ESR study of the twinning structure of the superconducting single crystals Y–Ba–Cu–O

E. F. Kukovitskiĭ, S. G. L'vov, Yu. I. Talanov, G. B. Teitel'baum, and V. A. Shustov
Kazan' Physicotechnical Institute, Academy of Sciences of the USSR

(Submitted 30 November 1989)
Pis'ma Zh. Eksp. Teor. Fiz. **51**, No. 1, 61–64 (10 January 1990)

Copper–oxygen complexes characteristic of two types of twins and of the boundaries between them are studied by the ESR method using single crystals with developed twinning.

One of the most characteristic disruptions of the homogeneity of high-T_c superconducting materials is twinning, the study of which by x-ray and other methods provides useful information on the real structure of these materials.[1,2] Unique information on the local properties of such defects can be obtained by means of ESR. However, the characteristics of the magnetic state of copper ions in high-T_c superconducting compounds considerably complicate the observation of resonance on paramagnetic centers with orthorhombic symmetry,[3,4] characteristic of superconducting single crystals. The observed signals are usually attributed to various kinds of defects and impurity phases.[4–7] In our study of Y–Ba–Cu–O single crystals, whose homogeneity is disrupted primarily by twinning, we were able to observe not only the ESR signals of orthorhombic symmetry but also to use this method to study the structure of the twins and the boundaries between them.

The effects stemming from the presence of twinning boundaries are most distinct in systems where the number of copper ions belonging to the boundaries is sufficiently large. Such a situation takes place in two cases: When there is system of coherent boundaries with a large total length, or when one deals with so-called extended boundaries,[2] where the transition from one twin to another takes place at distances much greater than the lattice constant. For the same length of the boundaries, their volume in the second case is much greater.

We have studied the first case. The material chosen for study was a single crystal of $YBa_2Cu_3O_x$ with a well-developed domain structure, whose period, measured with a polarization microscope, is 0.1 μm. Its parameters are: $x = 6.75$, $T_c = 88$ K, transition width, 1 K; lattice constants $a = 3.822$ Å, $b = 3.880$ Å, $c = 11.702$ Å; dimensions, $2.5 \times 1.3 \times 0.3$ mm. The x-ray studies and polarization microscopy indicate a high degree of monocrystallinity, and no indications of the green phase were noted. The ESR measurements were conducted with a BER-418S Bruker microwave spectrometer at a frequency of 9.4 GHz at temperatures between 6 K and 300 K.

The ESR spectrum, recorded in a constant magnetic field $\mathbf{H} \| \mathbf{c}$, has one signal, whose width decreases (Fig. 1) as the temperature is lowered from 300 K to 100 K, $\Delta(\delta H)/\Delta T \approx 1.3$ G/K. At $T = 110$ K, it amounts to 130 G, and the g factor is 2.030 ± 0.003. Near $T = 90$ K, the signal broadens markedly, but its intensity falls off, and the line disappears. In the superconducting state, almost no resonance is observed,

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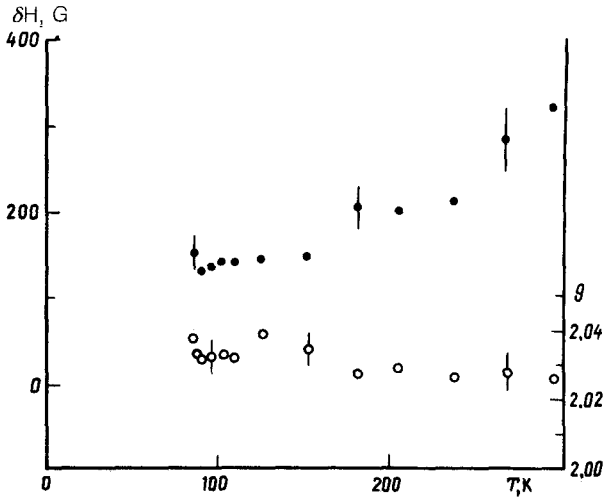

FIG. 1. Temperature dependence of the linewidth (●) and the g-factor (○) of $YBa_2Cu_3O_{6.75}$ sample for $\mathbf{H}\|\mathbf{c}$.

and it can be detected only at the lowest temperatures (~ 10 K), where its width is 500 G.

