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State of Atoms and Interatomic Interactions in Complex Perovskite-Like Oxides:

XIV.[1] Interatomic Interactions and Local Environment of Paramagnetic Atoms in Complex Cuprates by Mössbauer Spectroscopy

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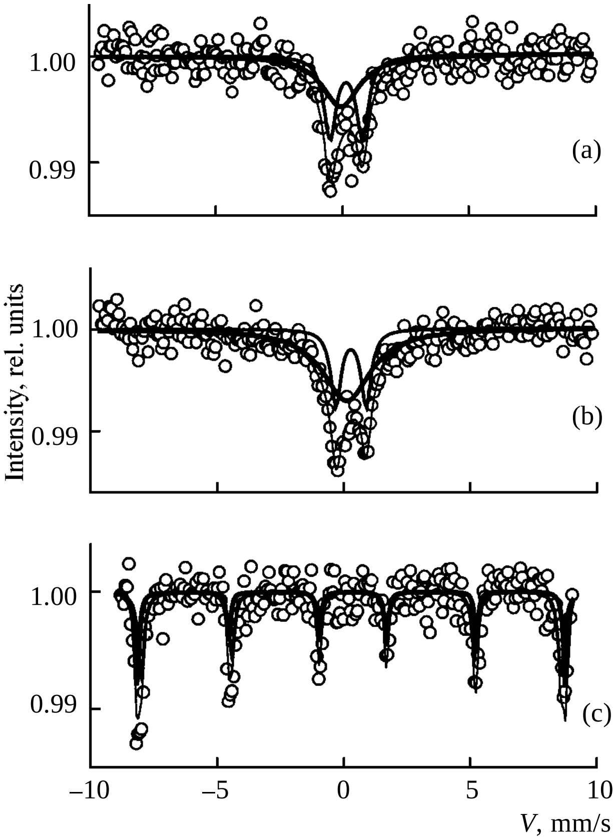
Abstract—The Mössbauer study of strontium- and barium-containing solid solutions on the basis of superconducting cuprates, including ^{57}Fe as Mössbauer probe, allowed estimation of the size of nanoclusters formed by paramagnetic atoms.

Mössbauer spectroscopy is a highly informative microscopic method that allows determination of the state of Mössbauer atoms and their local environment. The "Mössbauer probe" technique has been used to success for studying the state of copper atoms in iron-doped superconducting cuprates [2, 3]. In iron-doped complex oxides La_2CuO_4 and $La_{1.85}Sr(Ba)_{0.15}CuO_4$ iron occupies the same octahedral positions as copper, since Cu^{2+} and Fe^{3+} have close radii. Introduction of small amounts of iron (0.5–1 mol %) into cuprates has almost no effect on magnetic interactions. The antiferromagnetic transition point (T_n) of $La_2Cu_{0.95} \cdot Fe_{0.05}O_4$ is almost the same as that of individual La_2CuO_4 (318 and 320 K, respectively [2]); therefore, iron is a suitable Mössbauer probe for local environment studies on copper atoms.

Unfortunately, there have been no systematic Mössbauer studies on cuprates, and there is still no commonly accepted notion of the state of copper atoms, and the question of local distortions of crystal structure, e.g. whether there are low-temperature magnetically ordered regions in $La_{2-x}Sr(Ba)_xCuO_4$, is under discussion [3–5]. The oxide systems $La_{2-x}Sr_x \cdot CuO_4$ and $La_{2-x}BaxCuO_4$ have been studied by different authors, but the Mössbauer spectra of these systems have not been compared.

The present work deals with the Mössbauer spectra of the complex oxide $La_{1.85}Sr_{0.15}FeO_4$ and of solid solutions on the basis of $La_{1.85}Sr(Ba)_{0.15}CuO_4$, containing 1 mol% of ^{57}Fe. The spectra are given in the figure. The solid solutions all contained 10 mol% of



Mössbauer spectra of samples (a) **III**, (b) **II**, and (c) **I**.

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[1] For communication XIII, see [1].

