

CHARACTERIZATION OF TRANSITION METAL-CONTAINING OXIDE SYSTEMS BY MÖSSBAUER SPECTROSCOPY

ZOLTÁN HOMONNAY, ERNŐ KUZMANN*, ZOLTÁN NÉMETH, ZOLTÁN KLENCÁSÁR*, SÁNDOR I. NAGY, ATTILA VÉRTES

Department of Nuclear Chemistry, Eötvös Loránd University, Budapest 1518 P.O.Box 32, Hungary

**Research Group for Nuclear Methods in Structural Chemistry, Hungarian Academy of Sciences, Budapest 1518 P.O.Box 32, Hungary*

E-mail: homonnay@ludens.elte.hu

Submitted September 17, 2004; accepted October 25, 2004

Keywords: Mössbauer spectroscopy, High temperature superconductors, Colossal magnetoresistance, Isomer shift, Metallicity

High-temperature (high- T_c) superconductors and colossal magnetoresistant (CMR) materials belong to the most promising materials of the past 2-3 decades for technical applications. Most of them are oxides and the crucial element which determines their useful physical properties is often a transition metal (Cu, Co, Fe, Mn). ^{57}Fe Mössbauer Spectroscopy can be used to characterize the electronic and structural properties of transition metal-containing oxides by providing information on the local electronic structure of the lattice site where the Mössbauer probe is accommodated. By reviewing several Mössbauer studies, it is demonstrated how the layered (2D) electronic structure of high- T_c superconductors can be deduced from the analysis of the Mössbauer isomer shift and quadrupole splitting. We also show how the Mössbauer isomer shift indicates metallicity of the ferromagnetic phase in the CMR material $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$.

INTRODUCTION

Mössbauer Spectroscopy has been extensively used to characterize transition metal compounds in the past decades since the most conveniently measurable Mössbauer nuclide is a transition metal: iron. When iron is a natural constituent element of a material, interpretation of the ^{57}Fe Mössbauer spectra is rather straightforward in a sense that the information obtained is characteristic for the host compound. Iron may be substituted for other transition metals in compounds containing no iron, and then the ^{57}Fe Mössbauer probe gives information on the hyperfine interactions at the lattice site where the probe is accommodated. In these cases, careful considerations are needed to explain the observed Mössbauer parameters and their relevance to the physical and chemical properties of the host compound. Transition metal-containing oxides are of particular importance due to some unique electronic and magnetic properties such as high-temperature superconductivity [1] and colossal magnetoresistance [2]. In these cases electron mobility is usually high enough to get rid of the so called "after effects" which perturb emission Mössbauer spectra, due to the radioactive decay of ^{57}Co , the mother nuclide of ^{57}Fe . Thus both ^{57}Co and ^{57}Fe can be readily used to probe lattice sites where these elements can be accommodated.

In this paper, we demonstrate the application of both techniques on two classes of materials which have no natural iron content in general.

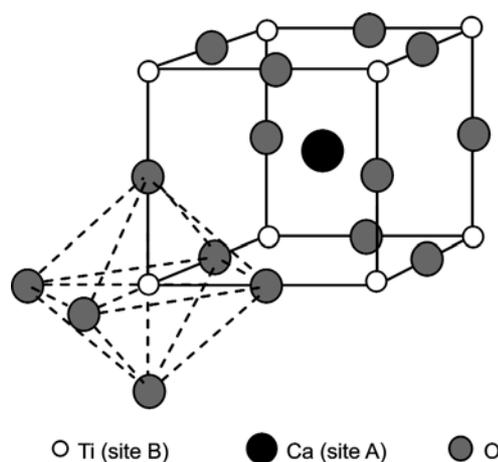


Figure 1. The unit cell of perovskite with indicating the coordination environment of site B.

Paper presented at the conference Solid State Chemistry 2004, Prague, September 13 -17, 2004.

Characterization of high- T_c superconductor cuprates with ^{57}Fe -Mössbauer Spectroscopy

High-temperature cuprate superconductors which have mostly orthorhombic or tetragonal structure derived from the ABO_3 type cubic perovskite CaTiO_3 (see figure 1) do not contain iron, however, copper can be readily substituted by iron or cobalt for a Mössbauer study. Such substitution raises questions of where and how Fe/Co is accommodated in the lattice. Although an absolute answer cannot be given (there is no independent method to check it), the large number of Mössbauer works published so far allow us to draw important conclusions on the electronic structure of these mixed oxide systems.

The problem of substitution may be addressed through the general structural features of high- T_c cuprates. Practically all known structures (unit cells) can be built up by combining the perovskite structure with rock salt type and/or fluorite type layers. The pure cubic perovskite structure has not yet been found superconducting, so the insertion of various layers and thereby enforcing an overall layered structure seems to be a

prerequisite for superconductivity. The layers created in this way have different functions which is demonstrated in a rather convenient nomenclature suggested by Shaked et al. [3]. According to this nomenclature, the "four number naming scheme", the lattice of high- T_c superconductors may be built up from insulating layers, spacing layers, separating layers and conducting layers, and the number of such layers in a unit cell (normalized to the smallest integers) is shown in the notation in the quoted sequence. For example, the compound $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ belongs to the "1223" structure and contains one [TlO] insulating layer, two [BaO] spacing layers, two [Ca] separating layers and three conducting [CuO₂] layers. The unit cell is shown in figure 2. It is common to start the name with the element which forms the insulating layer, so a more informative name for the above compound is Tl1223. (This rather simple naming system may not be used universally; for more complicated cases see the quoted literature.) Since high- T_c cuprates only contain one transition metal, Cu, it is generally accepted that when Fe or Co is introduced for a Mössbauer study, it will substitute for Cu.

