PSEUDOROTATIONAL AVERAGING OF EPR SPECTRUM OF Cu(II)O$_5$ COMPLEX IN YBa$_2$Cu$_3$O$_{7-\delta}$ IN LOW TEMPERATURES

J. STANKOWSKI, W. KEMPIŃSKI AND Z. TRYBULA

Institute of Molecular Physics, Polish Academy of Sciences
Smoluchowskiego 17, 60-179 Poznań, Poland

In low temperatures the condensation of oxygen was found to occur at O5 site in an elementary cell of YBa$_2$Cu$_3$O$_{7-\delta}$ being the fifth ligand forming the CuO$_5$ complex around Cu1 copper in chain. This change of coordination from CuO$_4$ to CuO$_5$ is the origin of a pseudorotation related to a strong vibronic coupling of two distorted configurations: a tetragonal pyramid C_{4v} and a trigonal bipyramid D_{3h}, which yields a pseudocubic EPR spectrum in low temperatures. The averaged spectroscopic splitting coefficient is related to a superposition of vibronically coupled orbital states $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$. The averaged spectrum was for the first time observed in low temperatures since the oxygen condensation in YBa$_2$Cu$_3$O$_{7-\delta}$ at O5 site of the chain occur only when oxygen undergoing fast diffusion among the chains, gets localized with decreasing temperature. The activation energy of oxygen desorption from the O5 site is 36 K.

1. Introduction

Anisotropic EPR spectrum is characteristic for a copper ion Cu(II)L$_4$ of four ligand square coordination in a crystal. The ground state of the ion of d^9 configuration is the orbital singlet $|x^2 - y^2\rangle$ and its typical g tensor values are: $g_\parallel \approx 2.40$ and $g_\perp \approx 2.06$.

Five-coordinated Cu(II)L$_5$ complexes feature instability of orbital ground state which can be either $|x^2 - y^2\rangle$ or $|3z^2 - r^2\rangle$ state. The quadratic pyramid of C_{4v} symmetry and trigonal bipyramid of D_{3h} symmetry correspond to these extreme cases, respectively [1, 2].

High-amplitude ligand vibration couples both states which makes that the ground state is a superposition $|\rangle = a|x^2 - y^2\rangle + b|3z^2 - r^2\rangle$, so in consequence it is responsible for isotropic character of EPR spectrum. The appropriate co-efficient of spectroscopic splitting equals to $g = (1 - b^2)g_{sp} + b^2 g_{bpt}$, where g_{sp} and g_{bpt} are the mean values of g-factor for the square pyramid (sp) and trigonal bipyramid (bpt). The value of b^2 is a measure of trigonal distortion of the resultant ground state. Assuming the above given values of the g tensor components $g_{\parallel}^{(sp)} = 2.40$ and $g_{\perp}^{(sp)} = 2.04$ for the square pyramid and the values $g_{\parallel}^{(bpt)} = 2$ and $g_{\perp}^{(bpt)} = 2.4$ for the trigonal bipyramid, the mean values we get for the extreme cases are: $\langle g \rangle_{sp} = 2.16$ and $\langle g \rangle_{bpt} = 2.29$. Hoffmann [3] and the others [2] analysed vibronic excitations of five-coordinated copper complexes and proved that a transition from one trigonal bipyramid orientation to another trigonal bipyramid orientation involves the state of deformed square pyramid (Fig. 1).
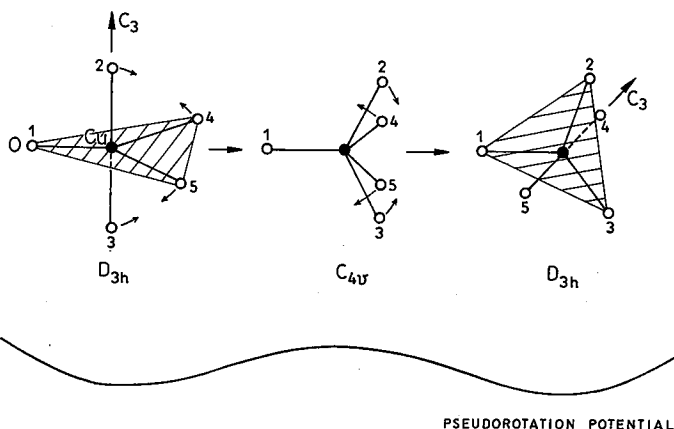

PSEUDOROTATION POTENTIAL

Fig. 1.　Pseudorotation of CuO$_5$ complex.

