Kinetics and Catalysis, Vol. 41, No. 6, 2000, pp. 794–798. Translated from Kinetika i Kataliz, Vol. 41, No. 6, 2000, pp. 873–877.
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Effect of Reductive Treatment on the Magnetic Properties of $HoBa_2Cu_3O_y$ and $NdBa_2Cu_3O_y$ Oxide Systems

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Received June 7, 1999

Abstract—The effect of the reductive treatment of perovskite-like $RBa_2Cu_3O_y$ (R = Ho, Nd) complex oxides in a CO atmosphere on their superconducting and magnetic properties is studied by ESR spectroscopy. ESR spectra of initial $RBa_2Cu_3O_y$ phases exhibit only a low-field absorption signal in the zero field ($T = 77$ K). This signal disappears after the exposure of test samples to carbon monoxide. The analysis of ESR spectra of reduced samples points to the formation of regions with high local concentrations of isolated Cu^{2+} ions and Cu^{2+}–Cu^{2+} dimers. The concentration of these paramagnetic species significantly decreases with an increase in the degree of reduction.

INTRODUCTION

Recent discovery of high-temperature superconductivity (HTSC) in multicomponent $RBa_2Cu_3O_y$ oxides, where R is a rare-earth element, has stimulated intensive studies of this compounds [1]. Laminated cuprates with such a composition are also of interest because they can be used as a basis for selective oxidation catalysts.

Prospects for the use of these compounds as catalysts for redox reactions depend on their properties, such as the high mobility of oxygen in a crystalline structure, low activation energies [2, 3], and the anionic nonstoichiometry y that can be changed over a wide range while preserving a sample as a single-phase system [4].

However, the structure and properties of $RBa_2Cu_3O_y$ compounds exposed to the reaction mixture may considerably change under real conditions of a heterogeneous catalytic process. This paper presents the ESR study of the effect of reductive treatment of laminated $RBa_2Cu_3O_y$ cuprates (R = Ho, Nd) in a CO atmosphere on their superconducting and magnetic properties.

EXPERIMENTAL

The samples of $RBa_2Cu_3O_y$ (R = Ho, Nd) were synthesized by a high-temperature solid-phase reaction using the procedure described in [5]. The existence of a single phase in prepared oxides was monitored by XRD using an RD7 diffractometer (Freiberger Prazisions Mechanik) with CuK_α radiation. The oxygen nonstoichiometry of samples was determined by iodometric titration [6].

The test complex oxides were reduced by carbon monoxide under non-steady-state conditions at 473 and 673 K using a pulse microcatalytic method. The experimental conditions are described in detail in [7].

ESR spectra were recorded at 77 and 298 K with an EMX spectrometer (Bruker) operating with a frequency of 9.4 GHz. The Bruker SimFonia program was used for simulating spectra. The values of the g factor were determined by the simultaneous measurements of the magnetic field intensity and frequency.

RESULTS AND DISCUSSION

The ESR spectrum of the initial $HoBa_2Cu_3O_y$ phase recorded at the temperature of liquid nitrogen exhibited only a low-field absorption signal in the zero field (Fig. 1). This nonresonance signal is typical of high-temperature superconductors with the composition $RBa_2Cu_3O_y$ [8, 9]. The absorption in low fields is due to the penetration of a magnetic field in HTSC ceramic granules. The intensity of a low-field signal is proportional to the amount of superconducting phase, and this relationship can be used for the rapid diagnostics of electrophysical properties of $RBa_2Cu_3O_y$ oxides [8]. No signal other than the low-field signal was observed in the spectra of initial $RBa_2Cu_3O_y$ phases (R = Ho, Nd) measured at room temperature and 77 K. This pointed to the fact that the samples of laminated cuprates were mainly present in a single phase.

After the treatment of $RBa_2Cu_3O_y$ samples with carbon monoxide at 473 or 673 K, their magnetic properties substantially changed. Of course, the nonresonance absorption disappeared because, according to our data [7], the thermal treatment of $RBa_2Cu_3O_y$ samples in a CO atmosphere resulted in the removal of weakly bound oxygen from their structures and, hence, in the

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† Deceased.

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loss of their superconductivity. The removal of oxygen favored the formation of a defective structure of complex oxides with a high concentration of anionic vacancies and the partial degradation of the laminated cuprate surface. Evidently, the degradation concerned only a small subsurface region of crystallites because, according to the XRD data, the crystalline structure of the samples after reductive treatment did not change. When reduced samples were reoxidized by oxygen, the low-field signal in the zero field appeared in the ESR spectra again; that is, the superconductivity of samples was restored.