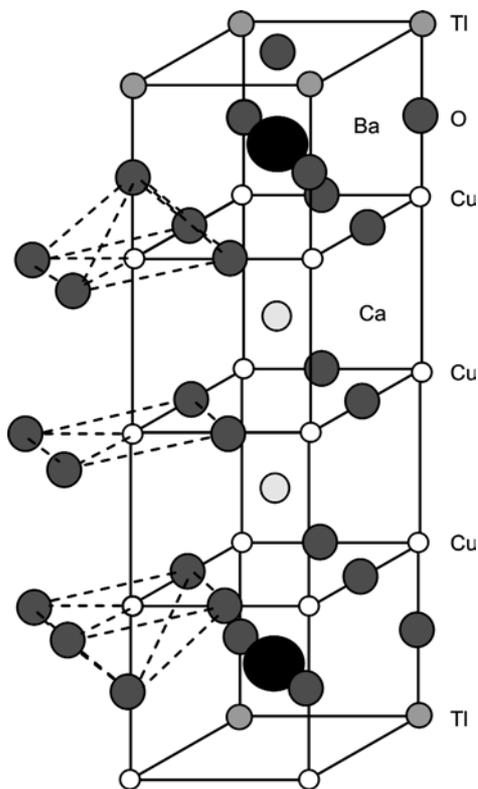


Figure 2. The idealized unit cell of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$, i.e. Tl1223 showing the oxygen coordination environments of Cu.

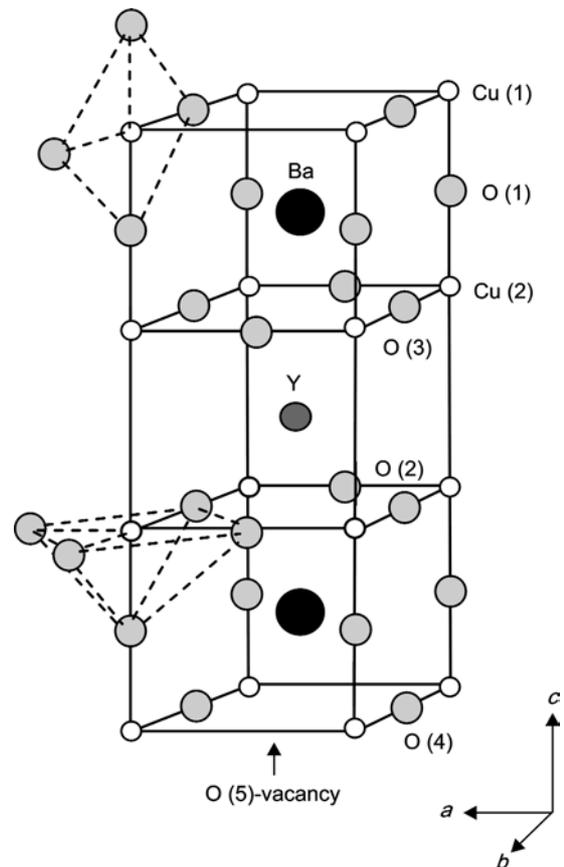


Figure 3. The unit cell of the Cu1212 type $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

For Mössbauer Spectroscopy, it is very interesting that Cu is not always found in the conducting/superconducting [CuO₂] layers, but sometimes also in insulating layers. In fact, the most studied 90 K superconductor YBa₂Cu₃O_{7-δ} belongs to this class of compounds and partly this is the reason why it caused so much headache for many researchers. Its name in the four number naming system is Cu1212, thus one of the three copper atoms (Cu(1)) in the unit cell is in an insulating layer and the other two (Cu(2)) are in conducting layers (figure 3). Looking back to the history of high-*T_c* research, it was a rather unlucky situation that this relatively simple compound was a lot more complicated for Mössbauer Spectroscopy than several other compounds with much larger unit cells and more contributing elements.

A Mössbauer probe in a host lattice gives information on the local hyperfine interactions. Namely, the Mössbauer isomer shift (δ) characterizes the local elec-

tron density at the Mössbauer nucleus, the quadrupole splitting (Δ) is connected with the non-spherical electron density distribution around the Mössbauer nucleus, and the magnetic hyperfine splitting indicates any magnetic field (as characterised by the flux density *B*) sensed by the Mössbauer nucleus. These measured parameters should be characteristic of the host compound which is not trivial in an impurity Mössbauer study. However, reviewing a large number of studies and comparing Mössbauer data obtained on various but related cuprate structures may allow reliable conclusions on the electronic structure of high-*T_c* compounds. The Mössbauer dopant can be either ⁵⁷Fe or ⁵⁷Co. ⁵⁷Co is the mother element of ⁵⁷Fe, namely, the generator of the excited ⁵⁷Fe nuclei at the Co-substituted sites of the lattice in an "emission Mössbauer experiment".

The intense research on high-*T_c* superconductors has shown that for practical applications the most promising materials are Tl- and Bi-containing compounds which are

Table 1. Mössbauer data obtained for selected high-*T_c* cuprates at room temperature. The applied Mössbauer dopant concentration (⁵⁷Fe) in the cited studies was mostly around 1% relative to the Cu-content except in the ⁵⁷Co emission experiment (100 ppm ⁵⁷Co). δ : isomer shift relative to α -Fe; Δ : quadrupole splitting.