The barrier between the subsequent states is very small which means that the trigonal pyramid axis undergoes very fast rotation. This pseudorotation brings the effect of averaging the EPR spectrum, similarly as it happens in the so-called dynamic Jahn–Teller effect, but it is temperature independent and depends only on the degree of the trigonal distortion so on the b^2 parameter. This distortion appears for the five-coordinated Cu(II)L$_5$ complex but does not occur at all for Cu(II)L$_4$.

Such a pseudorotation at room temperature was detected for a crystal of Cu(NH$_3$)$_4$(ClO$_4$)$_2$ [4, 5]. By changing the concentration of ammonia in the solution from which the studied crystals were grown, we obtained the crystals with different concentration of five-coordinated Cu(II)(NH$_3$)$_5$ complexes. The EPR spectra of Cu(NH$_3$)$_4$(ClO$_4$)$_2$ were anisotropic, typical of rigidly fixed Cu(II)(NH$_3$)$_4$ (Fig. 2).

After the crystal has been saturated with ammonia i.e. having introduced the fifth molecule of ammonia into the coordination sphere of copper ion
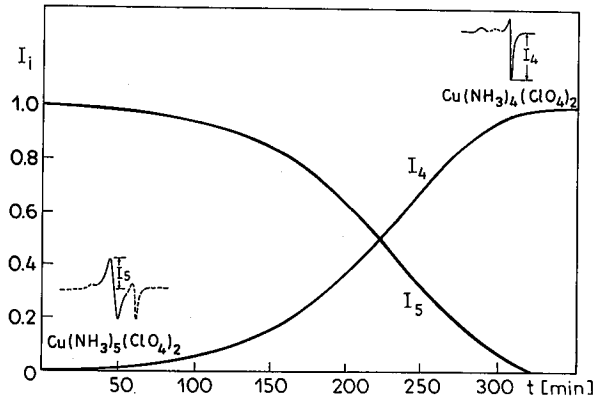
Fig. 2.   Concentration of I_4 four- and I_5 five-coordinated complexes versus the time of ammonia desorption from the crystal $Cu(NH_3)_4(ClO_4)_2$ at room temperature.

$Cu(II)(NH_3)_4 \xrightarrow{NH_3} Cu(II)(NH_3)_5$ a symmetric EPR line was observed. From $\langle g \rangle$ coefficient a value of $b^2 = 0.47$ was determined [4]. Figure 2 illustrates the changes in the averaged spectrum (left side) as ammonia gets vaporized (right side). The fifth ammonia weakly bounded with the complex has the desorption time of $t = 300$ min. Assuming that desorption is a thermally activated process $\tau = \tau_0 \exp(E_{des}/RT)$, we get the energy of desorption $E_{des} = 23$ kcal/mol, which is a reasonable value for copper complexes [7]. The pseudorotation process depends on the degree of coupling between the states $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ and thus can occur even at the lowest temperature considered, as a quantum exchange process between the two complex configurations. An analogous phenomenon takes place in the structure of $YBa_2Cu_3O_{7-\delta}$. Mechanically induced copper complexes in $YBa_2Cu_3O_{7-\delta}$ have, in high temperatures, a spectrum typical of $Cu(II)O_4$ square coordinated in planes or in chains [6]. Oxygen atoms undergoing fast diffusion among the chains make quick jumps among O5 sites and do not attach to Cu1 copper making flat $Cu1(O4)_2(O1)_2$ complexes in the chains (Fig. 3). At a low temperature range, below 45 K, the EPR spectrum of Cu^{2+} changes becoming pseudo-cubic below 25 K. The reason for this is the break up of the Cu1–Cu2 complex due to the condensation of the fifth oxygen as a ligand of Cu1 copper at the O5 site. With increasing concentration of five-coordinated complexes, their trigonal distortion, and thus EPR line intensity, increase.