ESR spectra of the $HoBa_2Cu_3O_y$ sample reduced by CO at 673 K were recorded at 77 and 298 K (Fig. 2). The shape of these spectra is the result of the superposition of a broad line and the spectra with a well-resolved hyperfine structure (hfs) (Fig. 3). As is seen from Fig. 2, the shape of the broad line, its intensity, and the g factor strongly depended on the measurement temperature, whereas the central part of the spectrum retained almost all its characteristic properties at both temperatures. Well-resolved hfs pointed to diamagnetic dilution in the region where paramagnetic centers were localized. The shape of the ESR spectrum obtained in the presence of air was similar to that observed in a vacuum of 10^{-2} Torr. The absence of broadenings of the hfs components from the ESR spectra obtained in the presence of paramagnetic oxygen molecules on the surface of the sample is evidence that paramagnetic centers were located in the sample bulk. The parameters of the ESR spectra (Table 1) pointed to the presence of paramagnetic species of two types: isolated Cu^{2+} cations and isolated Cu^{2+}–Cu^{2+} ion pairs.

When the sample was treated under mild conditions (CO, 473 K), the contribution of the broad line was insignificant. The ESR spectrum was the superposition of a weak signal from Cu^{2+}–Cu^{2+} pairs, the anisotropic spectrum of isolated Cu^{2+} ions (with unresolved HFS), and the exchange-narrowed signal of Cu^{2+} ions (g_{iso} = 2.11) (Fig. 4, Table 1). Comparison of the ESR spectra of the samples treated in a CO atmosphere at 673 and 473 K suggested that the types of isolated Cu^{2+} ions and copper pairs did not change. The broadening was probably due to the effects of a strong spin–spin interaction between Cu^{2+} isolated ions in the $HoBa_2Cu_3O_y$ sample reduced at 473 K. The enhancement of the spin–spin interaction may be caused by an increase in the concentration of the corresponding copper ions.

It is well known that the ESR spectrum of isolated Cu^{2+} ion is radically different from that of the Cu^{2+}–Cu^{2+} ion pair [10]. At a certain distance between Cu^{2+} ions, the coupling of two unpaired electrons resulted in the splitting of the system into the triplet (s = 1) and singlet (s = 0) states. Only the triplet state is paramagnetic.

In the ESR spectrum of the $HoBa_2Cu_3O_y$ sample treated by CO at 673 K (Fig. 4), two groups of lines (A and A') in the fine structure of the spectrum (Δm_s = ±1 transition of the triplet state) corresponded to ion

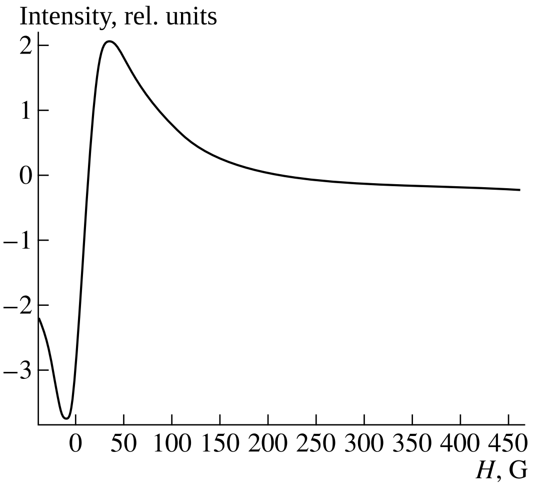

Fig. 1. Low-field absorption signal in the ESR spectrum of $HoBa_2Cu_3O_y$ phase measured at the temperature of liquid nitrogen.

