Fluctuations of the local magnetic fields on Er^{3+} and Yb^{3+} rare-earth impurity ions in the superconductor $YBa_2Cu_3O_{6.85}$

I. N. Kurkin, I. Kh. Salikhov, L. L. Sedov, M. A. Teplov, and R. Sh. Zhdanov

V. I. Ul'yanov-Lenin State University, Kazan

(Submitted 23 August 1992)
Zh. Eksp. Teor. Fiz. **103**, 1342–1355 (April 1993)

The epr of Er^{3+} and Yb^{3+} in oriented $Y_{0.99}(Er,Yb)_{0.01}Ba_2Cu_3O_{6.85}$ powders has been studied at low temperatures $T < T_c \approx 85$ K). It is shown that the rare-earth ions are subject to a fluctuating molecular field of ≈ 160 Oe from the copper ions, independent of the kind of rare-earth ions and principally directed along the crystallographic c axis. The fluctuation rate of this field at $T > 6$ K increases exponentially with temperature: $W = 3.5 \cdot 10^{10} \exp(-25/T)$. On the basis of the measured dependence of the Yb^{3+} epr line intensity in $(Y,Yb)Ba_2Cu_3O_x$ on the oxygen content, and also taking account of experimental data in the literature on the Meissner effect and the calculated probabilities of the formation of clusters with the ortho-I structure in $YBa_2Cu_3O_x$, it is deduced that the observed Er^{3+}, Yb^{3+} signals and the dynamic effects in $YBa_2Cu_3O_{6.85}$ characterize the non-superconducting ortho-III phase, present in specimens to a noticeable degree ($\approx 30\%$ of the volume) in the form of layers (or drops) between the grains of the superconducting ortho-I phase.

INTRODUCTION

The physical properties of the superconductor $YBa_2Cu_3O_x$ are very sensitive to the oxygen content in the range of values $6.9 < x < 7.0$, i.e., within the limits of the so-called "90 K plateau."[1–6] In particular, the value 7.0 of the oxygen index corresponds to the maximum Meissner effect,[1] while the maximum critical temperature is reached at some value $x_m < 7.0$. Due to the known difficulties in finding the absolute oxygen concentration it has not so far been possible to determine the exact value of x_m and according to different authors the value of x_m is 6.90,[2] 6.92,[4] 6.94,[1] 6.95,[3] and 6.96.[5] Recent experiments[4] revealed a two-phase composition of crystals with $x > x_m$: it appeared that the second phase has the lattice parameter c_0 about 0.02 Å less than the main phase and replaces it as x increases. At the same time the critical temperature of crystalline specimens is little sensitive to the hydrostatic pressure for $x > x_m$ ($dT_c/dP \approx 0.04$ K/kbar), while for $x < x_m$ the derivative dT_c/dP increases rapidly and reaches 0.4 K/kbar for $x = 6.8$ (Ref. 6). It is also known that a change occurs in the sign of the thermoelectric force and in the derivative $d\chi/dT$ (Ref. 5) for $T > T_c$ (χ is the spin susceptibility). Nuclear magnetic resonance (NMR) of copper and oxygen[7] established that a Fermi liquid model is appropriate for describing the temperature dependences of the static spin susceptibility and the rate of nuclear spin-lattice relaxation in "heavily doped" (overdoped) $YBa_2Cu_3O_x$ specimens ($x > x_m$). It is characteristic of "weakly doped" (underdoped, $x < x_m$) specimens that an energy gap exists in the magnetic excitation spectrum opening up at $T \approx 130$ K. Inelastic (magnetic) neutron scattering experiments[8] showed that the width of the gap depends on the oxygen content: when the oxgyen index is reduced the gap narrows from 325 K at $x = 6.92$ to 185 K for $x = 6.69$. Results have recently appeared[9] on the temperature dependence of the microwave surface impedance R_s of a $YBa_2Cu_3O_x$ crystal ($T_c = 91.5$ K). Although the exact value of the oxygen content in this specimen remained unknown, according to certain indirect criteria (the large width ≈ 4 K of the superconducting transition, the existence of the "35 K anomaly" in the $R_s(T)$ dependence, see below) this crystal should evidently be ascribed to the "weakly doped" category. Analysis of results[9] shows that the scattering rate of thermally excited quasiparticles in the temperature range from 80 K to 60 K changes according to the law $\tau^{-1} = \tau_0^{-1} \exp(-E/kT)$, where the energy $E = 320$ K coincides with the width of the "spin gap" found by inelastic neutron scattering for $x = 6.92$ (Ref. 8), while $\tau_0^{-1} = 4.5 \times 10^{14}$ s^{-1} agrees with the fluctuation rate of the hyperfine magnetic field on copper Cu(2) nuclei in the CuO_2 planes found earlier in NQR (Ref. 10) and NMR (Ref. 11) experiments, i.e., with the rate of copper spin fluctuations for $T > T_c$.

Results of Bonn *et al.*[9] not only confirm, as it seems to us, the magnetic nature of quasi-particle scattering in specimens with $x < x_m$ for $T < T_c$, but also indicate the existence of one other singular point on the temperature scale: this point $T_{c2} = 35$ K corresponds to the maximum of the measured surface impedance. We note that anomalies of the physical properties of $YBa_2Cu_3O_x$ ($x \approx 6.9$) compounds at low temperatures were also observed earlier. For example, in NQR experiments on copper[12–16] speeding up of spin-spin relaxation of Cu(2) nuclei was recorded at 35 K, while it was established[17] that this effect is only observed in specimens with $x < 6.95$. In the temperature range from 45 K to 25 K the electron paramagnetic resonance (epr) spectra of copper also undergo appreciable changes:[18,19] as the temperature decreases, instead of a narrow asymmetry of the epr line a wide symmetric epr line appears, as though motion takes place in the system of electron spins which changes its nature at $T \approx 35$ K and stops at helium temperatures. Bondar' *et al.*[12] suggest that at $T \approx 35$ K either a second-order phase transition occurs or a rearrangement of the dynamic state of the intrinsic defects in $YBa_2Cu_3O_x$. In Ohkawa's view[20] the anomalies in the physical properties at the point T_{c2} are due to a second superconducting transition.