2. Experimental

The initial high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ obtained in the form of bulk ceramic did not show any EPR signal. Ceramic samples were powdered into granules of 0.18 mm in diameter. The granulated sample, below $T_c = 91.5$ K, showed a very strong Josephson absorption related to the so-called low-field maximum of magnetically modulated microwave absorption (MMMA) [8]. This
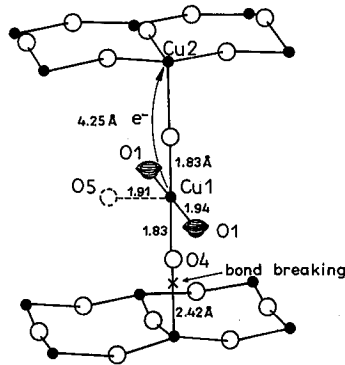
Fig. 3.   A fragment of $YBa_2Cu_3O_{7-\delta}$ structure [11]. The fifth oxygen is condensed at O5 site in the vicinity of Cu1 copper in low temperatures.

absorption made taking EPR signal impossible as its amplitude is hundred times greater than that of EPR signal. In view this finding, the sample was subject to heating at 740°C in helium atmosphere for 10 minutes. The annealed sample after having been cooled down to room temperature in helium atmosphere revealed strong microwave absorption below 60 K and this value of T_c pointed to oxygen desorption to the value $\delta = 0.3$. Next day the phase of $T_c = 91$ K appeared again in result of redisitribution of oxygen in the sample.

The sample prepared in this way did not reveal strong Josephson absorption which could mean that oxygen had been absorbed within the grains while in the intergrain regions oxygen had been in deficiency. This resulted in the superconducting regions being moved from the grain boundaries which form a system of weak Josephson links. This effect resembled that of Josephson absorption decay observed with decreasing size of ceramic granules [9]. Owing to its occurrence we could study the shape and intensity of EPR spectrum in the absence of disturbing Josephson absorption in the whole temperature range.

EPR spectra were recorded on a standard spectrometer RADIOPAN SE/X with double modulation of a magnetic field of a frequency of 100 kHz. A rectangular resonance cavity with the wave TE_{102} stabilized the klystron frequency at $f = 9.4$ GHz. Temperature was changed and stabilized with the aid of a helium flow-cryostat made by Oxford Instruments. At a room temperature the spectrum of Cu^{2+} is typical of powdered sample with $g_\parallel = 2.218$ and $g_\perp = 2.06$. It corresponds to a complex rigidly fixed in the superconductor lattice. EPR spectra given in Fig. 4 illustrate the change in the EPR line shape between 55 K and 9.2 K. The smallest amplitude has been observed for the line recorded at 55 K and its shape resembles that of the room temperature recorded line. In the temperatures 45–47 K, the line significantly broadens. From 25 K to 10 K the line is symmetric
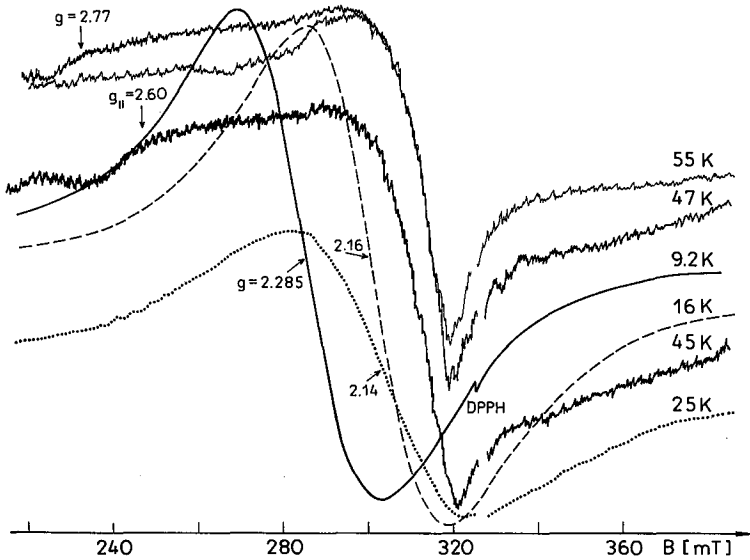
Fig. 4. EPR lines due to Cu(II) centre in the partly deoxygenated $YBa_2Cu_3O_{7-\delta}$ sample. The powder line – 55 K, the broadened line 45–47 K, the symmetric line of small amplitude – 25 K and of large amplitude – 9.2 K.