Compound (Mössbauer impurity nuclide at Cu sites)	Four-number symbol	δ (mm/s)	Δ (mm/s)	rel. amount (%)	coordination environment of Fe at the substituted Cu-site	Ref.
(Tl _{0.57} Pb _{0.4})(Ba _{0.2} Sr _{0.8}) ₂ Ca ₂ Cu ₃ O _y (⁵⁷ Fe)	(Tl.Pb)1223	0.24	1.36	72.1	square planar	
		0.25	0.93	27.9	pyramidal	
(Tl _{0.57} Pb _{0.4})(Ba _{0.2} Sr _{0.8}) ₂ Ca ₂ Cu ₃ O _y (⁵⁷ Fe) (stoichiometry of starting material)	(Tl.Pb)1223 with considerable (Tl.Pb)1212 impurity	0.25	1.42	73.8	square planar	[4]
		0.25	0.85	26.2	pyramidal	
(Tl _{0.57} Pb _{0.4})(Ba _{0.2} Sr _{0.8}) ₂ Ca ₂ Cu ₃ O _y (⁵⁷ Co)	(Tl.Pb)1223	0.23	1.50	100	square planar	[5]
(Hg _{0.3} Pb _{0.4})(Ba _{0.2} Sr _{0.8}) ₂ Ca ₂ Cu ₃ O _y (⁵⁷ Fe)	(Hg.Pb)1223	0.22	1.42	69.8	square planar	[6]
		0.24	0.52	30.2	pyramidal	
		0.26	1.48	36	square planar	
(Tl _{0.5} Pb _{0.5})(Ba _{0.2} Sr _{0.8}) ₂ Ca ₂ Cu ₃ O _y (⁵⁷ Fe - 1% rel. to Cu)*	(Tl.Pb)1223	0.24	1.17	31	pyramidal	[7]
		0.21	0.51	32	square planar	
					or pyramidal, with one additional oxygen	
Bi ₂ Sr ₂ CaCu ₂ O _{8+d} (⁵⁷ Fe)	Bi2212	0.23-0.25	0.65-0.78	-	octahedral	[8]
		0.23-0.25	1.73-1.84	-	pyramidal	
(Bi _{0.93} Pb _{0.17}) ₂ Sr _{1.9} Ca _{2.05} Cu ₃ O _y (⁵⁷ Fe)	(Bi.Pb)2223	0.23	1.18	68.3	square planar	[9]
		0.27	0.80	31.7	pyramidal	
(Tl _{0.74} Bi _{0.25})(Ba _{0.2} Sr _{0.8}) ₂ Ca ₂ Cu ₃ O _y (⁵⁷ Fe)	(Tl.Bi)2223	0.25	1.64	56.3	square planar	[9]
		0.22	0.68	43.7	pyramidal	
La ₂ SrCu ₂ O ₆ (⁵⁷ Fe)	0212	0.24	0.31	100	octahedral	
La _{1.6} Sr _{0.4} CaCu ₂ O ₆ (⁵⁷ Fe)	0212	0.22-0.26	~0.3	**	octahedral	[10]
		0.22-0.26	~1.0	**	pyramidal	
La _{1.8} Sr _{0.2} Cu _{0.4} (⁵⁷ Fe)	0201	0.27	1.49	~100	octahedral	[11]

* Data for 2% and 3% Fe were also reported (very similar).

** Comparable amounts; octahedral positions became more abundant upon oxygenation treatment.

very hard to synthesize in a phase-pure form (note that purity proved to be not very important for good superconducting properties!) due to their large unit cell and thus a readiness to decompose to closely related structures during the synthesis or further heat treatments. Thus the early Mössbauer data on such compounds were rather confuse and discouraging. More careful investigations were carried out later when the hope for a fast solution of the puzzle of how high- T_c superconductivity actually works was clearly over. Table 1 shows selected Mössbauer data obtained for various compounds which contain Cu in different oxygen coordination environments from square planar to square pyramidal to octahedral. In all of these compounds, Cu positions are solely in conducting sheets. Since the suggested assignments of Mössbauer doublets to possible oxygen coordination environments do not always meet the available coordination environments of Cu sites in that particular structure, the latter are listed in table 2.

Table 2. Oxygen coordination environments for Cu in some high- T_c cuprates.

four-number symbol	<i>c</i> -axis oriented			other:
	square planar	pyramidal	octahedral	
0201	No	No	Yes	-
0212	No	Yes	No	-
(Tl,Bi...)1223	Yes	Yes	No	-
(Tl,Bi...)1212	No	Yes	No	-
(Tl,Bi...)2212	No	Yes	No	-
Cu1212	No	Yes	No	Cu(1)*
(Tl,Bi...)2223	Yes	Yes	No	-

* in insulating layer: square planar in *bc* plane or linear along the *c* axis

The following facts are remarkable in these tables:

1. The number of different Mössbauer microenvironments (ligand environments) observed can be either lower or higher than that of the available Cu-environments in the cuprate host material. For example, in the ^{57}Co study of the Tl1223 system [5], although pyramidal and square planar environments are readily available, the Mössbauer spectrum contained only one doublet which was assigned to the square planar environment. Note that in parallel ^{57}Fe Mössbauer studies [4] both environments were found. This difference was interpreted on the basis of the different chemical behavior of Fe and Co, namely in an emission experiment, the Co dopant prefers lower coordination number than Fe. At the same time, in practically the same material, but obviously under somewhat different conditions (oxygenation) not only a square planar and a pyramidal environment but also a third one involving an extra oxygen atom were found (transforming pyramidal to octahedral and square planar to pyrami-

dal) [7]. Furthermore, $\text{La}_{1.6}\text{Sr}_{0.4}\text{CaCu}_2\text{O}_6$ contains only pyramidal Cu positions but the Mössbauer spectrum showed two doublets, assigned to pyramidal and octahedral positions [10]. We note here that there are several other literature data where even more components are reported in the Mössbauer spectra, however, we have selected examples where phase purity was well demonstrated or impurity phases were convincingly identified.

