of the high-T_c materials and their constituents, they yield rich but complex spectra. Spectra of (1) CuO, (2) $BaCuO_2$, (3) $CaCuO_2$, (4) $Y_2Cu_2O_5$, (5) La_2CuO_4, (6) $La_{2-x}M_xCuO_4$ (M = Sr, Ba), (7) Y based-123, (8) Bi based-2201, 2212, 2223, (9) Tl based-2223 and (10) Hg based-1212,1223 have been studied. One thing common to all these materials is the CuO_2 plane which gets fragmented on deoxygenation and the inherent antiferromagnetic coupling is partially destroyed which results in the appearance of the spectra.

The spectra recorded have been identified to be due to (1) Cu-monomer, (2) Cu-dimer, (3) Cu-tetramer, (4) Cu-octamer and (5) one signal at very low field which could not be identified because there was no structure in it and may be due to fragments higher than octamers. Very big fragments do not give any spectra because the original AF order probably remains intact in them. It is expected that when the fragments become magnetically isolated from the bulk, they produce EPR spectra. Most of the spectra have been analyzed and their spin-Hamiltonian parameters determined. The spectra of these species vary a little in terms of g-value and fine-structure splitting constant from sample to sample or even in the same sample and this may be attributed to some extra oxygen attachments retained with these species. Most frequently occurring species is the Cu-tetramer, $(CuO)_4$. As $(CuO)_4$ represents the unit cell of the all important two-dimensional CuO_2 plane of the high-T_c materials, its spectra have been argued to provide some clue to the mechanism of high-T_c superconductivity. The tetramer $(CuO)_4$ is a four one-half spin system and is essentially 16-fold degenerate by Heisenberg isotropic exchange, it is split into 6 components: one pentet, three triplets and two singlets. In superconductors the pentet appears to be the ground state and in the non-superconducting constituents the singlets seem to form the ground state as revealed by the temperature variation studies. In the case of $La_{1.854}Sr_{0.146}CuO_4$ we have found the signature of quantum stripe formation. The high-T_c superconductivity theories involving spin bag, antiferromagnetic spin fluctuations and magnons can be explained on the basis of Cu-tetramers.

Keywords. Deoxygenated high temperature superconductors; EPR study.

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1. Introduction

High temperature superconductors (HTSC) are EPR silent [1–5]. But they yield EPR spectra when oxygen content is reduced especially in the CuO_2 plane or oxygen is displaced from their equilibrium positions in the structure, which is achieved by quenching the samples from their preparation temperatures. On quenching, the all important CuO_2 planes are broken into fragments of various sizes. The bigger ones do not give spectra because the original AF order remains intact in them, the intermediate ones give a broad signal at very low field but without any structure, and hence, their detection is not possible. In the smaller fragments, Cu-octamers, tetramers, dimers and monomers have been detected by their fine structure and hyperfine structures. Nearly all kinds of high-T_c superconductors and their constituents have been tried. The constituents have been tried because CuO_2 plane is common to them also. Following substances have been studied by EPR after deoxygenation: (1) CuO, (2) $BaCuO_2$, (3) $CaCuO_2$, (4) $Y_2Cu_2O_5$, (5) La_2CuO_4, (6) $La_{2-x}M_xCuO_4$ (M = Sr, Ba), (7) Y based-123, (8) Bi based-2201, 2212, 2223, (9) Tl based-2223 and (10) Hg based-1212,1223 [6–12]. Some representative spectra will be reproduced. The important findings in this series of investigations will be discussed. The most frequently occurring species in all the compounds have been found to be Cu-tetramer, i.e., $(CuO)_4$. This can be considered as the unit cell of two-dimensional CuO_2 plane which is responsible for superconductivity. The role of $(CuO)_4$ unit as the seed of superconductivity will be discussed.

2. Experimental

All the samples were prepared by the usual solid state reaction routes. X-ray diffraction (XRD) spectra of as-prepared and quenched samples were taken and they did not show any significant difference indicating that there was a marginal loss of oxygen content or displacement of oxygen ions from their equilibrium positions. All the spectra were recorded on the EPR spectrometer (JEOL-RE2X) with 100 kHz field modulation.

