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Mössbauer study of ^{57}Fe -doped $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$

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Abstract

Mössbauer and magnetization measurements have been performed on the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}^{57}\text{Fe}_{0.022}\text{O}_3$ compound in the temperature range $100\text{ K} < T < 293\text{ K}$. It was shown that the most probable electronic state of the iron probe ions is a formal 4+ high-spin one. Such electronic Fe ion configuration is associated with the metallicity and confirms the delocalized e_g electron character. The paramagnetic single-line component together with a broadened magnetic splitting was observed in the Mössbauer spectra well below the magnetic ordering temperature. This peculiarity is interpreted in terms of a La-rich inhomogeneity containing Co^{3+} ions mainly in the low-spin state as well as irregular $\text{La}^{3+}/\text{Sr}^{2+}$ ion distribution in the surroundings of the iron probe ions. The mechanism of the magnetic interactions is discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system has drawn great attention from researchers due to the intriguing correlation of magnetic and transport properties. There are three main mechanisms in the explanation of the unusual magnetic properties of cobaltites: (1) the ‘superexchange model’ based on the localized electron interactions via an oxygen ion; (2) the ‘Zener double exchange’, and (3) the ‘itinerant-electron ferromagnetism’ [1–5]. These approaches can explain some of the physical properties, but none can provide a universal model.

It is suggested that the ‘double exchange’ mechanism is more appropriate for the origin of magnetic interaction in the cobaltites and manganites, though there are too strong distinctions in their properties. Thus, in the cobaltites a concentration transition from metal to insulator state occurs simultaneously with ferromagnetic onset [6–15], in contrast with manganites, where an insulating ferromagnetic range exists. Such an interesting property is worthy of some

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comments. Thus the LaCoO_3 compound is a diamagnetic semiconductor at $T \rightarrow 0$ K, whereas LaMnO_3 exhibits an antiferromagnetic (AF) ordering with $T_N = 140$ K. The $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system at a low doping level has an AF ordered insulating phase, which eventually evolves into a ferromagnetic insulator and then into a ferromagnetic metal. In the cobaltite materials with a low doping of divalent alkali-earth elements, many of the magnetic properties can be simply explained by the formation of short-range-ordered ferromagnetic clusters. At temperatures above T_C , superparamagnetic clusters in a nonmagnetic matrix are observed. Their coalescence is revealed with temperature decrease and their magnetic moment starts to block into the local magnetic anisotropy fields [16].

The differences in the magnetotransport properties of the cobaltites and manganites are mainly revealed in the following: (i) the optimally doped manganites (like $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [17]) exhibit the first-order metal–insulator (M–I) and ferromagnetic–paramagnetic (FM–PM) transitions at the same temperature, whereas for the cobaltites the resistivity has a rather complicated behaviour, thus above the magnetic percolation threshold and at the temperatures $T > T_C$ the cobaltites have a metallic-like conductivity; (ii) for manganites the magnetoresistance has its maximum value near T_C , whereas in the cobaltites the absolute magnetoresistance value is significantly lower as compared with the manganites and one can demonstrate its increase as temperature decreases.

Another interesting peculiarity of both the manganite and cobaltite materials is the presence of the magnetic inhomogeneity in a wide concentration range. Likely, such inhomogeneity causes a phase segregation, which can have structural, chemical or electronic origin. Recent NMR works [18, 19] clearly establish the inhomogeneous magnetic nature of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system, with coexistence of the regions of ferromagnetic, spin-glass and low-spin Co ions. However, the origin of such inhomogeneities in most of the cobaltites and manganites is still an open issue.

Immediate information concerning a microscopic magnetic structure of the sample may be obtained using Mössbauer spectroscopy. A small percentage of ^{57}Fe substitution for Co in cobaltites is sufficient as a microprobe for detecting the local structure and magnetic state of the Fe environment in the Mössbauer experiments. In this work we present the temperature-dependent ^{57}Fe Mössbauer spectra measured in order to obtain evidence for localized versus itinerant d electrons as well as to elucidate the origin of the observed inhomogeneities.