- The assignments of the Mössbauer doublets to Cu-environments may seem to be inconsequent, because the same (or very similar) quadrupole splittings are often assigned to different ligand environments. The only systematic rule is that within one spectrum the quadrupole splitting should decrease in the sequence: square planar > pyramidal > octahedral. In most cases, however, this inconsequency can be readily explained by different lattice constants in the various cuprate structures.
- Although it would be reasonable, there is no substantial preference of the Mössbauer dopant for ligand environments with higher coordination number. On the contrary, in some cases lower coordination is preferred [4,6,9].
- The most striking fact of these data is the narrow range of the isomer shifts we find. All listed isomer shifts fall between 0.21 and 0.27 mm/s (relative to $\alpha\text{-Fe}$).

The Mössbauer isomer shift directly depends on the electron density at the nucleus where mostly *s* electrons can be found with non-zero probability (this is a good approximation for ^{57}Fe but not necessarily for much heavier elements). Nevertheless, due to the electron-electron interaction, the Fe3d density affects the *s* density in the nucleus, namely, if the 3d density increases, the *s* density in the nucleus decreases and this results in an increase of the isomer shift [11]. Thus the isomer shift is sensitive to the valence state and not only to this but to much finer electron-density changes in the valence shell of the Mössbauer atom.

The typical isomer shift range for (high spin) Fe^{3+} compounds is roughly 0.2 to 0.6 mm/s [12]. To learn something about the electron density at the Cu-sites in the superconducting cuprates one may compare the observed values with isomer shifts found in the closest possible relatives of the cuprates. There are several iron-based perovskites with known Mössbauer parameters. For example, the defect perovskite $\text{Sr}_7\text{Fe}_2\text{O}_5$ which is isomorphous with brownmillerite and thus contains alternating layers of tetrahedrally and octahedrally coordinated Fe^{3+} , has two distinct ionic Fe^{3+} sites with isomer shifts 0.37 mm/s (octahedral oxygen coordination) and 0.17 mm/s (tetrahedral oxygen coordination) [13]. Note that both iron states are Fe^{3+} and the lower

isomer shift for the tetrahedral positions is due to the lower coordination number: instead of six, only four O²⁻ ions donate electrons to the 3d shell of iron (ionic state with some covalency), thus a lower 3d density results in a lower isomer shift. SrFeO₃ is a much more complicated case; it is metallic, and formally contains Fe⁴⁺. Its synthesis is difficult; with slight oxygen deficiency, the observed isomer shifts are in a range of -0.06 to 0.36 mm/s indicating ionic Fe³⁺ and fractional valence states between +3 and +4 due to delocalized electrons [14]. Note that the completely ionic Fe⁴⁺ would have an isomer shift around -0.1 mm/s.

From the Mössbauer data of the high-*T_c* cuprates it can be seen that the isomer shift is lower than that for a basically ionic octahedrally coordinated Fe³⁺. The decrease may be due to either a lower coordination number or a higher oxidation state. The latter is not likely because Fe substitutes bivalent or trivalent Cu, so a formally tetravalent Fe would destabilize the structure with its too high ionic charge. Thus we are left with lower coordination number, but this explanation is also untenable because the isomer shift is practically independent on the coordination number (table 1). There are only small variations, sometimes even with negative correlation, i.e., lower coordination with higher isomer shift.

It is known that in the investigated superconductor cuprates, iron (or cobalt) substitutes for copper in the conducting planes, therefore they become part of a delocalized electron system. Now it is very reasonable to assume that the initially ionic Fe³⁺ state (this is expected because synthesis and doping is carried out under highly oxidative conditions, i.e. in O₂ flow at 800-900°C) is forced to donate electrons to the delocalized system, and the resultant 3d density loss is responsible for the reduced isomer shift (from a level of ~0.4 mm/s). In other words, the primary determining factor for the isomer shift is the metallicity of the [CuO₂] sheets.

The coordination environment of the Mössbauer dopants in the investigated cases has a common feature: the sheet oxygens are always there. Therefore, the fact that the isomer shift is independent on the coordination number really means that it is independent on the presence or absence of the apical oxygens (either naturally occurring in the lattice or brought by the dopant as extra oxygen). This further supports the determining role of the conducting planes in the electronic structure, and leads us to an important conclusion. If the apical oxygens do not contribute to the 3d electron density of Fe (and inherently of Cu), the chemical bond between them cannot be metallic/covalent but rather ideally ionic. This readily explains that these apical oxygens do not affect the isomer shift but they do affect the quadrupole splittings. One may add that the surprising absence of site preference of the Mössbauer dopant (Fe) for a par-

ticular site also supports this. It appears as if there was no bonding between the Mössbauer probe and the apical oxygen, it acts as an independent Coulomb charge.

Our findings thus clearly demonstrate that the structural diagrams of the unit cells showing pyramidal and octahedral Cu positions in various structures are misleading. The real ("effective") coordination number for Cu is always 4, and the apical oxygens "chemically" belong to the neighboring sheets.