However that may be, the experimental facts reported above can evidently be taken as evidence of a qualitatively new state of the copper electron spin system for $T < 35$ K in

 1063-7761/93/040657-06$10.00

$YBa_2Cu_3O_x$ compounds with the oxygen content, $x < x_m$ (within the limits of the "90 K plateau"). The aim of the present work was to study the static and dynamic characteristics of this state. Using the epr method we established that the rare-earth ions (REI) Er^{3+} and Yb^{3+} introduced into the compound $YBa_2Cu_3O_{6.85}$ as probes are subject to a molecular field of ≈ 160 Oe at low temperatures, which is almost independent of the kind of REI and is directed along the crystallographic c axis. The fluctuation rate of this field grows with increasing temperature as $\exp(-25/T)$ and reaches the value 2. 10^{10} s^{-1} at 40 K.

EXPERIMENT

The epr measurements were carried out with a 3 cm IRÉS-1003 spectrometer. The specimens were $Y_{0.99}Er_{0.01}Ba_2Cu_3O_{6.85}$ and $Y_{0.99}Yb_{0.01}Ba_2Cu_3O_{6.85}$ powders ($T_c \approx 85$ K) with particle dimensions less than 10 μm,[21,22] mixed with epoxy resin and oriented in a magnetic field of 59 kOe. No contaminant phases were revealed in the specimens by x-ray measurements. The magnitudes of the oxygen indices were estimated by comparing the critical temperature and crystal lattice parameter c_0 with what is known from the literature[1,23] of the $T_c(x)$ and $c_0(x)$ dependences; the error in such an estimate is at most ± 0.05.

The Er^{3+} and Yb^{3+} epr spectra in $YBa_2Cu_3O_{6.85}$ are described by a spin Hamiltonian of rhombic symmetry.[22] However, since the difference between the g-tensor components in the ab plane is small, we assume in what follows that $g_a = g_b = g_\perp$, $g_c = g_\parallel$. Figures 1 and 2 show the temperature dependences of the g-factors and the linewidth $\Delta\omega_{pp}^{\alpha} = (g_\alpha \mu_B/\hbar)\Delta H_{pp}^{\alpha}$ from the peak to the absorption derivative peak. To complete the picture, results are also given in Fig. 2 of the magnitudes of the epr linewidth $\Delta\omega_{pp}$ of Yb^{3+} calculated on the basis of the results of measuring epr of unoriented $Y_{0.99}Yb_{0.01}Ba_2Cu_3O_{6.85}$ powder[21] (denoted by the symbols Δ) and an estimate of the spin-lattice relaxation rate of ytterbium ions from the temperature dependence of the $^{170}Yb^{3+}$ Mössbauer spectra in a $Y_{0.97}Yb_{0.03}Ba_2Cu_3O_x$ specimen with $x \approx 7.0$ (Ref. 24) (symbols ▲); both these sets of additional results are calculated according to known rules (see Ref. 25 and Eq. (1) below) on the assumption that the line-width at helium temperatures is $\Delta\omega_{Yb} = 0.31 \cdot 10^{10}$ rad/s. Without so far discussing the temperature dependence of the g-factors of Er^{3+} and Yb^{3+} ions, we turn to the fact that both the $\Delta\omega_{pp}^{\parallel}(T)$ curves in Fig. 2 have a minimum at some temperature $T_{\min}$. The measurements showed that the line shape of both RE ions at the temperatures $T \approx T_{\min}$ are close to Gaussian (see, e.g., Fig. 3). To the right of the minimum the $\Delta\omega_{pp}^{\parallel}(T)$ and $\Delta\omega_{pp}^{\perp}(T)$ curves for each of the RE ions practically coincide. Their rapid fall with increasing temperature is produced by the strong 4f-electron-phonon interaction [an Orbach spin-lattice relaxation process in the case of Er^{3+} and a Raman process for Yb^{3+} (Ref. 26)] and will not concern us further. We only note that from our results the temperature dependence of the spin-lattice relaxation rate of Yb^{3+} ions does not have a singularity at $T = T_c$. This conclusion agrees with a previous conclusion by Hodges *et al.*[24] To the left of the minimum the magnitude of $\Delta\omega_{pp}^{\parallel}$ increases in both cases and only becomes constant for $T < 6$ K, while the line width $\Delta\omega_{pp}^{\perp}$ remains constant for $T < 20$ K. Additional measurements at a frequency of 37 GHz showed that the linewidth $\Delta\omega_{pp}^{\perp}$ at low temperatures is