When the magnetic field is turned to the basal ab plane, the signal is split into two intense lines and one line approximately an order of magnitude weaker. All the signals have an angular dependence with a period of 180° during the rotation of the magnetic field about the c axis (Fig. 2). The intense signals (dotted and solid lines in Fig. 2) have maximum values of the g factors (2.182 ± 0.005) in the directions $\mathbf{H}\|[100]$ and $\mathbf{H}\|[010]$ (minimum $g = 2.058 \pm 0.002$). In the case of a weak signal (dot-dashed line in Fig. 2), maxima are observed in the $\mathbf{H}\|[110]$ orientation $g_{max} = 2.190 \pm 0.005$, $g_{min} = 2.052 \pm 0.003$).

Such a spectrum suggests that there are three types of paramagnetic complexes which differ in the nature of the environment of the Cu^{2+} ion. The magnitude of the deviation from the pair of different components of the g factors of these signals is due to different degrees of unfreezing of the orbital motion (due to the spin-orbit coupling) in each of the complexes, and makes it possible to draw qualitative conclusions about the nature of the electron density distribution in the corresponding d state of Cu^{2+}. This in turn makes it possible to determine the positions in the structure of the compound to which the complexes we are studying correspond. It is easy to see that the two strongest lines (A and B) belong to complexes differing by a 90° rotation of the a and b axes. This makes it possible to refer them to two types of twinning domains. The possibility that these complexes are related to the CuO_2 plane must be ruled out because the copper ions located in it are bound by strong exchange, and the orthorhombic nature of their environment is slight. It follows that these signals belong to planar tetracoordinated complexes of copper from chain planes spread by 90° relative to one another. The displacement of the extrema of the g factor of the third signal

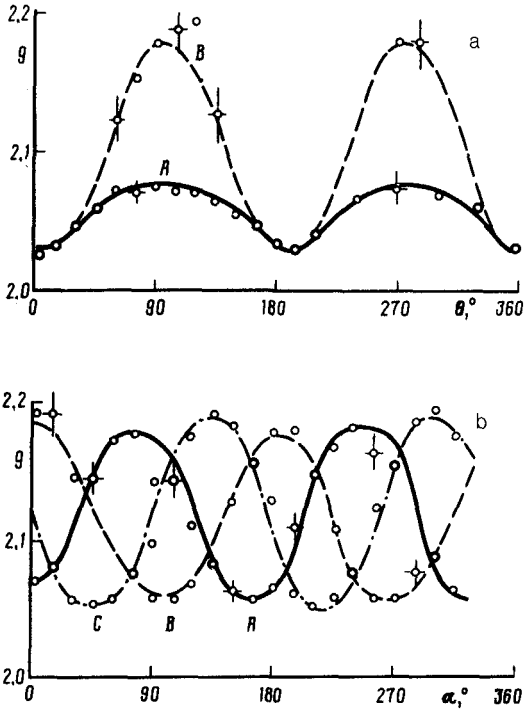

FIG. 2. Dependence of the g-factors of observed signals on the angles ϑ and α between the field H and the axes [001] (a) and [100] (b) at $T = 110$ K. (The lines —, - - -, -·-·- pertain to complexes A, B, and C, respectively. Boldface circles denote the points of superposition of the signals).

(complex C) by 45° from the [100] direction indicates that this factor belongs to the twinning boundary.