There have been attempts to calculate Mössbauer quadrupole splittings for some of these cuprates. For example, Yang Li et al. [7] used simple assumptions (ionic charges derived from bond valence sums) and the point charge model to calculate quadrupole splittings in Tl1223. They have found that measured quadrupole splittings matched the calculated ones if the Fe dopant atoms are slightly off-positioned in their polyhedra along the *c* axis. Our findings show that in such calculations the chemical bond-type difference in the sheets and in the apical direction may not be neglected (the somewhat longer apical Cu-O bond has long been known) and it is possible that the assumption of Fe displacement is not necessary.

These facts support theories which try to explain the mechanism of high-*T_c* superconductivity with 2D models [15-17].

One may not forget here the Mössbauer works on Cu1212 (i.e., YBa₂Cu₃O_{7-δ}) which also contains Cu in insulating layers. The most commonly accepted evaluation of the Mössbauer spectra involves 4 doublets assigned to various Cu-substitutions and Fe coordination environments. Table 3 shows Mössbauer data and doublet assignments based mainly on emission Mössbauer studies where the dopant is at very low concentration so the host material is not much perturbed.

This kind of spectrum evaluation (i.e., the obtained set of Mössbauer parameters) is widely accepted, including assignments of A, B and C to Cu(1) sites. D is somewhat debated but mostly assigned to Cu(2). Further details may differ from author to author.

Table 3. Mössbauer parameters for Cu1212 (YBa₂Cu₃O_{7-δ}) [18]. δ: isomer shift relative to α-Fe; Δ: quadrupole splitting.

Mössbauer doublet	δ (mm/s)	Δ (mm/s)	Assigned species
A	0.02	1.97	Square planar in <i>b-c</i> plane at Cu(1)
B	0.01	0.99	5-coordinate, trigonal bipyramidal, with basal plane in the <i>a-b</i> plane at Cu(1)
C	-0.12	1.49	5-coordinate, square pyramidal, with basal plane in the <i>b-c</i> plane at Cu(1)
D	0.2	0.6	<i>c</i> -axis oriented square pyramidal at Cu(2)

For Cu1212, it is common in all Mössbauer works that the majority of the Mössbauer dopant prefers Cu(1) substitution, the fraction of doublet D in the spectra is typically 10-20% only. Thus one can probe the electronic structure of the insulating layer, too.

We have already pointed out with the help of Mössbauer spectroscopy [19] that the Cu(1)-O chains in the "insulating" layer have delocalized electron structure for we use now quotation marks when calling this layer insulating. The metallicity of the chains is further supported by the observed isomer shifts. The surprisingly low isomer shifts cannot be explained by a valence state higher than 3+ because of the already discussed reasons. While species C and B contain one more extra oxygen at the otherwise vacant O(5) site [20,21] (figure 2) and disappear promptly upon slight deoxygenation, species A survives down to an oxygen stoichiometry $\sim O_6$ with slightly increasing isomer shift [19]. This isomer shift ranging from 0.02 mm/s to 0.08 mm/s upon deoxygenation is characteristic of a valence state somewhere between Fe³⁺ and Fe⁴⁺ while at these stoichiometries the average valence state of Cu changes from 2.33 to 1.67 only. Thus the reduction of the isomer shifts should be explained by the electron withdrawing behavior of the delocalized electron system of the chains (presumably the Cu3dO2p band). The variations in the isomer shifts for species A to C indicates that the effectiveness of Fe3d electron donation to the chains depends on the structure of the ligand environment, and it seems to overdominate the effect of the coordination number.

It is noteworthy that Boolchand et al. [22] reported two new species in YBa₂Cu₃O_{7- δ} after rigorous oxygenation treatment, and although they were short lived, the one which was assigned to octahedral coordination at Cu(1) had Mössbauer parameters $\delta = 0.28$ mm/s and $\Delta = 0.2$ mm/s. One may conclude that once the coordination in the *a-b* plane reaches 4, should it be in the chains, the isomer shift will fall into the "right" interval (for species A, B and C the number of oxygens in the *a-b* plane is 2, 3 and 3, respectively).

The fact that all isomer shifts related to the Cu(1)-substituted ⁵⁷Fe probe are lower than that belonging to Cu(2) is in agreement with the chemical bond theory calculations of Gao et al. [23] who found that the covalency is 0.41 for Cu(1)-O bonds, and 0.28 for Cu(2)-O bonds. This shows (rather interestingly) that the chains can really pull electrons from the Fe3d orbitals stronger than the Cu(2) sheets. These authors did not differentiate between basal and apical Cu-O bonds.

One more experimental fact is noteworthy about the electronic structure of the chains (the layer containing the Cu(1)-O chains). There is a longstanding controversy in Mössbauer studies concerning the direction of the principal axis of the electric field gradient (EFG) at the Cu(1) site for various Mössbauer species. On the

basis of geometrical considerations, one expects that the principal EFG axis lies in the b-direction for species A and C and it may lie in the c-direction for species B. However, very careful measurements seem to have confirmed many former results and settled this question rather convincingly [24] that for all the four species (including D for which it is logical, however,) the EFG points to the c-direction. This finding shows that not only in the conducting layers but also in the "insulating" Cu(1) layer, the in-plane delocalization of electrons determines the local electronic properties, such as the electron density and its spatial distribution. Apical oxygens have hardly any effect.

Our final conclusion is that Mössbauer measurements strongly support the layered (2D) electronic structure of cuprate high-*T_c* superconductors not only in the superconducting planes but also in the "insulating" Cu(1)-O planes of the Cu1212 system. Conduction properties of the latter may have to be reconsidered.