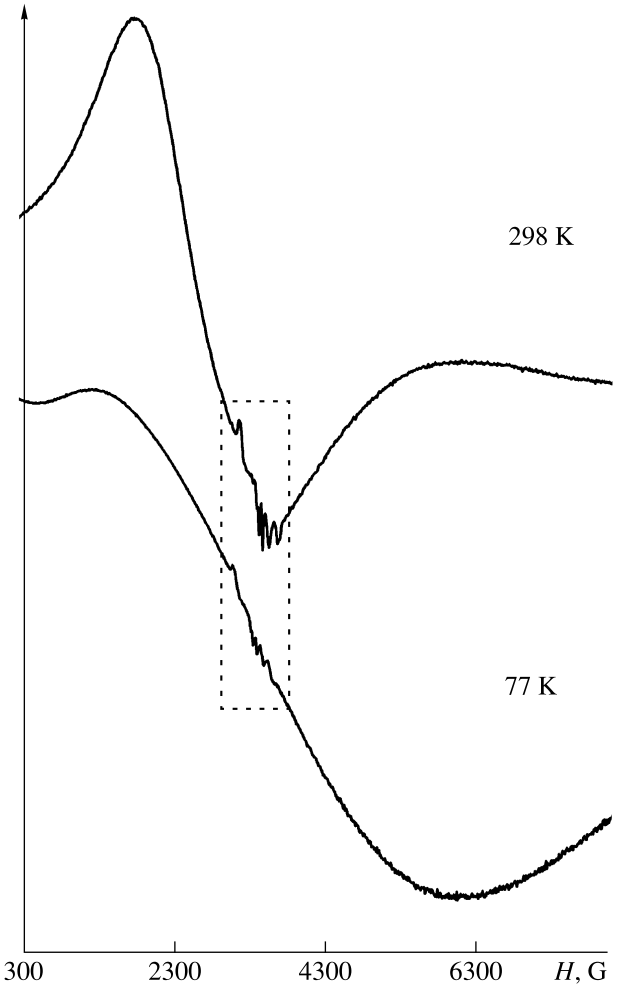

Fig. 2. ESR spectra of an $HoBa_2Cu_3O_y$ sample treated with CO (the spectra were recorded at 298 and 77 K).

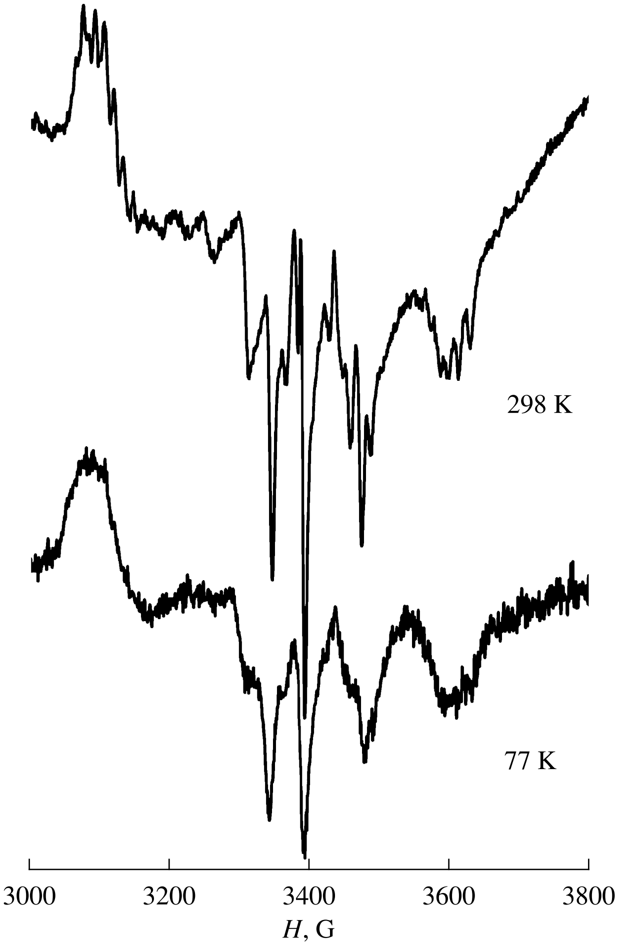

Fig. 3. The part of the ESR spectra enclosed by the dotted line in Fig. 2. The base line is subtracted from the spectra.

pairs (dimers). The hyperfine structure consisting of seven components with an intensity ratio of 1 : 2 : 3 : 4 : 3 : 2 : 1 resulted from the interaction of unpaired electron with two equivalent ^{63}Cu and ^{65}Cu nuclei ($I = 3/2$). The values of the g factor ($g_\perp$), the fine structure splitting constant ($d_\perp$), and the hfs splitting constant ($A_\perp$) were found by computer simulation of the experimental ESR spectrum (Table 1).