Figure 3 shows the structure of these complexes. Considering complex A as a fragment of the CuO_6 octahedron, infinitely stretched along the tetragonal axis, one can see the most advantageous configuration of the electron density is $d_{x^2-y^2}$. The x, y plane in this case contains all four oxygens that surround the copper ion. From a comparison of the expressions for the components of the g factor $g_i = g_0 - 2\lambda/\Delta_i$ with their experimental values, one can estimate the distances between the different levels of the Cu^{2+} multiplet: $\Delta_x = E_{xz} - E_{x^2-y^2} = 35.9|\lambda|$, $\Delta_y = E_{yz} - E_{x^2-y^2} = 71.42|\lambda|$, $4\Delta_z = E_{xy} - E_{x^2-y^2} = 44.4|\lambda|$. Here $g_e = 2.0023$, and $\lambda(<0)$ is the spin-orbit coupling constant (~ 500 cm^{-1}). If the rotation of the coordinate system is taken into account (Fig. 3), these results also apply to case B. Complex C, which corresponds to tetracoordinated copper, has an anisotropy axis which is specified by the intersection of the basal plane with the twinning plane. Its stability is achieved by a small displacement of the copper ion along the anisotropy axis; this results in a more symmetric arrangement of oxygen ions with respect to the plane that passes through the copper ion at right angles to this axis. As a result, the ground state of Cu^{2+} resembles a four-leaved rose in this plane, which accounts for the principal values of the g tensor characteristic of cases A and B (with allowance for a 45° spread).

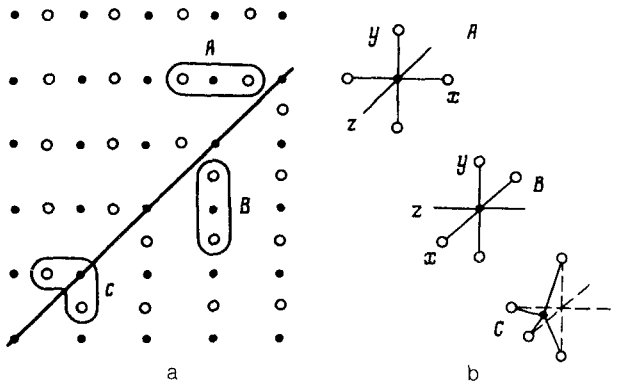

FIG. 3. Arrangement of complexes *A*, *B*, *C* in the chain plane (a) and their structure (b).

The appearance of tetracoordinated divalent copper indicates the presence of a hole at one of the oxygens of the surroundings. This assumption is confirmed by the results of NMR[9] and x-ray absorption[10] studies, which detected the presence of positive oxygen holes in the barium plane. Their localization near the twinning boundaries, when the total length of the latter is large, makes it possible to observe ESR in a twinned single crystal.

The correlation between the observed signals and twinning has also been established on the basis of the estimates of the number of spins in the resonance, based on the integrated line intensities. Approximately 10^{18} spins correspond to signals *A* and *B*, which amounts to $\sim 10\%$ of all the copper ions in the chains, and $\sim 10^{17}$ spins correspond to signal *C*. In order of magnitude, this number agrees exactly with the number of spins located within the twinning boundaries. We note that the weak line *C* which we observed is associated with only one orientation of the domain boundaries (along [110]). The fact is that there apparently are fewer twinned complexes in which the domain boundaries are misaligned by 90°, and the corresponding type *C* signal is located beyond the sensitivity limits of the spectrometer.

When the average size of the domains increases, and the total length of the boundaries decreases, the ESR signals decrease in amplitude and disappear. Thus, in $YBa_2Cu_3O_{6.9}$ crystals with $T_c \approx 92$–93 K, in which the domain width is $\gtrsim 1$ μm, no resonance could be observed. This again confirms the conclusion that the paramagnetic centers which we observed belong to the twinning boundaries.

Taking all the experimental results into account, we can draw some unambiguous conclusions about the properties of copper-oxygen complexes in the twinning boundaries and near them.

We wish to thank M. V. Eremin for a helpful discussion and V. E. Kataev for assistance in this work.

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Translated by A. Peiperl