3. Results and discussion

Some important EPR spectra are shown in figures 1–7. The fine and hyperfine structures in the spectra (figures 1–7) established the identity of the species. In the above figures the

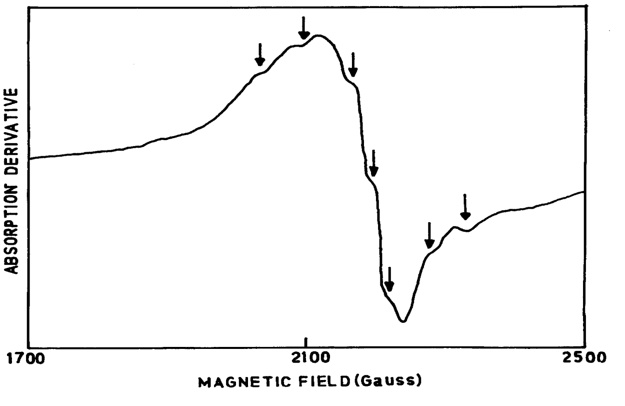

Figure 1. Hyperfine structure of Cu-dimer in CuO. $g = 3.20$, $A = 54$ Gauss.

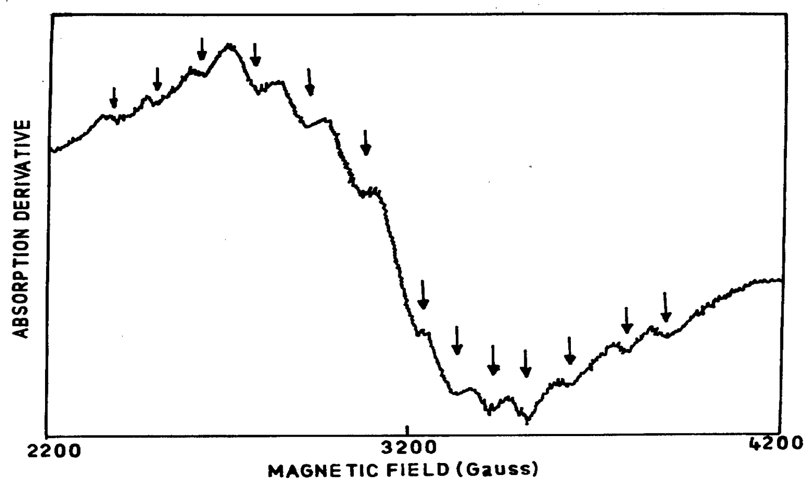

Figure 2. Hyperfine structure of Cu-tetramer in CuO. $g = 2.12$, $A = 130$ Gauss.

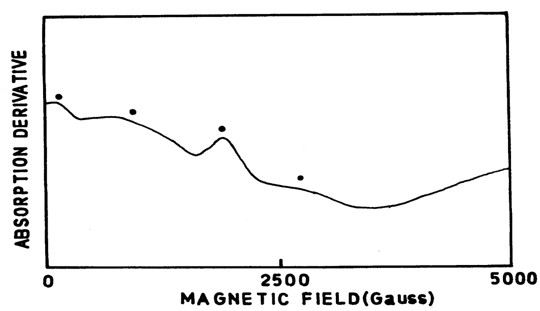

Figure 3. Fine structure of Cu-tetramer in Hg-1223. $g = 5.10$, $D = 845$ Gauss.

tetramer spectra shown in different compounds do not have the same g value. It may be due to the fact that Cu-tetramers assume different configurations in different systems, i.e., square planar, square pyramidal structure with attachment of one oxygen ion, distorted octahedral structure due to attachment of two oxygen ions, etc. Using the spin-Hamiltonian proposed by Stankowski and Mackowiak [13] the parameters for the spectra shown in figures 1–7 are given along with their figure captions. Some g values reported here deviate considerably from the usual $g \approx 2$ range. The values reported are the experimental values obtained by the relation $h\nu = g_{\text{exp}}\beta H_{\text{obs}}$. But the true g values may be quite different from the g_{exp}. As there is ferromagnetic coupling of the spins in the Cu clusters, the effective field may be quite different from the applied field due to demagnetization effects. The demagnetization field strength depends upon the shape and size of the sample. In such cases, the resonance absorption condition is written as $h\nu = g\beta(HB)^{1/2}$ where $B =$ magnetic induction or for cylindrical samples, $h\nu = g\beta(H + 2M)$ where $M =$ intensity of magnetization. As M is positive for ferromagnetic samples, it may happen that the effective field is of such a value that it will keep the g values in the proximity of 2. In the fragments which