Study of the colossal magnetoresistant material La_{0.8}Sr_{0.2}Co(Fe)O₃ by ⁵⁷Fe-Mössbauer Spectroscopy

The analysis of the Mössbauer parameters proved to be also powerful in the investigation of colossal magnetoresistant [25] materials. These materials show a substantial change in their electric conductivity when even a small external magnetic field is applied. This phenomenon is mostly observed in the vicinity of the magnetic ordering temperature, in some cases (manganites) it may be explained by the double exchange mechanism of spin coupling.

La_{0.8}Sr_{0.2}Co_xFe_{1-x}O_{3- δ} has been thoroughly investigated by various methods [26-28], and Mössbauer spectroscopy offers two possibilities to probe the system: either through the naturally contained iron or by doping with radioactive ⁵⁷Co. Thus the localization of the Mössbauer probe after the doping process is never dubious: in the first case, the Fe-sites, in the second case, the Co-sites are probed. In this compound, large dependence of the CMR-effect on the Fe-content was observed. The valence and spin state of Fe and Co is crucial for the mechanism of the CMR phenomenon; the superexchange interaction Fe³⁺ - O - Co⁴⁺ \leftrightarrow Fe⁴⁺ - O - Co³⁺ responsible for the ferromagnetic coupling was proposed by Maignan et al. in SrFe_{1-x}Co_xO₃ [29].

In La_{0.8}Sr_{0.2}Co_{0.7}Fe_{0.3}O₃, only high-spin Fe³⁺ state was found [28], which is remarkable because when La³⁺ is substituted by Sr²⁺ at site A of the perovskite unit cell (our reference now is La^{III}(Co^{III},Fe^{III})O₃), the missing charge is supposed to be compensated by the generation of Fe⁴⁺ at the expense of Fe³⁺ at site B. Oxygen stoichiometry is, rather surprisingly, reported to be very close to 3. This could seem to be logical on the basis of

the chemistry of Co and Fe: Co^{4+} is a stronger oxidant than Fe^{4+} (at least in conventional aqueous solutions), thus Fe^{4+} should form much more readily than Co^{4+} .

At the same time, it is deduced from magnetic studies of $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ that in these compounds Co can be found in low or intermediate spin Co^{3+} and Co^{4+} states [30,31]. Since the spin state can substantially alter redox properties, it is plausible to assume that in the solid perovskite lattice a low (or intermediate) spin Co^{4+} state is more stable than a high spin Fe^{4+} . In other words, the roles of reducing and oxidizing agents are switched between iron and cobalt. Macroscopic magnetic measurements cannot differentiate whether a certain magnetic effect is due to iron or cobalt moments in a mixed compound. Since substituting Fe for Co is expected to bring more oxygen to the lattice due to higher affinity, it is very unlikely that, in an iron containing material, a decreased oxygen stoichiometry would compensate for the missing charge at site A of the perovskite lattice due to La^{3+} to Sr^{2+} exchange. Now, if the total iron content is in high spin Fe^{3+} state according to the Mössbauer spectra, one should conclude that Co must be in Co^{4+} state, at least partially, which is feasible only in low or intermediate spin state. Thus a ^{57}Fe Mössbauer measurement

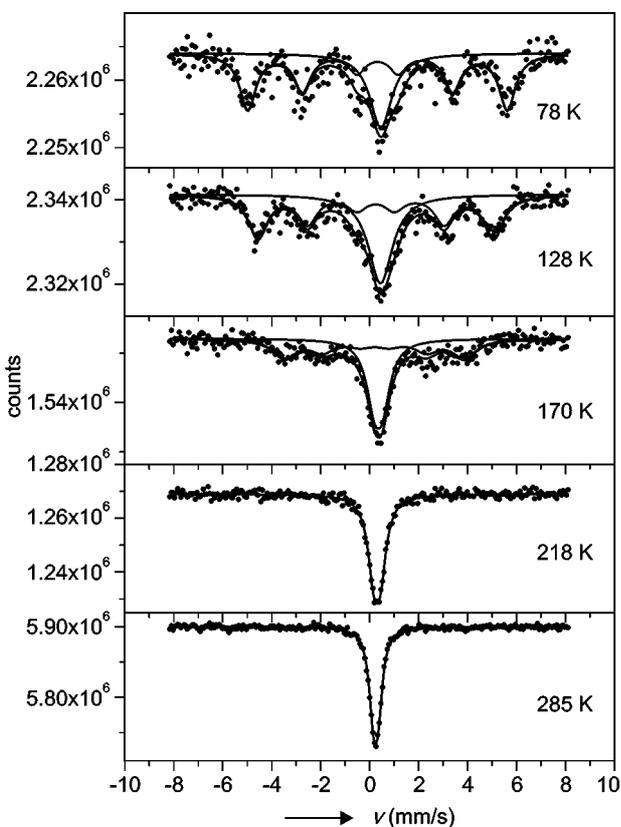


Figure 4. Selected emission Mössbauer spectra of ^{57}Co -doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ recorded at the indicated temperatures. The velocity scale refers to $\alpha\text{-Fe}$ [32].

can support (in an indirect way) that cobalt ions are in low or intermediate spin state in the mixed perovskite CMR compound $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$.

We have recently studied $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ with the help of the emission Mössbauer technique, by doping this material with ^{57}Co . In this case we can study one extreme of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ system, namely, when $x \rightarrow 1$. Details of the study will be published elsewhere [32].

The transition from paramagnetic to ferromagnetic state showed typical superparamagnetic-like behavior, with the coexistence of the two phases from 200 K down to below 78 K (!). Some selected Mössbauer spectra can be seen in figure 4. There are two features of the transition which are noteworthy.