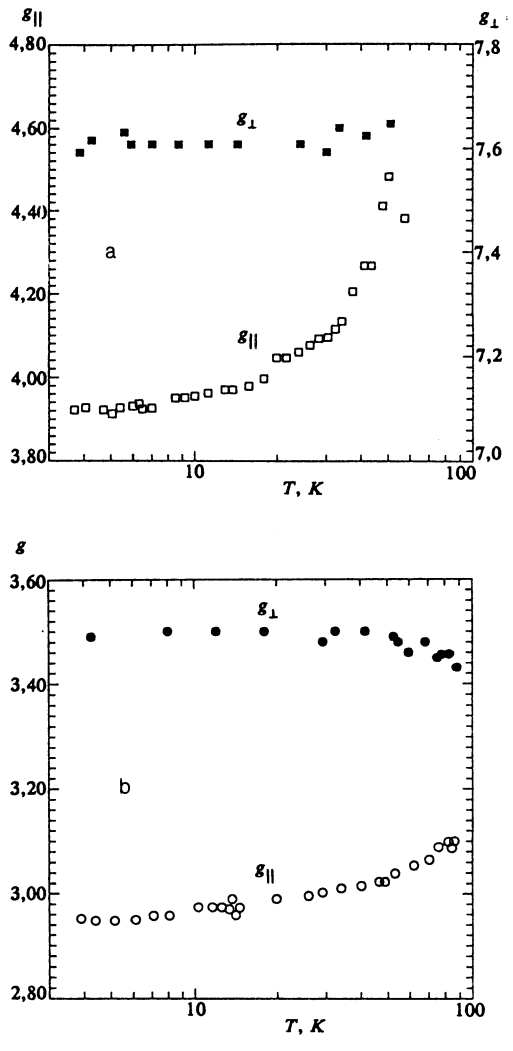

FIG. 1. Temperature dependence of the g-factors of a) Er^{3+} and b) Yb^{3+} ions in $YBa_2Cu_3O_{6.85}$.

related roughly linearly to the magnitude of the external d.c. field H_0. Such behavior of $\Delta\omega(H_0)$ ususally characterizes inhomogeneous epr line broadening due to a spread of the g-factor caused by local distortions of the electric crystal field (ECF).

DISCUSSION

The reduction in the value of $\Delta\omega_{pp}^{\parallel}(T)$ (see Fig. 2) in the range from helium temperatures to $T_{\min}$ leads one to consider the effect of the narrowing of resonance lines due to rapid motion.[27] The results of our experiments can be explained if it is assumed that the inhomogeneous linewidth $(\Delta\omega_{pp}^{\perp})_{LT}$ measured at low temperatures is mainly due to static local distortions of the CEF due to defects in the crystal structure [dipole-dipole interaction of the REI magnetic moments can only give a small contribution (~2–3%) to the epr linewidth for their relative concentration of ~1%], while an appreciable contribution to the width $(\Delta\omega_{pp}^{\parallel})_{LT}$ also comes from a spread (or slow fluctuations) of magnetic fields produced by copper ions and preferentially directed along the crystallographic c axis. If it is assumed further that for $T > 4$ K these molecular fields start to fluctuate as a result of some thermally activated motion of the copper-oxygen phase and the fluctuation rate W grows rapidly with increas-

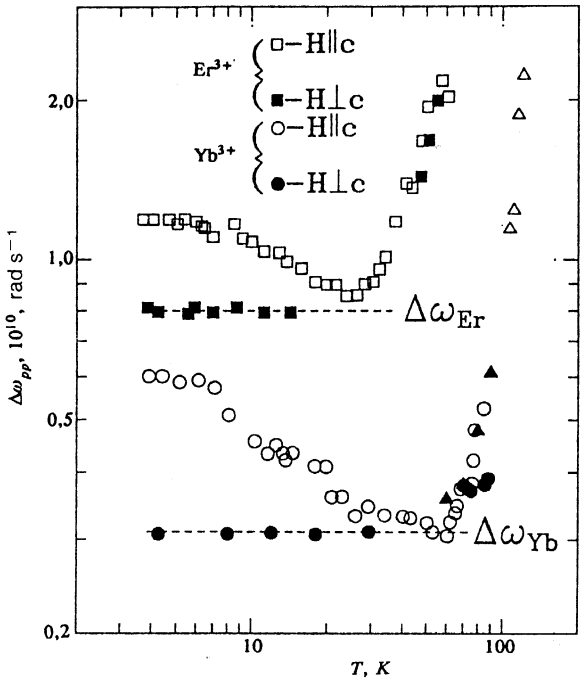

FIG. 2. Temperature dependence of the linewidths of Er^{3+} and Yb^{3+} in $YBa_2Cu_3O_{6.85}$; circles and squares show the present work, △, ▲ are estimates of $\Delta\omega_{pp}^{\perp}$ for Yb^{3+} ions according to results of, respectively, Abdulsabirov *et al.*[21] and Hodges *et al.*[24]

ing temperature, then we arrive naturally at the effect of narrowing of the epr line, when the rate $W(T)$ becomes commensurate with the value of $(\Delta\omega_{pp}^{\parallel} - \Delta\omega_{pp}^{\perp})_{LT}$. In order to estimate the magnitudes of the molecular field and of the fluctuation rate we assume that in the absence of a molecular field the line width at low temperatures would be independent of the specimen orientation in the magnetic field and would be equaL to $(\Delta\omega_{pp}^{\perp})_{LT} = \Delta\omega$ (a better justification for such an assumption is the general character of the $\Delta\omega_{pp}^{\alpha}(T)$ curves for different REI's shown in Fig. 2). Then knowing that the narrowing of a resonance line due to motion should have a Lorentzian shape,[28] we can find from the experiment the halfwidth of this line at half-maximum using the following equation:[25]

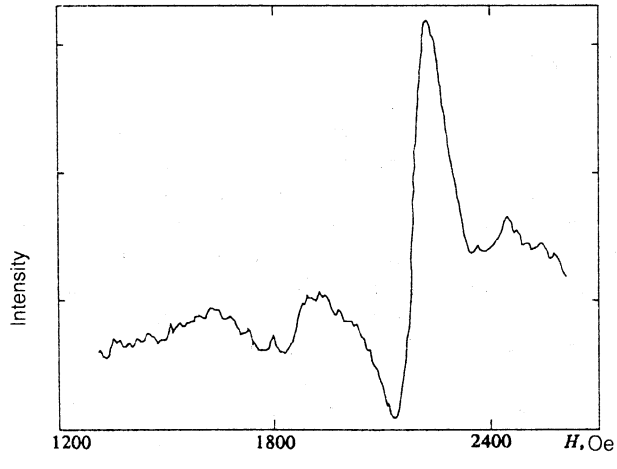

FIG. 3. Epr spectrum of Yb^{3+} ions in $YBa_2Cu_3O_{6.85}$ for $\mathbf{H}\|c$ and $T = 49.4$ K; the strong-field and weak-field lines are due to powder particles with the c axis parallel and perpendicular to the magnetic field, respectively.