Parameters of the Mössbauer spectra of samples **I**–**III**

Sample no.	Pattern, hyperfine structure	*S*, %	δ, mm/s	Linewidth	Δ, mm/s	H_{ef}, kOe
I	Sextet 1	46.2	0.350 ± 0.008		0.071 ± 0.016	526.264 ± 0.030
	Sextet 2	53.8	0.341 ± 0.012		0.097 ± 0.024	515.301 ± 0.059
II	Doublet	30.5	0.317 ± 0.018	0.483 ± 0.098	1.203 ± 0.043	
	Singlet	69.5	0.148 ± 0.064	2.310 ± 0.213		
III	Doublet	49.4	0.167 ± 0.025	0.574 ± 0.143	1.291 ± 0.084	
	Singlet	50.6	–0.035 ± 0.112	1.808 ± 0.406		

a paramagnetic component (Cu + Fe). The diamagnetic solvent for solutions on the basis of $La_{1.85}Sr_{0.15}\cdot CuO_4$ and $La_{1.85}Ba_{0.15}CuO_4$ were $LaSrAlO_4$ and $LaBaAlO_4$, respectively. The starting materials for the synthesis were La_2O_3, $SrCO_3$ ($BaCO_3$), CuO, Al_2O_3, and $^{57}FeC_2O_4\cdot 2H_2O$. Our original synthetic procedure for cuprates has been described in [6]. Solid solutions containing ^{57}Fe were prepared by a modified ceramic procedure. The X-ray phase analyses and magnetic susceptibilities showed that the resulting samples are the complex oxide $La_{1.85}Sr_{0.15}FeO_4$ (**I**) and homogeneous single-phase solid solutions 0.1 $(La_{1.85}Sr_{0.15}\cdot Cu_{0.9}Fe_{0.1}O_4)$–0.9($LaSrAlO_4$) (**II**) and 0.1 $(La_{1.85}\cdot Ba_{0.15}Cu_{0.9}Fe_{0.1}O_4)$–0.9($LaBaAlO_4$) (**III**).

The strontium-containing solid solutions has the layered K_2NiF_4-type structure ($LaSrAlO_4$). In this structure Cu (Fe) atoms reside in tetragonally distorted oxygen octahedra. The barium-containing solid solutions has the β-K_2SO_4-type structure (solvent $LaBaAlO_4$), with paramagnetic atoms in tetrahedral oxygen environment. Thus, introduction of various substituents in the La sublattice gives rise to various crystallographic environments of the paramagnetic atom: octahedron or tetrahedron of oxygen atoms.

The Mössbauer spectrum of sample **I** was measured with the aim to assess the behavior of the Mössbauer probe in the crystal lattice in study. The spectrum is approximated by two sextets with close isomer shifts relative to α-Fe (δ) and quadrupole splittings (Δ). The difference in the H_{ef} values is larger: 526 and 515 kOe. The areas (*S*) of the corresponding sextets are 46.2:53.8. The spectral parameters are given in the table. The δ values (0.35 mm/s) fall in the range of the isomer shifts of different spin states of iron. These values are most close to those for Fe(III) (*S* 3/2), Fe(II) (*S* 1), and Fe(III) (*S* 5/2) [7]. Intermediate spin states may arise when the local environment of the paramagnetic atom is sufficiently strongly distorted. Parameters of sextet 2 better agree with this assumption. Sextet 1 may relate to Fe(III) atoms in a less distorted octahedron. The presence of two states of iron can be associated with a complex character of *d*-electron density distribution in the magnetically concentrated system, resulting in appearance of intermediate spin states. The spectral assignment is confirmed by the fact that the two sextets has close but different H_{ef} values indicative of the presence of two magnetically ordered iron sublattices.

In iron-doped (1 mol %) solid solutions no inter-sublattice magnetic bond should be observed, and in the absence of magnetic splitting iron atoms can be considered as Mössbauer probe.

Actually, unlike the spectrum of the individual oxide, the spectrum of the lanthanum cuprate–strontium solid solution containing 9 mol % of copper and 1 mol% of ^{57}Fe (sample **II**) shows no magnetic splitting. The spectrum of sample **II** is approximated by a doublet and a singlet with the area ratio *S* : *S* 30.5 : 69.5 (to the Mössbauer coefficient). The linewidths and the δ values for the doublet and singlet are much different (see table). The isomer shift for the doublet (0.32 ± 0.02 mm/s) is typical of Fe(III). The larger qudrupole splitting (1.20 ± 0.04 mm/s) suggests that a third of positions occupied by Fe and Cu atoms has a strongly distorted local environment. The singlet signal is difficult to interpret because of the large linewidth (2.3 ± 0.2 mm/s), which is an order of magnitude larger than the instrumental width, and the low isomer shift δ. The values of δ give grounds to state that two third of positions are occupied by iron in a state close to metallic or in the state of strong exchange (electron delocalization like in the metal). Obviously, in the oxide system the second case is realized.