and its width does not change much. Below 18 K there is a significant increase in the line amplitude which cannot be described by the Curie law. With decreasing temperature, the value of $g_{\parallel}$ slightly decreases and reaches a sharp minimum at a temperature above T_c (Fig. 5). Below $T_c = 91$ K the value of $g_{\parallel}$ turns out to be the same as that the sample had at 120 K. Since it is difficult to determine an accurate value of $g_{\perp}$, in Fig. 4 the value of g_{min}, corresponding to the minimum in the absorption derivative, is marked. The values of g_{min} reveal a weak anomaly above T_c. A systematic decrease in $g_{\parallel}$ with decreasing temperature as well as the $g_{\parallel}$ minimum above T_c are related to the fluctuations of the superconducting phase which screen the field seen by the paramagnetic complex. Below T_c, the high T_c-superconductor is in the mixed state and the local field takes again the value of the external field. Further temperature decrease is accompanied by a break-up of the two-centered Cu2-Cu1 complex [6]. The condensation of the fifth oxygen at O5 site increases the dynamics of the chain complex $Cu1O_5$ while an increase in superconductivity screens the $Cu2O_4$ complexes in planes. Both effects decouple the two-centred complex. In the temperatures ranging from 50 to 28 K the EPR spectrum significantly changes, apart from a vanishing peak of EPR signal in the vicinity of $g_{min} = 2.05$, a wide absorption appears which then constitutes a single EPR line. Below 25 K the EPR spectrum is composed of a single symmetric EPR line of $g = 2.14$ corresponding to reorientating complex of $g_{\parallel} = 2.40$ and $g_{\perp} = 2.06$. Below 18 K the averaged coefficient of spectroscopic splitting rapidly increases with decreasing temperature. At 9.3 K, g reaches a value of 2.28 which
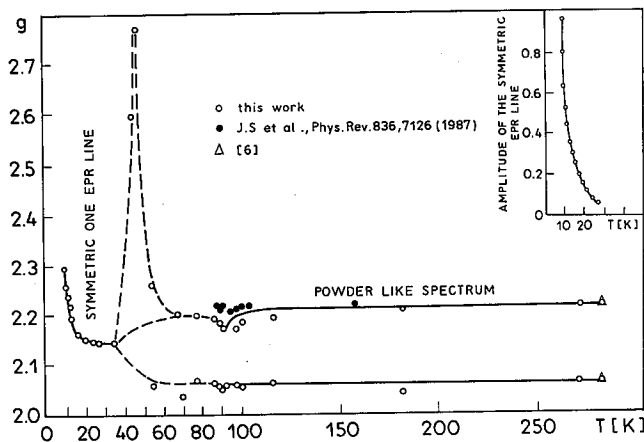
Fig. 5.   Temperature dependences of $g_{\parallel}$, $g_{\perp}$ and $g_{\min}$. The upper right corner insert presents the temperature dependence of EPR signal amplitude.

corresponds to full trigonal distortion. This is also pointed to by a weak asymmetry of the EPR line suggesting that $g_{\parallel}^{bpt} \approx 2$. The reciprocal asymmetry $(g_{\parallel} < g_{\perp})$ is a consequence of trigonal bipyramid pseudorotation which occurrence is proved by dramatically rising EPR signal amplitude (see the insert in Fig. 5). The width of this line is constant and equal to $\Delta B_{pp} = 33.5$ mT.