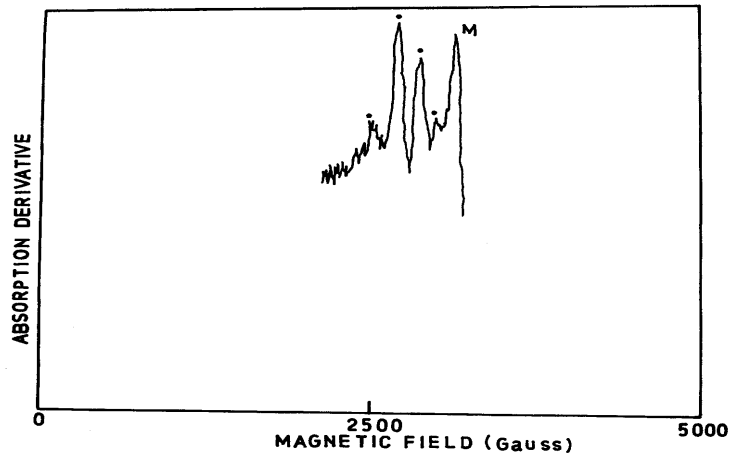

Figure 4. Fine structure of Cu-tetramer in Bi-2223. $g_x = 2.317$, $g_y = 2.524$, $g_z = 2.470$; $D = 210$, $E = 18$, $a = -20$, $b = -3$, $c = -8$ (Gauss).

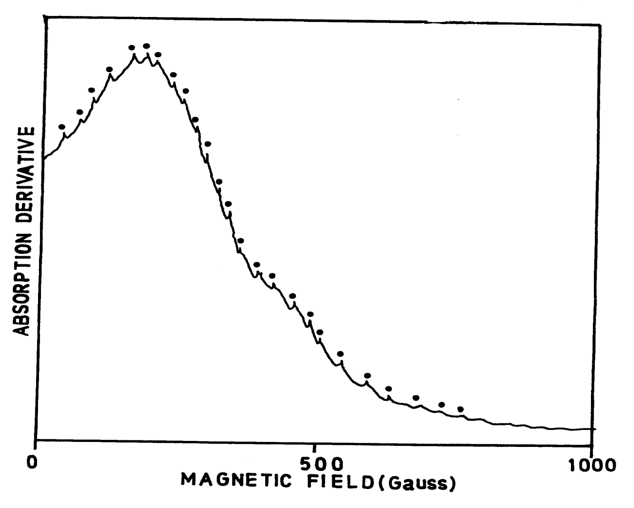

Figure 5. Hyperfine structure of Cu-octamer in Bi-2201. $G = 19.94$, $A = 29$ Gauss.

show EPR spectra, the spins of the Cu ions are ferromagnetically coupled through superexchange via the intervening oxygen ions. For example in $(CuO)_4$, the electronic spins of the four Cu ions add up to $(4 \times 1/2 = 2)$ and the nuclear spins equal to $(4 \times 3/2 = 6)$.

Two important findings have been noted: (1) Quantum stripe formation in $La_{1.854}Sr_{0.146}CuO_4$ [12]. It has been noted that in the temperature variation of the spectra of the compound (figure 7) there is a great instability in the signal at 100 K, which coincides with the temperature of quantum stripe formation in HTSC [14]. This is the first detection of quantum stripe formation by EPR. (2) Second important observation is the difference in Cu-tetramer signal of a non-superconductor $CaCuO_2$ and a superconductor $La_{1.854}Sr_{0.146}CuO_4$, though in both cases, they arise from their respective CuO_2 planes. In