Thus, directed synthesis followed by Mössbauer examination of solid solutions allows experimental separation of the contributions in the magnetic properties of exchanging paramagnetic atoms and of individual Fe(III) atoms in a strongly delocalized oxygen environment.

To assess the effect of the nature of local crystal lattice distortion on the state of paramagnetic atoms, we studied solid solutions with part of La atoms substituted by Ba (sample **III**). Here metal atoms (Cu or Fe) have a tetrahedral oxygen environment (rather than octahedral as in the above-described strontium-containing systems.

The Mössbauer spectrum of sample **III** (see table), too, is approximated by a singlet and a doublet ($S:S = 50.6:49.4$). Like in the above case, the doublet can be associated both with Fe(III) in distorted oxygen environment and with strongly exchanging iron atoms. The β-K_2SO_4 structure is distorted stronger than K_2NiF_4, as evidenced by larger linewidths and quadrupole splitting for the doublet (compared with the strontium-containing system). Larger Mössbauer linewidths are commonly interpreted in terms of variation in the local environment of metal sites, i.e., here, the parameters of the Mössbauer spectrum reveal inhomogeneity of the crystallographic environment of the paramagnetic atom. The singlet has reduced linewidth and δ. The isomer shift tends to δ values typical of Fe(II), implying stronger electron density localization near the magnetic atom.

Based on the area ratio of the doublet and singlet, we can construct a model of the arrangement of iron atoms in the lattice, which is directly related to the arrangement of copper atoms. In constructing such a model, one should assume a planar structure of the cluster and take account of the structural features of the lattices. No interplanar interaction takes place. Within the plane containing Al, Cu, and Fe atoms, there are two kinds of Cu and Fe atoms: exchanging and not exchanging with a strongly distorted environment. The paramagnetic atoms are arranged in a planar cluster, the first reside inside the cluster and the second form its outer layer. The ratio of these two kinds of atoms, measured (to the Mössbauer coefficient) by the area ratio of the siglet and doublet (see table), shows that the fraction of the outer atoms is 3 : 5 with Sr and Ba, respectively, of the total number, i.e. the number of atoms in the cluster is limited, and, consequently, the size of clusters relates to the nanometer range. On the assumption of square nanoclusters, their size can be estimated at ~3.8 nm for the strontium systems and at ~2 nm for the barium systems.

The above results provide convincing evidence for the two states of Cu and Fe atoms in complex cuprates. Partly these atoms, as follows from the Mössbauer spectra, is in the exchange-coupled state, i.e. they are involved in local nanoaggregates. The high degree of electron delocalization in such systems confirms our earlier hypothesis as to the existence of exciton-forming nanoclusters in superconconducting systems.

Exciton-like interactions in cuprates replace the usual ferrimagnetic interaction of iron atoms in the isomorphous system containing no copper.

EXPERIMENTAL

The magnetic susceptibilities were measured by the Faraday method at 77–400 K. The error was no higher than 1–2%. The unit cell parameters were determined from the diffraction patterns measured on a DRF-2.0 instrument (CuK_α radiation) with an accuracy of ±0.005Å for *a* and *b* and ±0.01 Å for *c*.

The Mössbauer spectra were measured on a Wissel spectrometer in the constant accelerations mode. The measurements were performed at room temperature. The source was ^{57}Co–Rh, activity 20 mCi. The spectra were treated by the least-squares method with Newton linearization.

The solid solutions $0.1(La_{1.85}Sr_{0.15}Cu_{0.9}Fe_{0.1}O_4)$–$0.9(LaSrAlO_4)$ and $0.1(La_{1.85}Ba_{0.15}Cu_{0.9}Fe_{0.1}O_4)$–$0.9(LaBaAlO_4)$, containing 1 mol % of ^{57}Fe, were synthesized by the nitrate decomposition procedure. Calculated amounts of chemically pure grade La_2O_3, $SrCO_3$, $(BaCO_3)$, CuO, Al_2O_3, and ^{57}Fe oxalate were mixed, the mixture was evaporated and heated at 750 K until nitrogen oxides had been completely removed. The residue was ground, pressed in pellets, and calcined for 30 h at 1573 K and then for 10 h at 1673 K. The optimal calcination time was determined by the results of X-ray phase analysis and magnetic susceptibility mesurements.

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