3. Theory of the averaged EPR spectrum of Cu²⁺ ion

The divalent copper Cu^{2+} state ^2D of the configuration $3d^9$ is an orbital quintet $(L = 2)$ and its ground state in axial crystalline field is characterized by a half spin, $S = 1/2$. In the case of square coordination of oxygen, CuO_4, or tetragonal pyramid, CuO_5, where the distance copper–oxygen in plane is shorter than the Cu–O distance in the vertical direction, the ground state is the orbital state $|x^2 - y^2\rangle$. The symmetries of CuO_4 and CuO_5 complexes are D_{4h} and C_{4v}, respectively. The orbital ground state of the complex $|3z^2 - r^2\rangle$ is characteristic of the squeezed CuO_6 octahedron of the symmetry O_h in which the Cu–O distance in plane is greater than the Cu–O distance in the vertical direction, five-coordinated CuO_5 complex of trigonal bipyramid symmetry (D_{3h}) or a linear copper coordination CuO_2. The complexes of a square coordination of CuO_4 pyramid are characterized by great stability, and the energies of their $E_{x^2-y^3}$, $E_{3z^2-r^2}$ and E_{xy} levels are -0.914Δ, -0.086Δ and $+0.086\Delta$, respectivety. A value of Δ is the orbital splitting of the levels in the cubic field which for a typical copper complex equals to about 10^4 cm^{-1}. Since the energy is so high, the ground state $|x^2 - y^2\rangle$ is made of rigid objects characterized by the axial g tensor of the following principal

values:

$$g_\parallel \approx 2 - 8\frac{\lambda}{E_{xy} - E_{x^2-y^2}}, \tag{1a}$$

$$g_\perp = 2 - 2\frac{\lambda}{E_{xz,yz} - E_{x^2-y^2}}. \tag{1b}$$

This tensor is averaged as soon as the complex begins fast reorientation. In a crystal the averaging of the axial tensor may occur in result of the dynamical Jahn–Teller effect which takes place in high enough temperatures, at which for some complexes the EPR spectrum anisotropy disappers due to thermally activated rotation, and a pseudocubic EPR spectrum characterized by the following averaged coefficient of spectroscopic splitting appears:

$$\langle g \rangle_{\mathrm{JT}} = \frac{g_\parallel + 2g_\perp}{3}. \tag{2}$$

Quite different is the behaviour of a paramagnetic complex CuO_5 when five oxygen atoms located around the central copper ion form a trigonal bipyramid of D_{3h} symmetry. The lowest energy $E_{3z^2-r^2} = -0.493\Delta$ has the state $|3z^2 - r^2\rangle$, and there are two states in its vicinity: $|x^2 - y^2\rangle$ and $|xy\rangle$ whose energy $E_{x^2-y^2} = E_{xz} = -0.282\Delta$. For a trigonal bipyramid CuO_5 of D_{3h} symmetry as well as for a linear CuO_2 molecules of $D_{\infty h}$ symmetry, the principal values of the g tensor are determined by after expressions:

$$g_\parallel = 2, \tag{3a}$$

$$g_\perp = 2 - 6\frac{\lambda}{E_{xz,yz} - E_{3z^2-r^2}}. \tag{3b}$$

In the case of dynamical averaging relation (2) is valid but $\langle g \rangle_{\mathrm{bpt}} > \langle g \rangle_{\mathrm{sp}}$. A close distance between $|x^2 - y^2\rangle$ state and the ground state $|3z^2 - r^2\rangle$ makes that vibronic excitation favours pseudorotation of trigonal bipyramid (Fig. 1) and the complex orbital ground state is superposition of two states:

$$|\rangle = \sqrt{1 - b^2}|x^2 - y^2\rangle + b|3z^2 - r^2\rangle. \tag{4}$$

A five-coordinated CuO_5 complex of the combined orbital state (4) is characterized by a pseudocubic EPR spectrum. In the terms of the crystal field theory Neimark and Zaritzsky [10] discussed the possible copper coordinations in IITS assuming that oxygen ions O^{2-} make the nearest surrounding of a copper ion Cu^{2+}(II). As it follows from their analysis, the ground state of a strongly deformed square coordination CuO_4 as well as of a linear CuO_2 coordination is $|3z^2 - r^2\rangle$. The ground state of non-deformed CuO_6 and CuO_4 complexes is $|x^2 - y^2\rangle$ and the principal values of the g tensor, obtained from their EPR spectra obey the following

relation: $g_{\parallel} > g_{\perp}$. The number of ligands in the complexes is described by the coefficient of asymmetry defined as:

$$\gamma = \frac{g_{\parallel} - g_0}{g_{\perp} - g_0}. \tag{5}$$

For an octahedron of O_h symmetry and for a plane complex of D_{4h} symmetry, this coefficient takes the values 4 and 6, respectively. Thus, we may assume that the EPR spectrum of copper ion of $g_{\parallel} = 2.390$ and $g_{\perp} = 2.065$ observed by us, corresponds strictly to the square coordination CuO_4 of D_{4h} symmetry and is related to copper in the chains $Cu(1)(O1)_2(O4)_2$ or to the paramagnetic defect $Cu2(O2)_2(O3)_2$ in the oxygen-copper plane in the structure of Y–123. The paramagnetic complex in Y–123 is formed by breaking up the exchange bonding of the chain copper Cu1 with the plane [6]. The values $g_{\parallel} = 2.218$ and $g_{\perp} = 2.065$ observed for Y–123 at room temperature are the result of exchange interaction between two copper atoms Cu2–Cu1 which is responsible for paramagnetic excitation of the Y–123 structure through violation of charge equilibrium. These values of $g_{\parallel}$ and $g_{\perp}$ practically do not change up to 50 K. A slight decrease in $g_{\parallel}$ with decreasing temperature as well as a clear anomaly above T_c are related to the superconductivity fluctuations. The fluctuations screen the external field thus diminishing the local magnetic field acting on the paramagnetic center. Above T_c the screening effect vanishes due to the appearance of a mixed Abrikosov structure and the magnetic field inside the vortices is equal to the external field. With further decrease in temperature the exchange interaction gets disconjugated. The components of the two-copper complex become unstable which at 45 K leads to a very wide EPR spectrum. Beyond 45 K this complex is decomposed and the EPR line is due to the mobile CuO_5 complex which is formed in result of the condensation. At 25 K the g tensor gets averaged to the value of $\langle g \rangle = 2.14$ in consequence of the dynamical Jahn–Teller effect, which corresponds to the reorientation among the three possible positions of the tetragonal pyramid $g = (2.39 + 2 \times 2.065)/3$. With further temperature decrease, at 18 K a strong vibronic coupling takes place between the states: $\sqrt{1 - b^2}|x^2 - y^2\rangle$ and $\sqrt{b}|3z^2 - r^2\rangle$, and the trigonal distortion b^2 increases. The coefficient of spectroscopic splitting increases from 2.143 to 2.285 which is related to the change in b^2 from ~ 0 at $T = 25$ K to $b^2 \approx 1$ at $T = 9.3$ K. In the lowest temperature considered, the EPR spectrum reveals asymmetry in a strong field, which means that the symmetry of the $\langle g \rangle$ tensor has been changed from the elongated ellipsoid to an oblate one. The width of the symmetric line does not change in the temperatures ranging from 25 K to 9.3 K which means that the g tensor's anisotropy does not change. Only the population of the states $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ is changed in this temperature range with the anisotropy coefficient g, remaining the same. At 18 K the width of the symmetric EPR line was the least, with $\Delta B_{pp} = 32.6$ mT. With the temperature decreasing from 25 K to 9.3 K the amplitude of EPR line increases 17-times, see the insert in Fig. 5. Such a strong increase in the signal amplitude is related to an increase in the number of paramagnetic centers formed in the consequence of oxygen condensation at O5 site in the Y–123 structure.