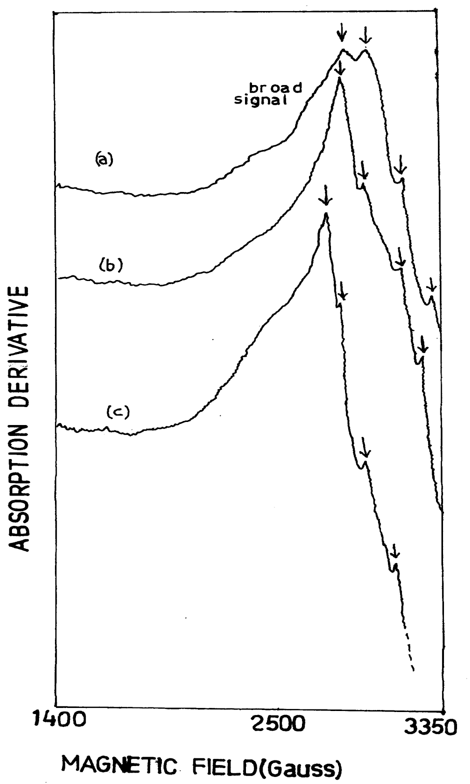

Figure 6. Hyperfine structure of Cu-monomer in La_2CuO_4 at different angles. $g_{11} = 2.11$, $g_{\perp} = 2.17$; $A_{11} = 125$, $A_{\perp} = 108$ (Gauss).

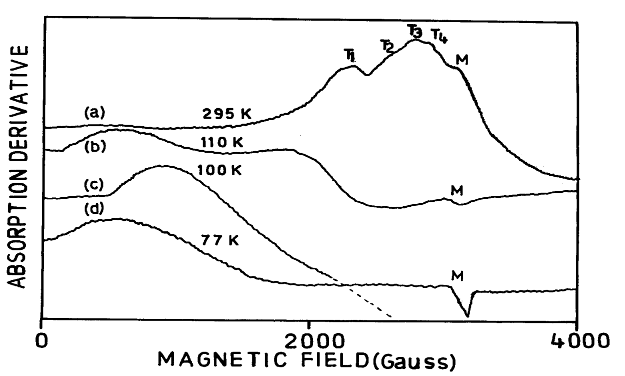

Figure 7. (**a**) Cu-tetramer (T1–T4) and monomer (M) in $La_{1.854}Sr_{0.146}CuO_4$ at RT, (**b**) spectra at 110 K, (**c**) spectra at 100 K, (**d**) spectra at 77 K. At RT, $g = 2.40$, $D = 208$ Gauss; At 77 K, a single broad signal with $g = 10.60$.

$CaCuO_2$, the tetramer signal is reduced in intensity as the temperature is lowered but in $La_{1.854}Sr_{0.146}CuO_4$ it gains intensity. The tetramer $(CuO)_4$ is a four one-half spin system and is essentially 16-fold degenerate. By Heisenberg isotropic exchange, it is split into 6 components: one pentet, three triplets and two singlets. In non-superconductors, the singlet seems to be the ground state but in superconductors the pentet is the ground state.

The CuO bond is nearly 12.5% covalent. The breaking of 8 Cu–O bonds in the immediate vicinity of $(CuO)_4$ to isolate it from CuO_2 plane is equivalent to the introduction of a hole in it. Because of covalency factor, the following equality should hold good: Isolated $(CuO)_4 = (CuO)_4$ of the actual superconductor + a hole inside it. Further, as the conductivity in the superconductors is through holes, the study of the behavior of isolated Cu-tetramers may throw light on the properties of the bulk superconductors.

It seems that in the consideration of mechanism of high temperature superconductivity, especially in the magnetic mechanisms, the $(CuO)_4$ can play an important role. For example, in the spin-bag theory [15], spin fluctuation theory, magnetic bipolaron, magnon theories [16,17] physical quasi-particles can be taken as Cu-tetramers with spin=2 instead of spin-1/2 fermions. The magnetic coupling will be stronger for the tetramers with total electronic spin ($S=2$) than for the spin $= 1/2$ particle and may explain the higher transition temperatures.

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