2. Experiment

Polycrystalline samples of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}\text{Fe}_{0.022}\text{O}_3$ were fabricated from La_2O_3 , Co_3O_4 , Fe_2O_3 (90% enriched in ^{57}Fe) and SrCO_3 starting materials by standard solid-state reaction methods. The starting powder was ground, calcined in air for 3 h at 1150°C , then sintered in air for 12 h at 1240°C , and after that slowly cooled down to room temperature. Structural characterization was performed by x-ray diffraction (XRD). The XRD confirms that the samples are single-phase ones (an XRD pattern for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}\text{Fe}_{0.022}\text{O}_3$ sample is shown in figure 1). The Fe-doped sample has a cubic structure (space group $Pm\bar{3}m$) with a lattice parameter $a = 3.833$ Å and a unit cell volume of 56.298 Å³. The best computer fitting of the x-ray pattern for the Fe-free compound was obtained by assuming $R\bar{3}c$ space group with minimal distortions (the unit cell volume is 56.283 Å³). The magnetization measurements were performed using an OI-1001 commercial vibrating-coil magnetometer in the temperature range 4.2 K $< T < 250$ K and in applied magnetic fields up to 15 kOe. The Mössbauer spectra of the samples were recorded with a ^{57}Co (Rh) source in transmission geometry. The Mössbauer data were computer fitted by the NORMOS program [20]. Isomeric shifts are given in relation to α -Fe.

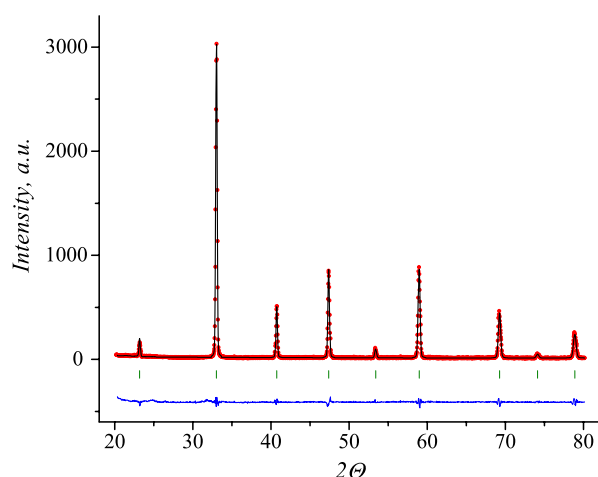


Figure 1. The refined x-ray diffraction pattern for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}^{57}\text{Fe}_{0.022}\text{O}_3$ sample at 300 K. The observed intensities are shown by dots and the calculated ones by the solid line. The positions of the Bragg reflections are shown by the small vertical lines below the pattern. The line at the bottom indicates the intensity difference between the experimental and the estimated data.

3. Results

The temperature dependences of the magnetization of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}^{57}\text{Fe}_{0.022}\text{O}_3$ and of the Fe-free sample $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ are shown in figure 2. Both field cooled (FC) and zero-field cooled (ZFC) data are presented; the field cooling was performed in a magnetic field of 100 Oe. At 220 K the $M(T)$ dependence of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}^{57}\text{Fe}_{0.022}\text{O}_3$ sample shows a sharp increase in the FC magnetization, confirming sample uniformity. The ZFC magnetization curve has a nonmonotonic behaviour with a peak close to the temperature which is approximately 15 K below T_C . In these compounds the magnetization curve in low external magnetic field may be governed by a local anisotropy field [21], and magnetic moments of the spins are probably frozen in directions energetically favoured by their local anisotropy or by the external field when the samples are cooled down in the ZFC or in the FC modes, respectively. The $M(H)$ curve measured for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}^{57}\text{Fe}_{0.022}\text{O}_3$ does not saturate at moderate magnetic fields (~ 15 kOe); however, it is possible to conclude that the magnetic moment per Co ion should be larger than $1.5 \mu_B$, which is consistent with previous works [7, 22, 23], in which magnetization values of about 1.6 – $1.92 \mu_B$ were reported. It should be noted that Fe doping leads to some T_C decrease (about 5 K regarding to Fe-free compound, figure 2) and to the increase of coercive field up to 1 kOe at 5 K ($H_C = 386$ Oe in the Fe-free $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ compound according to [24]).

The Mössbauer spectra were measured at room temperature (RT), 100 K and at temperatures close to the magnetic ordering temperature (220–190 K). The measurements were performed at two velocity ranges: a small velocity range with optimal energy resolution and a large velocity range at which all other spectra were measured and at which the entire magnetic hyperfine splitting could be observed (see figure 3). The small velocity spectrum (see the inset of figure 3) shows that the spectrum measured for the sample in the nonmagnetic state (RT) consists clearly of a single line ($\text{IS} = 0.18 \text{ mm s}^{-1}$); this suggests that crystalline symmetry around the Fe atoms is cubic. The spectra measured at temperatures in the range 220–190 K, i.e., near the magnetic ordering temperature, reveal that at 220 K (figure 3) the