It is known that hfs $A_\perp$ constant for the pairs of equivalent ions is almost two times smaller than that for the initial paramagnetic ions, while the values of the g factor components ($g_\parallel$ and $g_\perp$) remain the same [10]. The comparison of ESR parameters of isolated (1)Cu^{2+} ions ($g_\perp = 2.042$, $A_\perp = 26$ G) and (1)Cu^{2+}–(1)Cu^{2+} dimers ($g_\perp = 2.042$, $A_\perp = 13$ G) in the sample treated at 673 K suggested that these isolated Cu^{2+} ions were responsible for the formation of copper ion pairs.[1] It can also be assumed that the spectrum of these ions in the sample subjected to mild treatment (CO, 473 K) transformed into the signal (1)Cu^{2+} (CO, 473 K) with unresolved hfs as a result of the enhancement of spin–spin interaction and an increase in the concentration. At the same time, the parallel component of the spectrum with $g_\parallel = 2.224$ and $g_\perp = 2.045$ appeared (Table 1, Fig. 4).

If the parameters of the ESR spectrum of ion pairs are available, it is possible to calculate the Cu^{2+}–Cu^{2+} distance either from the intensity ratio of the signals observed at $\Delta m_s = 2$ (forbidden transition) and those obtained at $\Delta m_s = 1$ (allowed transition) or, under certain restrictions, from the values of the g factors and the fine-structure parameters $d_\perp$ and $d_\parallel$ [10]. However, the components corresponding to the forbidden transition and to the parallel part of the allowed transition ($\Delta m_s = 1$) are virtually impossible to determine because of their low intensity and overlapping with an intense broad line. Therefore, this evaluation method is unacceptable in our case. Assuming that the splitting of levels in the zero field (D) is mainly governed by dipole–dipole interaction and neglecting the exchange component, one can follow another way of evaluating the distance r between copper ions in the pair. The above assumption is confirmed to some extent by the retention of the general view of the central part of the ESR spectrum when the recording temperature decreased from 298 to 77 K (see Fig. 3). In this approximation and using the formula [11] for the evaluation of D

$$|D| = 10^{20}\frac{(2g_\parallel^2 + g_\perp^2)}{2r^3}\beta^2$$

(where D is in joules; r is in nanometers; and the Bohr magneton β is in m$^{2.5}$ kg$^{0.5}$ s^{-1} [12]) and the relationship between D and parameters of ESR spectrum is

$$D = d_\perp g_\perp \beta$$

(in the latter equation, Bohr magneton is in J/G), we obtained that $r = 0.40 \pm 0.03$ nm.

According to published data, the distance r in the Cu^{2+}–Cu^{2+} pair depends on the nature of a sample. Thus, it equals 0.34 nm in the Cu^{2+}/CeO$_2$ system. In the Cu^{2+}/ThO$_2$ system, r was found to be 0.51 nm [10]. From crystallographic data, it follows that this distance may be equal to 0.34 nm in our system [4]. With the above assumptions, this value is in good agreement with an obtained value of 0.40 nm. Thus, Cu^{2+}–Cu^{2+} ion pairs may belong to the defective structure of HoBa$_2$Cu$_3$O$_y$.

The central part in the ESR spectrum of the HoBa$_2$Cu$_3$O$_y$ sample (CO, 673 K) exhibited the lines of isolated Cu^{2+} ions of another type (Table 1, Fig. 4) and, probably, the lines of defective and contaminant sites. The identification of these paramagnetic sites was complicated by the low intensities and overlapping of lines. Comparison of the parameters of experimental ESR

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[1] Numbers 1, 2, and 3 denote different types of copper isolated ions in the reduced samples. It is likely that these ions differ in the symmetry of oxygen environment. The parameters of their spectra are presented in Table 1.

spectra for isolated copper ions with the published data allowed us to assign the above lines to Cu^{2+} ions in octahedral coordination with a different degree of tetragonal distortion. Because of the complex shape of the ESR spectrum, it was difficult to precisely determine the concentration of isolated Cu^{2+} ions from the experimental data; however, the order of magnitude can be evaluated: it is ~5 × 10^{16} spin/g and corresponds to 0.01% of the total copper concentration in the sample.

The parameters of the broad line in the ESR spectrum (see Fig. 2) are presented in Table 2. With a decrease in the ESR recording temperature, the width of the broad line in the spectrum significantly enlarged, the intensity increased by more than an order of magnitude, and the value of the *g* factor changed. A similar spectrum was observed in the reduction of the Cu^{2+}/CeO_2 system by hydrogen [13]. This spectrum was interpreted assuming either strong exchange interaction or ferromagnetic interaction.