1. As can be seen, the paramagnetic to ferromagnetic transition occurs in an anomalously wide temperature range. It starts at ~ 190 K and is not yet finished at the lowest temperature applied, 78 K. The transition resembles superparamagnetism, however in this case the particle size cannot limit the magnetic domain size, thus it is an intrinsic property of the bulk material to form ferromagnetic clusters with a wide size distribution as a function of temperature.

It has been proposed that the crucial common feature of colossal magnetoresistance found even in materials with no possibility for double exchange is this superparamagnetic-like behavior [33]. Our finding is not in perfect agreement with this idea because in the series of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ with $x = 0$ to 1, actually the Fe-free compound is the poorest CMR material.

2. The second remarkable feature of the transition is made clear by the observed isomer shifts. Contrary to regular paramagnetic to ferromagnetic transitions (or even to paramagnetic spin relaxation), the isomer

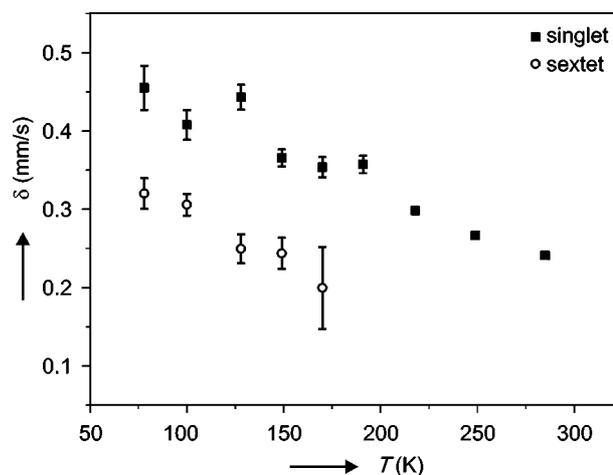


Figure 5. Temperature variation of the isomer shift (relative to $\alpha\text{-Fe}$) in ^{57}Co -doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ in the paramagnetic and the ferromagnetic phase represented by a singlet and a sextet, respectively [32].

shift of the Mössbauer probe - the probe is now "nucleogene" ^{57}Fe formed from the mother nuclide ^{57}Co at the Co-site of the perovskite lattice - is not the same in the paramagnetic and in the magnetically ordered (ferromagnetic) phase. We find that the ferromagnetic phase has significantly lower isomer shift at all temperatures measured (figure 5).

On the basis of our arguments used in the case of high- T_c superconductors, the lower isomer shift is in perfect agreement with the metallicity of the ferromagnetic phase and it clearly demonstrates that magnetic ordering and metallicity are strongly correlated in CMR materials. Furthermore, it is a direct proof that the decrease in resistivity belongs to the ferromagnetic phase only. It is unique in Mössbauer spectroscopy that in contrast to macroscopic magnetic measurements, the ratio of the paramagnetic and magnetically ordered phase can also be obtained from the analysis of the spectra.

CONCLUSIONS

The characterization of high-temperature superconductors (HTSC) and colossal magnetoresistant (CMR) materials with Mössbauer spectroscopy was demonstrated by reviewing selected studies. It was shown that for many cuprate superconductors, despite the great variability of the structure and chemical composition, the isomer shift of the Mössbauer probe falls in a very narrow range, while the quadrupole splitting shows large variation. These are explained by the 2D electronic structure of the (super)conducting Cu-O₂ planes in the perovskite-related lattice of HTSC, namely, the in-plane oxygens being covalently bonded to the Cu(Fe) center determine the isomer shift, and the apical oxygens, if there is any, with basically ionic bonding contribute to the quadrupole splitting only. The relatively low isomer shift is explained by the metallicity of the planes.

The decreased isomer shift due to metallicity, observed in the structurally related ^{57}Co -doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3.6}$ perovskite, binds HTSC cuprates and CMR materials together. It is demonstrated that in $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3.6}$, the low isomer shift is found solely in the ferromagnetic phase (coexisting with the paramagnetic phase in a surprisingly wide temperature range), which confirms the correlation between magnetic ordering and electric conductivity in CMR materials.

Acknowledgement

The authors are thankful for the support of the studies mentioned in this paper to the Hungarian National Research Fund (OTKA T043565, T034839, T043687)

and to the Hungarian Academy of Sciences (AKP 2000-143 2,4). Preparation of materials and helpful discussions are also gratefully acknowledged to Prof. Dr. Gerhard Gritzner (Johannes Kepler University, Linz).