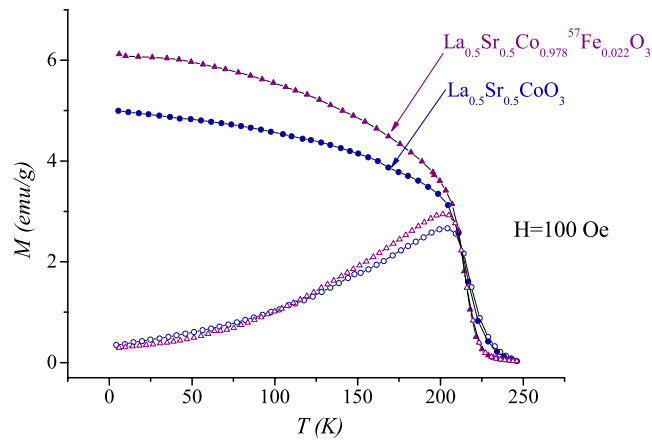


Figure 2. The temperature dependences of the magnetization for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}^{57}\text{Fe}_{0.022}\text{O}_3$ and Fe-free sample, measured in the FC (filled symbols) and ZFC (open symbols) modes at $H = 100$ Oe.

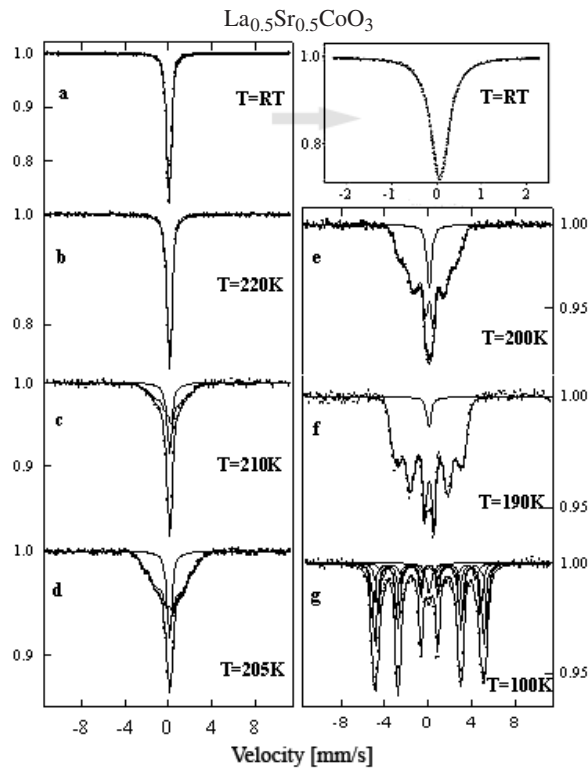


Figure 3. The Mössbauer spectra of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}^{57}\text{Fe}_{0.022}\text{O}_3$ upon cooling in zero field, measured at different temperatures. The reduced velocity pattern measured at room temperature is shown in the inset.

spectrum is purely nonmagnetic (single line), which means that the temperature of 220 K is above the transition temperature. A magnetically ordered fraction clearly appeared at 210 K.

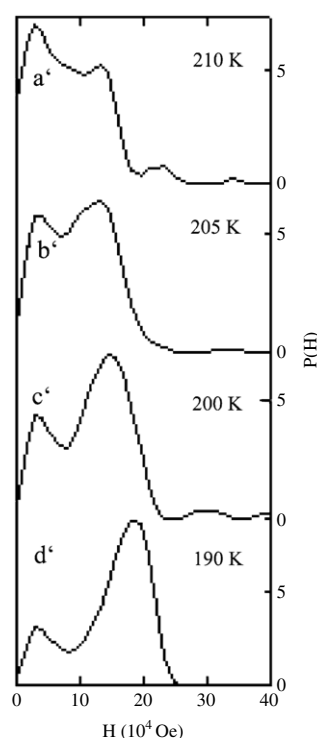


Figure 4. The Mössbauer spectra fitted with the $P(H)$ distributions at 210, 205, 200 and 190 K.