The emergence of such a signal pointed to the formation of a concentrated magnetic phase. Currently [14], such hyperexchange is believed to be feasible at certain interatomic distances between paramagnetic ions; apparently, this is the case in the system under consideration. Under mild conditions of treatment (473 K), the contribution of a broad line to the ESR spectrum was insignificant, because the regions with strong exchange interaction only began to arise. The structure of the sample was highly defective, and the concentration of oxygen vacancies was large in it. Under more severe conditions of reductive treatment (673 K), the contribution of the concentrated magnetic phase to the ESR spectrum became dominant. It is interesting that even when the exchange interaction was strong (in the $HoBa_2Cu_3O_y$ sample reduced by CO at 673 K), the regions in which isolated Cu^{2+} ions and Cu^{2+}–Cu^{2+} dimers were localized in a diamagnetic matrix were retained.

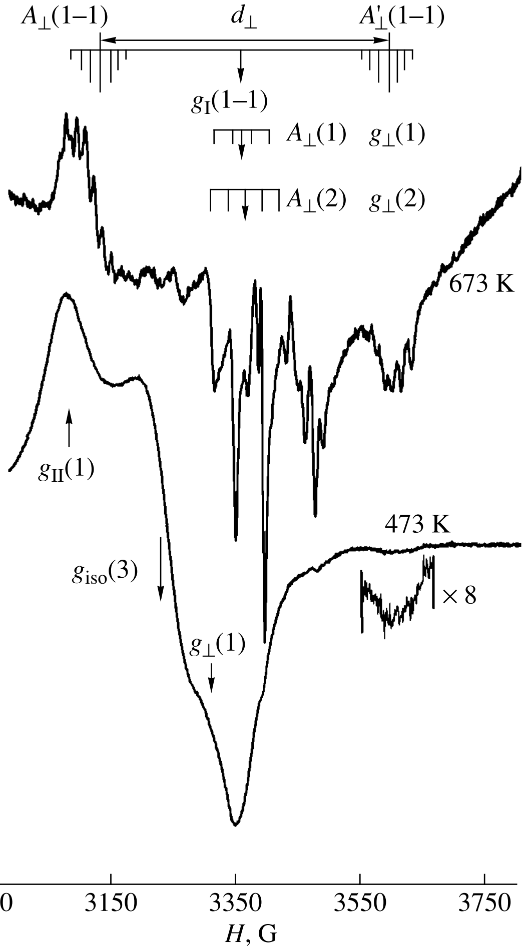

Fig. 4. ESR spectra of the $HoBa_2Cu_3O_y$ sample treated with CO at 673 and 473 K. Schematic diagram presents the transitions of the fine and hyperfine structures of Cu^{2+} ions and Cu^{2+}–Cu^{2+} pairs.

The results of ESR studies of the $NdBa_2Cu_3O_y$ phase are in complete agreement with the correspond-

Table 1. Parameters of the ESR spectra of Cu^{2+} ions and Cu^{2+}–Cu^{2+} pairs in the $HoBa_2Cu_3O_y$ sample exposed to CO atmosphere at 473 and 673 K (spectra were recorded at 298 K)

Treatment conditions	Spectrum	$g_\parallel$	$g_\perp$	*A*, G	g_{iso}	$d_\perp$, G
CO, 473 K	$(3)Cu^{2+}$	–	–	–	2.110	–
CO, 473 K	$(1)Cu^{2+}$	2.224	2.045	–	2.105	–
CO, 473 K	$(1)Cu^{2+}$–$(1)Cu^{2+}$ ($\Delta m = 1$)	–	2.042	–	–	470
CO, 673 K	$(2)Cu^{2+}$	–	2.040	37	–	–
CO, 673 K	$(1)Cu^{2+}$	–	2.042	26	–	–
CO, 673 K	$(1)Cu^{2+}$–$(1)Cu^{2+}$ ($\Delta m = 1$)	–	2.042	13	–	470
Computer-simulated spectrum	Cu^{2+}–Cu^{2+}	2.224	2.042	13	2.100	470

Table 2. Parameters of the ESR spectra of the $HoBa_2Cu_3O_y$ sample confirming strong exchange interaction

Treatment conditions	ESR recording temperature, K	g Factor	ΔH, G
CO, 473 K	298	2.7	1200
	77	~2	~4700
CO, 673 K	298	2.7	1780
	77	2.0	4700

ing data obtained for $HoBa_2Cu_3O_y$ complex oxide. The identity of the structure of ESR spectra and the closeness of their parameters led us to conclude that the changes caused by the reductive treatment of samples in a CO atmosphere observed in the present work are typical of complex oxides of $RBa_2Cu_3O_y$ composition.

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