References

1. Maple M. B.: Journal of Magnetism and Magnetic Materials 177, 18 (1998).
2. Nagaev E. L.: Physics Reports 346, 387 (2001).
3. Shaked H., Keane P. M., Rodriguez J. C., Owen F. F., Hitterman R. L., Jorgensen J. D.: Proc. 4th International Conference on Materials and Mechanism of Superconductivity - High-temperature Superconductors, Grenoble, 5.-9. July 1994, special publication by Argonne National Laboratory and Elsevier Science B. V.
4. Kuzmann E., Mair M., Klencsár Z., Vértes A., Homonnay Z., Gritzner G.: Physica C 319, 12 (1999).
5. Enengl M., Kuzmann E., Homonnay Z., Gritzner G.: Physica C 377, 565 (2002)
6. Kuzmann E., Mair M., Klencsár Z., Homonnay Z., Vértes A., Gritzner G.: J. Radioanal. Nucl. Chem. 246, 107 (2000).
7. Li Y., Baggio-Saitovitch E., Wang Y. B., Cao G. H., Chen N., Zhao Z. X., Wei L.: Physica C 315, 129 (1999).
8. Bhargava S. C., Chakrabarty J. S., Jhans H., Malik S. K.: J. Phys. Condens. Matter. 5, 4541 (1993).
9. Kuzmann E., König W. T., Mair M., Homonnay Z., Klencsár Z., Juhász G., Gritzner G.: Superconductor Science and Technology 14, 379 (2001).
10. Imbert P., Jehanno G., Debray P., Garcin C., Hodges J. A.: J. Phys. I France 2, 1405 (1992).
11. Kuzmann E., Homonnay Z., Nagy S., Nomura K.: Mössbauer Spectroscopy, in: Handbook of Nuclear Chemistry, volume 3, pp. 109-187, eds. Vértes A., Nagy S., Klencsár Z., Kluwer Academic Publishers, Dordrecht-Boston-London 2003.
12. Gütlich P., Link R., Trautwein A.: Mössbauer Spectroscopy and Transition Metal Chemistry, Springer Verlag, Berlin 1978.
13. Battle P. D., Gibb T. C.: J. Chem. Soc. Dalton Trans., p.667 (1985).
14. Gibb T. C.: J. Chem. Soc. Dalton Trans. 1455 (1985).
15. Mohammadzadeh M. R., Akhavan M.: Supercond. Sci. Technol. 16, 1216 (2003).
16. Balestrino G., Tebano A.: Supercond. Sci. Technol. 16, R29 (2003).
17. Levin G. A., Stein T., Almasan C. C., Han S. H., Gajewski D. A., Maple M. B.: Phys. Rev. Lett. 80, 841 (1998)
18. Homonnay Z. in: Mössbauer spectroscopy of sophisticated oxides, p.199, ed.: Vértes A., Homonnay Z., Akadémiai Kiadó, Budapest 1997.
19. Homonnay Z., Nath A., Wei Y., Jing T.: Physica C 174, 223 (1991).
20. Nath A., Homonnay Z.: Physica C 161, 205 (1989).
21. Homonnay Z., Nath A.: J. Supercond. 3, 433 (1990).

22. Boolchand P., McDaniel D.: *Hyperfine Interact.* 72, 125 (1992)
23. Gao F., Li D., He J., Tian Y., Yu D., Zhang S.: *Physica C* 371, 151 (2002)
24. Chechersky V., Nath A.: *Hyperfine Interactions* 72, 173 (1992)
25. Fontcuberta J.: *Physics World*, p.33, February 1999.
26. Tai L-W., Nasrallah M. M., Anderson H. U., Sparli D. M., Sehlin S. R.: *Solid State Ionics* 76, 259 (1995).
27. Barman A., Ghosh M., Biswas S., De S. K., Chatterjee S.: *Appl. Phys. Lett.* 71, 3150 (1997).
28. Cziráki Á., Geröcs I., Köteles M., Gábris A., Pogány L., Bakonyi I., Klencsár Z., Vértes A., De S. K., Barman A., Ghosh M., Biswas S., Chatterjee S., Arnold B., Bauer H.D., Wetzig K., Ulhaq-Bouillet C., Pierron-Bohnes V.: *Eur. Phys. J. B* 21, 521 (2001).
29. Maignan, A., Martin, C., Nguyen, N., Raveau, B.: *Solid State Sciences* 3, 57 (2001).
30. Senaris-Rodríguez M. A., Goodenough J. B.: *J. Sol. State Chem.* 116, 224 (1995).
31. Senaris-Rodríguez M. A., Goodenough J. B.: *J. Sol. State Chem.* 118, 323 (1995).
32. Homonnay Z., Németh Z., Kuzmann E., Klencsár Z., Gritzner G., Vértes A, (to be published).
33. Nath A., Klencsár Z., Kuzmann E., Homonnay Z., Vértes A., Simopoulos A., Devlin E., Kallias G., Ramirez A. P., Cava R.J.: *Phys. Rev. B* 66, 2401 (2002).

CHARAKTERIZACE OXIDŮ PŘECHODOVÝCH KOVŮ
MÖSSBAUEROVOU SPEKTROSKOPIÍ

Z. HOMONNAY¹, E. KUZMANN², Z. NÉMETH¹, Z. KLENCSÁR²,
S. I. NAGY¹, AND A. VÉRTEŠ¹

¹*Department of Nuclear Chemistry, Eötvös Loránd University,
Budapest 1518 P.O.Box 32, Hungary*

²*Research Group for Nuclear Methods in Structural
Chemistry, Hungarian Academy of Sciences at ELTE,
Budapest 1518 P.O.Box 32, Hungary*

Vysokoteplotní supravodiče a materiály s kolosální magnetorezistancí (CMR) patří k nejslibnějším materiálům pro technické aplikace posledních dvou až tří desetiletí. Ve většině případů jde o oxidy kovů a prvkem hlavně ovlivňujícím jejich užitečné fyzikální vlastnosti bývá často přechodový kov (Cu, Co, Fe, Mn). ⁵⁷Fe Mössbauerova spektroskopie může být užita k popsání elektronických a strukturních vlastností oxidů přechodových kovů díky informaci o lokální elektronické struktuře příslušní krystalové pozice, pokud je v ní Mössbauerovské jádro. Z několika studií používajících Mössbauerovu spektroskopii vyplývá, jak může být prokázána vrstevnatá (2D) elektronická struktura vysokoteplotních supravodičů z Mössbauerových izomerních posunů a kvadrupólového štěpení. Dále ukazujeme, jak Mössbauerův izomerní posun ukazuje na kovový charakter ferromagnetické fáze v CMR materiálu $\text{LaSr}_{1-x}\text{CoO}_3$.