$$\delta\omega = (\sqrt{3}/2\Delta\omega_{pp}^{\parallel})(\Delta\omega_{pp}^{\parallel 2} - \Delta\omega^2). \tag{1}$$

The main contribution to the linewidth (Eq. 1) should be given only by the quasi-adiabatic components of the molecular field, i.e., those with frequencies lying in the range from $-\delta\omega$ to $+\delta\omega$, so that the linewidth is determined by the relation:[28]

$$\delta\omega^2 \approx \overline{\delta\omega_0^2}\left(\int_{-\delta\omega}^{+\delta\omega} J(\omega)d\omega \Big/ \int_{-\infty}^{+\infty} J(\omega)d\omega\right), \tag{2}$$

where $\overline{\delta\omega_0^2}$ is the contribution from the second moment of the resonance line in the absence of motion, while $J(\omega)$ is the spectral density of the molecular field fluctuations. Assuming, as usual, that $J(\omega) = 2\tau_c/(1 + \omega^2\tau_c^2)$, where τ_c is the fluctuation correlation time, we obtain from Eq. (2)

$$\delta\omega^2 = \delta\omega_0^2(2/\pi)\mathrm{arctg}(\delta\omega\tau_c). \tag{3}$$

Analysis of the experimental results (Fig. 2) using Eqs. (1) and (3) gives the following results:

$$\begin{aligned} &Er^{3+}\ (T = 4{,}0 - 23\ \mathrm{K}):\\ &\Delta\omega = 0{,}88\cdot10^{10}\ \mathrm{rad/s}, \quad \left(\overline{\delta\omega_0^2}\right)^{1/2} = 0{,}55\cdot10^{10}\ \mathrm{rad/s},\\ &Yb^{3+}\ (T = 4{,}0 - 39\ \mathrm{K}):\\ &\Delta\omega = 0{,}31\cdot10^{10}\ \mathrm{rad/s}, \quad \left(\overline{\delta\omega_0^2}\right)^{1/2} = 0{,}38\cdot10^{10}\ (\mathrm{rad/s}). \end{aligned} \tag{4}$$

It follows from Eq. (4) that the root mean square value of the molecular field at low temperature, $h_0 = \hbar(\overline{\delta\omega_0^2})^{1/2}/g_{\parallel}\mu_B$, which is equal to 160 ± 22 Oe for Er^{3+} and 148 ± 20 Oe for Yb^{3+} is practically independent of the kind of RE ion. Moreover, the fluctuation rate $W = 1/\tau_c$ extracted from the Er^{3+} and Yb^{3+} epr spectra agree well with one another (Fig. 4) and make it possible to determine the form of the temperature dependence $W(T)$: for $T < 40$ K we have

$$W = W_0\exp(-U/T), \tag{5}$$

where $W_0 = (3.5 \pm 0.7)\ 10^{10}\ \mathrm{s}^{-1}$, $U = (25 \pm 3)$ K. These

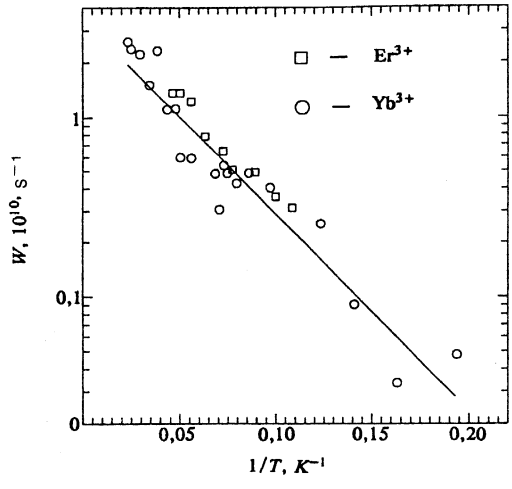

FIG. 4. Temperature dependence of the fluctuation rate of the molecular field on Er^{3+} and Yb^{+} ions in $YBa_2Cu_3O_{6.85}$.

facts provide the hope that the thermally activated motion which we have found is not connected with any perturbation introduced into the crystal lattice by the impurity RE ions but appears as a feature inherent to the compound $YBa_2Cu_3O_{6.85}$.