The oxygen condensation and desorption at these sites are thermally acti-

vated processes. The number of O^{2-} condensed at O5 sites N_{cond} can be found from the following expression:

$$N_{\text{cond}} = N_0(1 - e^{-E/kT}), \tag{6}$$

where N_0 is the number of O5 sites in the lattice. At the absolute zero temperature, $T = 0$, all free atoms of oxygen know their sites and $N = N_0$ while for T tending to infinity N tends to zero. The amplitude of the EPR signal in the logarithmic scale versus the inversed temperature is shown in Fig. 6. Applying Eq. (6), the
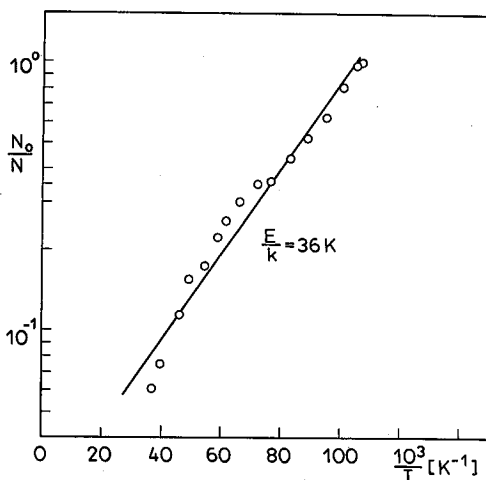

Fig. 6.   The amplitude of EPR signal N_0/N versus $1000/T$ for a symmetric line.

activation energy values was found for the temperatures from 9.3 K to 25 K to be $E/k = 36$ K. With respect to the g coefficient value, the temperature range $10 - 25$ K can be divided into two subranges. Between $25 - 18$ K the Jahn–Teller effect dominates, since $\langle g \rangle$ value is close to that obtained for the rotation of C_{4v} pyramid. The pseudorotation induced by a strong vibronic coupling takes place below 18 K where $\langle g \rangle$ strongly increases with decreasing temperature. Both these processes are, in this model, dependent on the number of oxygen atoms condensing at O5 sites.

4. Conclusions

The results are illustrated in Fig. 7. In a partly deoxygenated ceramic sample of $YBa_2Cu_3O_{7-\delta}$ oxygen is mainly desorbed from the links between the grains, which significantly reduces the microwave Josephson absorption. This effect permits the observation of EPR signals and their accurate analysis also below T_c. The paramagnetic centers formed in result of the ceramic refinement are composed of two-copper systems stable up to about 45 K. They are characterized by a typical
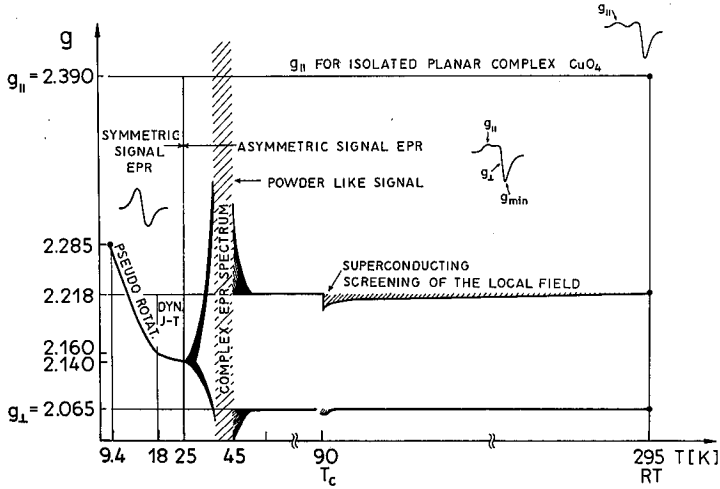
Fig. 7.   A schematic presentation of the EPR line shape changes with temperature.