We now consider the temperature dependence of the RE ion g-factors (Fig. 1). The overall character of the effect ($g_\perp \approx$ const. $dg_\parallel/dT > 0$) recalls the effect of diamagnetic shielding of the external magnetic field at low temperatures, especially noticeable for field orientations $\mathbf{H}_0 \| c$, i.e., perpendicular to the CuO_2 planes. Not ruling out the possibility of changes in the g-factors due to the temperature dependence of the CEF potential and to effects from the conduction electrons, we draw attention here to the fact that the shifts in the resonance lines in the orientation $\mathbf{H}_0 \| c$ [ΔH_0 (50 K) $\approx$ 170 Oe for Er^{3+} and 60 Oe for Yb^{3+}] observed on warming from helium temperatures are, in order of magnitude, close to the value of h_0 found above. Consequently, it can be suggested that the epr lines for $\mathbf{H}_0 \| c$ are shifted for the same reason as these lines are broadened at helium temperatures, i.e., the molecular fields due to the Cu(2) copper ions at the RE sites are not canceled out. The existence of a nonzero static field at the RE impurity sites at helium temperatures has already been mentioned above: 200 ± 100 Oe on Er^{3+} ions in $Y_{0.975}Er_{0.025}Ba_2Cu_3O_6$,[29] 1600 ± 800 Oe on Yb^{3+} ions in $Y_{0.97}Yb_{0.03}Ba_2Cu_3O_6$,[24] 2100 ± 1000 Oe on Yb^{3+} ions in $Y_{0.97}Yb_{0.03}Ba_2Cu_3O_{6.35}$.[30] The occurrence of a nonzero static field at RE sites can result either from the shift of the RE impurity ion from its centrosymmetric position Y or from a spread in the values and directions of the magnetic moments of the copper Cu(2) ions. It is evident that it will only be possible to find the correct explanation of the results of our measurements of $g(T)$ (as also the results of other experiments[24,29,30]) after special studies of a series of specimens with different oxygen content, but the following conclusions can already be drawn. If the epr line-shifts ΔH_0 are actually due to the unbalanced molecular fields of the eight Cu(2) ions, then it follows from symmetry considerations that the shifts observed in our experiments ($\Delta H_0^\parallel \neq 0$, $\Delta H_0^\perp = 0$) can appear in two cases: (a) when the RE ion is shifted from the center of a cube at the vertices of which there are Cu(2) ions, along its space diagonal; (b) when a pair of neighboring (along the c axis) Cu(2) spins from the CuO_2 planes adjacent to the RE ion undergo spontaneous reorientation. We will assume that the local fields from Cu(2) on an RE ion have a pure dipole nature. Then no reasonable shift of a RE ion can explain the magnitude of ΔH_0 observed in our epr experiments and, all the more, in the experiments of Hodges *et al.*[24,30] Only possibility (b) thus remains: when a pair of Cu(2) spins in neighboring planes are simultaneously reoriented ferromagnetic clusters arise from five copper spins (the same type as discussed by Hizhnyakov and Sigmund[31]), the RE ion appears inside a "sandwhich" of two such clusters and a field $\Delta H_0^\parallel \approx (1500 \text{ Oe}/\mu_B)\mu_{Cu}$ arises at its position. According to calculations,[8] the antiferromagnetic exchange energy between two Cu(2) layers in compounds with $x \leqslant 6.20$ is from 1.5 to 15 MeV, i.e., 17–170 K.

In the literature of the last three years experimental facts which are evidence of the appearance of low-frequency fluctuations of the internal magnetic and electric fields in cuprate layers at low temperatures have been referred to more than once. Borsa *et al.*[32] were the first to point out the appearance of "mobile" defects with small activation energies in CuO_2 planes doped with oxygen holes: they explained the spin-lattice relaxation of ^{139}La nuclei in the nonsuperconducting $La_{1.9}S_{0.1}CuO_{4-\delta}$ as the result of the action of internal magnetic fields on the nucleus, fluctuating at a rate $W = 5 \cdot 10^{14} \exp(-8/T)$. In work devoted to the study of the Mössbauer spectra of the superconductor $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ with $T_c = 62$ K, Wu *et al.*[33] noted fluctuations in the electric field gradient at $^{57}Fe^{3+}$ ions in Cu(2) positions; at temperatures below 30 K the activation energy was found to be (19 ± 6) K. Studies of Mössbauer spectra of $^{170}Yb^{3+}$ in $Y_{0.97}Yb_{0.03}Ba_2Cu_3O_{6.35}$ showed[30] that ytterbium nuclei are acted on by a molecular field of $\approx$2100 Oe inclined at an angle of $\approx$45° to the c axis, the fluctuation rate of which varies from 10^9–10^{10} s^{-1} at 4 K to $> 10^{12}$ s^{-1} for $T > 30$ K.

As we cannot deduce anything from these facts (neither the dynamic effects themselves nor their possible effect on the properties of a superconducting material are understood at present) we shall try to analyze our results using developments in the theoretical work of de Fontaine and his colleagues[34,35] and refined in experimental work[36] on the representation of the $YBa_2Cu_3O_x$ phase diagram. The oxygen index 6.85 belongs to the region in which two phases exist[34]: ortho-I ($x = 7.00$, all copper chains filled with O(I) atoms) and ortho-III ($x = 6.67$, pairs of "full" chains alternating with single "empty" chains, the lattice has a period $3a_0$). Note that the superlattice with lattice parameter $3a_0$ has been observed several times by electron diffraction and electron microscopy;[2,37–43] however, the most convincing demonstration of its existence was recently produced by Yang *et al.*[36] Our measurements show (Fig. 5) that the integrated intensity of the Yb^{3+} epr signal, expressed per unit mass of specimen, reaches a maximum value just at $x \approx 6.7$. Consequently, the RE ion epr signal and the observed dynamic effects can be attributed to the ortho-III phase. This phase is evidently not superconducting. We can come to this conclusion by comparing results for the Mössbauer effect[1] and the probability of formation of OI clusters[35] in specimens with

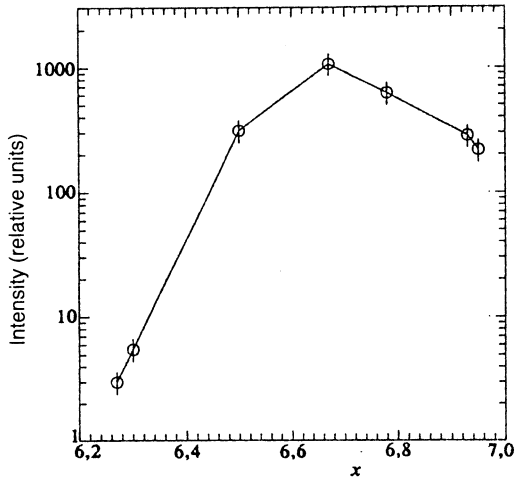

FIG. 5. Dependence of epr signal intensity of Yb^{3+} ions in $Y_{0.99}Yb_{0.01}Ba_2Cu_3O_x$ specimens on oxygen content.

different oxygen content. Experiment[1] shows that the volume fraction of superconductor in a specimen with $x = 6.85$ is $54 \pm 4\%$ of that observed in a specimen with $x = 7.00$. According to calculation,[35] OI clusters should have about such a weight (56%) in a specimen with $x = 6.85$, while the relative weight of OIII and disordered clusters with random single, double and triple chains of O(I) vacancies should be equal, respectively, to 33% and 11%.

Assuming the existence in one specimen of superconducting and nonsuperconducting phases, we should naturally consider the question of the dimensions of the "grains" (clusters) of these phases. We note first of all that the multiphase composition appears not only in polycrystalline (ceramic) specimens but also in high-quality single crystals. For example, Osofsky *et al.*[44] studying magnetization curves of $YBa_2Cu_3O_x$ crystals found that specimens with $x > 6.94$ behave as homogeneous superconductors in a magnetic field, while specimens with $x < 6.94$ behave as granular systems in a sufficiently strong field with the superconducting oxygen-rich regions divided by intermediate regions of oxygen-deficient material and the 90 K superconductivity is percolative (the percolation threshold is $x_c = 6.78 \pm 0.03$). One can approach an estimate of the minimum size of clusters of superconducting phase by using the suggestion of Jorgensen[45,46] of a concept of "structural coherence," according to which the main condition for superconductivity to arise in layered cuprates is the existence of translational symmetry of the CuO_2 planes. Jorgensen *et al.*[45,46] consider that local orthorhombic order (i.e., local structural coherence) in the form of orthorhombic fluctuations or microdomains may be sufficient to maintain superconductivity and that the critical structural coherence length should be of the same order as the superconducting coherence length $\xi_{ab} \sim 15$ Å. On the other hand, for superconductivity to arise a sufficiently high current carrier concentration is necessary in the CuO_2 planes which provides charge transfer from CuO chains. It was shown[47] that charge transfer is only possible from chain fragments Cu–O–...–O–Cu of length not less than $4b_0 \approx 15$ Å. We thus obtain an estimate of the minimum dimension of superconducting clusters $l_{\min} \sim 15$ Å. A value close to it, $l_{\min} \sim 30$ Å was given by Alekseevskiĭ *et al.*[48] in epr studies of Gd^{3+} in $(Y,Gd)Ba_2Cu_3O_x$. Although such small cluster dimensions are inaccessible to measurement by existing methods, we should nevertheless mention that it was possible by neutron diffraction to find "drops" of ortho-II phase with mean dimensions $10a_0 \times 24b_0 \times 2c_0$, i.e., $40 \times 90 \times 24$ Å^3 in the compound $YBa_2Cu_3O_{6.4}$ (Ref. 49). As regards the dimensions of non-conducting inclusions, they would be unlikely to differ greatly from those given above. For example, Vega *et al.*[50] estimated the minimum volume of a dielectric cluster per single O(I) vacancy as 12 elementary cells ($2a_0 \times 3b_0 \times 2c_0$).

It appears that the estimates given above are very crude, but they give an idea of the possible microscopic scales of the phase stratification in lightly doped $YBa_2Cu_3O_x$ compounds. This idea will evidently correspond better with reality if we take into account another specific structural feature of these compounds, the laminar structure. The assumed form of the structure of weakly doped compounds will occur when the assembly of superconducting ortho-I domains is in the form of thin plates alternating with layers of nonsuperconducting material (ortho-III and disordered phases). If thin layers of ortho-III phase (with special magnetic properties, as our experiments show) take part in the formation of weak interactions between superconducting ortho-I domains, then they will evidently produce scattering of Cooper pairs and will affect the observed magnetic and transport properties of $YBa_2Cu_3O_x$ specimens. We assume that the shift $\Delta H_0^{\parallel}$ and the width h_0 of Er^{3+} and Yb^{3+} epr lines in a field $H_0 \| c$ at helium temperatures are actually due to localization in the neighborhood of the RE ion of an antiferromagnetically coupled pair of ferromagnetic clusters (FMC) of Cu(2) copper with spins $S = 5/2$, formed in material weakly doped with oxygen holes.[31] The reduction of the shift and of the linewidth with increasing temperature can then be taken to be a result of thermally activated hops of these paired clusters from one RE ion to another. What basis is there for introducing discussion of a FMC pair here? An impurity RE ion is positioned between CuO_2 planes and leads to the appearance of defects (deformations) symmetrical in both planes. It is natural to expect that localization of FMC's will take place at such defects. Proceeding logically, we can assume further that at sufficiently low temperatures FMC's of copper will also maintain themselves near other point defects [such as O(I) oxygen vacancies], introducing asymmetrical distortions in adjacent CuO_2 planes. In such cases the probability of formation of stable, antiferromagnetically coupled pairs of FMC's should be small, while single localized FMC's with spin $S = 5/2$ should given an epr signal. In this model the following interpretation can, for example, be given for those transformations which the epr spectra of copper in $YBa_2Cu_3O_x$ undergo when the temperature decreases.[18,19] Single FMC's mobile at high temperatures start to "condense" at defects at $T \sim 35$ K and are fully localized at helium temperatures; the large epr linewidth at low temperatures may be associated with the existence of an unresolved fine structure.

Of course, all our discussions of pairs of FMC's are in the nature of unsubstantiated suggestions. However, it will be appropriate to mention here the following interesting fact in confirmation that these suggestions deserve serious attention: the temperature dependence of the spin susceptibility (χ_s) known from the literature and the NMR Knight shifts (K) of lightly doped $YBa_2Cu_3O_x$ compounds agree extremely well with the temperature variation of the susceptibility of a system of antiferromagnetically coupled pairs ($s_1 = 5/2, s_2 = 5/2$)[51]

$$\chi = \frac{Ng^2\mu_B^2}{3kT}\left\{e^{-\frac{35J}{2kT}} + 3e^{-\frac{31J}{2kT}} + 5e^{-\frac{23J}{2kT}} + 7e^{-\frac{11J}{2kT}} + 9e^{\frac{5J}{2kT}} + 11e^{\frac{25J}{2kT}}\right\}^{-1} \times\left\{6e^{-\frac{31J}{2kT}} + 30e^{-\frac{23J}{2kT}} + 84e^{-\frac{11J}{2kT}} + 180e^{\frac{5J}{2kT}} + 330e^{\frac{25J}{2kT}}\right\}. \quad (6)$$