powder EPR spectrum of the parameters $g_{\parallel} = 2.218$ and $g_{\perp} = 2.065$. Above T_c, the fluctuations of the superconducting state screen the external magnetic field. Below T_c, when the compound assumes the mixed-vortex state, the local field is close to the external field. At 45 K, the EPR spectrum becomes very broad because the two-copper complex gets decomposed and the paramagnetic excitations occur in a very wide range of magnetic field values, and two components of the EPR spectrum become apparent. Below 25 K the EPR spectrum takes the shape of a single symmetric line. Between $25 - 18$ K, single CuO_4 complexes characterized by $g_{\parallel} = 2.39$ and $g_{\perp} = 2.065$ are likely to be formed, and in consequence of the dynamical Jahn–Teller effect the g tensor gets averaged to $\langle g \rangle = 2.17$. In the range $18 - 9.3$ K the trigonal distortion of CuO_5 complex becomes more pronounced which leads to the pseudorotational averaging of the $\langle g \rangle$ tensor. The values of $\langle g \rangle$ increase with increasing b^2 reaching at 9.3 K $\langle g \rangle = 2.285$. The appearance of strong complex dynamics is related to the oxygen condensation at O5 sites and the formation of CuO_5 complexes. These complexes undergo both Jahn–Teller rotation and pseudorotation, which results in a symmetric EPR line. These two mechanisms of rotation are indicated by two clearly distinguished ranges of the $\langle g \rangle$ coefficient changes, one between $25 - 18$ K and the other $18 - 9.3$ K. The activation energy determined from the EPR line amplitude changes is $E/k = 36$ K.

The anomaly in g above T_c related to the fluctuations of the superconducting state in partially deoxygenated $YBa_2Cu_3O_{7-\delta}$, rapid increase in trigonal distortion below 18 K as well as other changes, like anomalous splitting of the EPR spectrum in the vicinity of 45 K and so on, related to the superconductivity will be the subject of our subsequent papers.

References

[1] I.B. Bersuker, *Jahn–Teller Effect and Vibronic Interactions* Nauka, Moscow 1987 (in Russian).

[2] D. Reinen, C. Friebel, *Inorg. Chem.* **23**, 791 (1984).

[3] S.K. Hoffmann, *Acta Phys. Pol.* **A49**, 253 (1976).

[4] J. Stankowski, *Adv. Mol. Phys.* **3**, 159 (1987) (in Polish).

[5] A. Dezor, K. Kędzia, M. Krupski, *Acta Phys. Pol.* **A57**, 81 (1980).

[6] J. Stankowski, W. Hilczer, J. Baszyński, B. Czyżak, L. Szczepańska, *Sol. State. Comm.* **77**, (2), 125 (1991).

[7] I.B. Bersuker, A.V. Ablov, *Chemical Bond in Complex Compounds*, Shtinca, Kishinev 1962, p. 147 (in Russian).

[8] R. Durny et al., *Phys. Rev. B* **36**, 2361 (1987); K.W. Blazey et al., ibid. p. 7241; J. Stankowski et al., ibid. p. 7126.

[9] J. Bohandy, B.F. Kim, F.J. Adrian, K. Moorjani, *Phys. Rev. B* **39**, 2733 (1989).

[10] E.I. Neimark, I.M. Zaritzky, *Superconductivity: Phys. Chem. Techn.* **2** (4), 63 (1989) (in Russian).

[11] R.J. Cava, B. Batlogg, R.B. Doves, D.W. Murphy, T. Siegist, J.P. Remeika, E.A. Rietman, S. Zahurak, G.P. Espinosa, *Phys. Rev. Lett.* **58**, 1676 (1987).