In fact, it is sufficient to take the exchange interaction constant in Eq. (6) as $J = -141$ K to describe the results of measurements of $\chi_s(T)$, $^{63}K(T)$ and $^{17}K(T)$ in $YBa_2Cu_3O_{6.63}$ ($T_c = 62$ K) in the temperature range 25–300 K (Ref. 52). This energy lies within the limits indicated by Rossat-Mignod *et al.*[8] for compounds with $x \leqslant 6.2$, while the value $2|J| = 282$ K, the energy interval between the

ground state singlet ($S = 0$) and the nearest excited ($S = 1$) states of the pair ($s_1 = s_2 = 5/2$), is close to the width of the "spin gap" a compound with $x = 6.92$, which was measured by inelastic neutron scattering.[8]

We note in conclusion that the present investigation could not reveal any feature of the spin dynamics at temperatures near T_{c2}. We postulate that for $T > 35$ K the character of the motion changes and the activation energy grows sharply, as happens for example in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ (Ref. 33), where the activation energy becomes equal to ≈ 120 K for $T > 30$ K. Such a tendency is just noticeable in Fig. 4, but the large inhomogeneous width and strong spin-phonon broadening of the epr lines of the RE ions interfere with its verification. Because of the technical difficulties of the experiment, associated with the low epr signal intensity and changes in the Q-factor of the vhf resonator, we were also unable to observe the jump in intensity for $T \geqslant T_c$ which could be expected on account of the appearance of an additional epr signal from the ortho-I phase.

The authors thank E. V. Kryukov, N. A. Logachev, I. V. Yasonov for help with the experiments and M. V. Eremin for discussion of the results. The work is supported by the Scientific Soviet for problems in HTSC, carried out under project No. 91001 of the Russian Government program "High-temperature superconductivity" and No. GR-21 of the Russian Government Interuniversity Scientific-technological program "High-temperature superconductivity."

[1]T. Graf, G. Triscone, and J. Muller, J. Less-Common Met. **159**, 349 (1990).
[2]S. Rusiecki, B. Bucher, E. Kaldis, E. Jilek, J. Karpinski, C. Rossel, B. Pümpin, H. Keller, W. Kündig, T. Krekels, and G. Van Tendeloo, J. Less-Common Met. **164–165**, 31 (1990).
[3]J. R. Cooper, S. D. Obertelli, A. Carrington, and J. W. Loram, Phys. Rev. B**44**, 12086 (1991).
[4]H. Claus, U. Gebhard, G. Linker, K. Röhberg, S. Riedling, J. Franz, T. Ishida, A. Erb, G. Müller-Vogt, and H. Wühl, Physica (Utrecht) C**200**, 271 (1992).
[5]G. Triscone, J.-Y. Genoud, T. Graf, A. Junod, and J. Muller, to be published in J. Alloys and Compounds.
[6]C. C. Almasan, S. H. Han, B. W. Lee, L. M. Paulius, M. B. Maple, B. W. Veal, J. W. Downey, A. P. Paulikas, Z. Fisk, and J. E. Shirber, Phys. Rev. Lett. **69**, 680 (1992).
[7]C. Berthier, Y. Berthier, P. Butaud *et al.*, Appl. Magn. Resonance **3**, 449 (1992).
[8]J. Rossat-Mignod, L. P. Regnault, C. Vettier, P. Bourges, P. Burlet, J. Bossy, J. Y. Henry, and G. Lapertot, Physica (Utrecht) C**185–189**, 86 (1991).
[9]D. A. Bonn, P. Dosanjh, R. Liang, and W. N. Hardy, Phys. Rev. Lett. **68**, 2390 (1992).
[10]O. N. Bakharev, R. Sh. Zhdanov, A. V. Egorov, M. V. Eremin, V. V. Naletov, M. S. Tagirov, and M. A. Teplov, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 383 (1988) [JETP Lett. **47**(8), 458 (1988)].
[11]C. H. Pennington, D. J. Durand, C. P. Slichter, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B**39**, 2902 (1989).
[12]A. V. Bondar', S. M. Ryabchenko, Yu. V. Fedotov, and A. A. Motuz, Pis'ma Zh. Eksp. Teor. Fiz. **50**, 133 (1989) [JETP Lett. **50**(3), 146 (1989)].
[13]A. Yu. Zavidonov, M. V. Eremin, O. N. Bakharev, A. V. Egorov, V. V. Naletove, M. S. Tagirov, and M. A. Teplov, Sverkhprovod. Fiz. Khim. Tekh. **3**, 1597 (1989) [Supercond. Phys. Chem. Technol. **3**(8), 1274 (1990)].
[14]M. Tei, H. Takai, K. Mizoguchi, and K. Kume, Z. Naturforsch. **45a**, 429 (1990).
[15]K. Kumagai, Y. Nakamichi, Y. Nakamura, T. Takatsuka, and H. Nakajima, J. Phys. Soc. Jpn. **59**, 2336 (1990).
[16]Y. Itoh, H. Yasuoka, and Y. Ueda, J. Phys. Soc. Jpn. **59**, 3463 (1990).
[17]M. Tei, K. Mizoguchi, and K. Kume, *The Physics and Chemistry of Oxide Superconductors* (eds. Y. Iye, H Yasuoka), Springer-Verlag, Berlin, (1992).
[18]J. Genossar, D. Shaltiel, V. Zevin, A. Grayevsky, and B. Fisher, J. Phys.: Condens. Matter **1**, 9471 (1989).
[19]J.Stankowski, W. Kempinski, and Z. Trybula, Acta Phys. Pol. A**80**, 571 (1991).
[20]F. J. Ohkawa, J. Phys. Soc. Jpn. **61**, 639 (1992).
[21]R. Yu. Abdulsabirov, R. Sh. Zhdanov, Ya. S. Izygzon, Sverkhprov. Fiz. Khim. Tekh. **2**, 52 (1989) [Supercond. Phys. Chem. Technol. **2**].
[22]M. V. Eremin, I. N. Kurkin, M. P. Rodionova, I. Kh. Salikhov, L. L. Sedov, L. R. Tagirov, Sverkhprov. Fiz. Khim. Tekh. **4**, 716 (1991) [Supercond. Phys. Chem. Technol. **4**(4), 625 (1991)].
[23]J. D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Klaus, and W. K. Kwok, Phys. Rev. B**41**, 1863 (1990).
[24]J. A. Hodges, P. Bonville, P. Imbert, and G. Jéhanno, Physica (Utrecht) C**184**, 259 (1991).
[25]G. M. Zhidomirov *et al.*, *Interpretatsiya slozhnykh spektrov ÉPR* [*The interpretation of complicated epr spectra*] (in Russian), Nauka, Moscow (1975).
[26]I. N. Kurkin and L. L. Sedov, Proc. 29th Soviet Conf. on Low-Temperature Physics, Kazan, June 1992, Part 3, Paper 65.
[27]N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).
[28]A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford (1961).
[29]J. A. Hodges, P. Bonville, P. Imbert, and G. Jéhanno, Physica (Utrecht) C**184**, 283 (1991).
[30]J. A. Hodges, P. Bonville, P. Imbert, G. Jéhanno, and P. Debray, Physica (Utrecht) C**184**, 270 (1991).
[31]V. Hizhnyakov and E. Sigmund, Physica (Utrecht) C**156**, 655 (1988).
[32]F. Borsa, M. Corti, T. Rega, and A. Rigamonti, Nuovo Cimento D**11**, 1785 (1989).
[33]Y. Wu, S. Pradhan, and P. Boolchand, Phys. Rev. Lett. **67**, 3184 (1991).
[34]G. Ceder, M. Asta, and D. de Fontaine, Physica (Utrecht) C**177**, 106 (1991).
[35]R. McCormack, D. de Fontaine, and G. Ceder, Phys. Rev. B**45**, 12976 (1992).
[36]S. Yang, H. Claus, B. W. Veal, R. Wheeler, A. P. Paulikas, and J. W. Downey, Physica (Utrecht) C**193**, 243 (1992).
[37]D. J. Werder, C. H. Chen, R. J. Cava, and B. Batlogg, Phys. Rev. B**38**, 5130 (1988).
[38]J. Reyes-Gasga, T. Krekels, G. Van Tendeloo, J. Van Landuyt, W. H. M. Bruggink, H. Verweij, and S. Amelinckx, Solid State Commun. **71**, 269 (1989).
[39]J. Reyes-Gasga, T. Krekels, G. Van Tendeloo, J. Van Landuyt, S. Amelinckx, W. H. M. Bruggink, and H. Verweij, Physica (Utrecht) C**159**, 831 (1989).
[40]C. J. Hou, A. Manthiram, L. Rabenberg, and J. B. Goodenough, J. Mater. Res. **5**, 9 (1990).
[41]M. A. Alario-Franco, Sverkhprov. Fiz. Khim. Tekh. **3**, 1689 (1990) [Supercond. Phys. Chem. Technol. **3**(8), 1362 (1990)].
[42]B. Raveau, C. Michel, M. Hervieu, D. Groult, and J. Provost, J. Solid State Chem. **85**, 181 (1990).
[43]T. Krekels, H. Zou, G. Van Tendeloo, D. Wagener, M. Buchgeister, S. M. Hosseini, and P. Herzog, Physica (Utrecht) C**196**, 363 (1992).
[44]M. S. Osofsky, J. L. Cohn, E. F. Skelton, M. M. Miller, R. J. Soulen, S. A. Wolf, and T. A. Vanderah, Phys. Rev. B**45**, 4916 (1992).
[45]J. D. Jorgensen, D. G. Hinks, P. A. Radaelli, P. Shiyou, P. Lightfoot, B. Dabrowski, C. U. Segre, and B. A. Hunter, Physica (Utrecht) C**185–189**, 84 (1991).
[46]J. D. Jorgensen, D. G. Hinks, B. A. Hunter *et al.*, to be published in *Lattice Effects in High-T_c Superconductors* (Eds. Y. Bar-Yam, T. Egami, J. Mustre de Leon, and A. Bishop), World Scientific, Singapore.
[47]G. V. Uimin, V. F. Gantmakher, A. M. Neminsky, L. A. Novomlinsky, D. V. Shovkun, and P. Brüll, Physica (Utrecht) C**192**, 481 (1992).
[48]N. E. Alekseevskiĭ, I. A. Garifullin, N. N. Garif'yanov, B. I. Kochelaev, A. V. Mitin, VI. Nizhankovskiĭ, L. R. Tagirov, G. G. Khaliullin, and E. P. Khlyubov, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 36 (1988) [JETP Lett. **48**(1), 37 (1988)].
[49]T. Zeiske, R. Sonntag, D. Hohlwein, N. H. Andersen, and T. Wolf, Nature (London) **353**, 542 (1991).
[50]A. J. Vega, W. E. Farneth, E. M. McCarron, and R. K. Bordia, Phys. Rev. B**39**, 2322 (1989).
[51]V. T. Kalinnikov and Yu. V. Rakitin, *Vvedenie v magnetokhimiyu. Metod staticheskoĭ magnitnoĭ vospriimchivosti v khimi [Introduction to magnetochemistry. The static magnetic susceptibility method in chemistry]* (in Russian), Nauka, Moscow (1980).
[52]M. Takigawa, A. P. Reyes, P. C. Hammel, J. D. Thompson, R. H. Heffner, Z. Fisk, and K. Van C. Ott, Phys. Rev. B**43**, 247 (1991).

Translated by Robert Berman