This magnetic component was fitted with a hyperfine field distribution, $P(H)$ (figure 4), and the average magnetic field estimated from the $P(H)$ distribution is about 8.7 T. The $P(H)$ distribution consists of two poorly separated peaks at about 3–4 and 13 T. The spectral fraction (area) of the $P(H)$ component is 54% and of the nonmagnetic single line is about 46%. With the decrease of temperature the average hyperfine field (hf) of $P(H)$ component increases and its spectral contribution also increases. At 205 K the average $H_{\text{hf}} = 10.1$ T, and the spectral area of the magnetic component ($P(H)$) is about 76% and of the single line component is about 24%. The shape of the $P(H)$ distribution becomes better resolved and still consists of the two peaks: at about 4–5 and 13 T. At 200 K the magnetic component ($P(H)$) is even better resolved. The average $H_{\text{hf}} = 12$ T. The $P(H)$ consists of two well resolved peaks: a smaller one at about 4 T and a larger one at 16 T. The area of the magnetic component is about 89% and of the single line about 11%. The magnetic component in the spectrum at 190 K is quite well resolved: $H_{\text{hf}} = 14.8$ T, and the relative spectral area of this component is about 96%. The $P(H)$ distribution consists mainly of a well resolved peak at 19 T and a much smaller one at low fields (about 3 T). The area of the single-line component decreases to below 4%. The isomer shift in this temperature range is about 0.21 mm s^{-1} for the single line and about 0.29 mm s^{-1} for the magnetic component; we should note that these values can be ascribed either to Fe^{4+} or Fe^{3+} ions. At the lowest temperature (100 K) the spectrum corresponds to an almost purely magnetically ordered sample. The spectrum was fitted with four sextets accompanied by a small single-line nonmagnetic component. The sextets reveal the following fields: 32.7, 30.9, 29.3 and 26.6 T. The isomer shifts of these sextets were 0.26, 0.24, 0.23 and 0.23 mm s^{-1} , respectively, and 0.23 mm s^{-1} for the single-line component. The areas of

Table 1. The fitted Mössbauer parameters for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}^{57}\text{Fe}_{0.022}\text{O}_3$ sample at different temperatures.

	T (K)	Area (%)				
		IS (mm s^{-1})	QS (mm s^{-1})	H (10^4 Oe)	Nonmagnetic Magnetic	
$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$	295	0.18	—	—	100	—
	220	0.21	—	—	100	—
	210	0.21	—	—	43	—
		0.29	—	8.7	—	57
	205	0.21	—	—	24	—
		0.30	—	10.1	—	76
	200	0.22	—	—	11	—
		0.29	—	12.0	—	89
	190	0.21	—	—	4	—
		0.29	—	14.8	—	96
	100	0.26	—	32.7	—	26
		0.24	—	30.9	—	36
		0.23	—	29.3	—	22
		0.23	—	26.6	—	11
0.21		—	—	4	—	

these components (sextets) were 26, 36, 22 and 11%, respectively, and 4% for the single-line component. The Mössbauer parameters are collected in table 1.

4. Discussion

At the present moment a number of Mössbauer investigations of the cobaltites and manganites are available. For the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ samples (^{57}Co was used in the samples) in [25] the authors interpreted the Mössbauer results in terms of a model according to which Fe ions have an oxidation state between those characteristic of high-spin (HS) trivalent iron Fe^{3+} (electronic configuration $t_{2g}^3 e_g^2$) and a low-spin (LS) tetravalent iron Fe^{4+} ($t_{2g}^4 e_g^0$), arising from the high-spin trivalent cobalt ($t_{2g}^4 e_g^2$) and low-spin tetravalent cobalt ions ($t_{2g}^6 e_g^0$), respectively (the claimed hyperfine field value for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ sample was about 316 kOe and the isomer shift was about 0.25 mm s^{-1}).

On the other hand, in [26] it is supposed that in the $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ compounds the Fe^{4+} ions have predominantly the high-spin electronic configuration with hf and isomer shift values of 330 kOe and 0.11 mm s^{-1} , respectively (at the parent SrFeO_3), which gradually changes to 296 kOe and 0.19 mm s^{-1} (SrCoO_3) correspondingly with an increase of cobalt concentration. It is worth noting that over the entire concentration range the $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ system retains a metallic-like resistivity.

Exploring the CaFeO_3 compound in [27], the authors noted that an application of a strong external pressure (~ 30 GPa) leads to an increase of the magnetic ordering temperature up to 800 K ($T_N = 290$ K at a pressure of 0.1 MPa) and to the first-order high-spin to low-spin transition of the Fe^{4+} ions. The observed hf value for the Fe^{4+} ions being in the low-spin state was about 16 T. This fact provides evidence in favour of the high-spin Fe^{4+} state stability.

Based on the Mössbauer data obtained (see table 1) and taking into account the results of [26, 27], one can suppose that the most probable valence state of Fe probe ions in the

$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ is a high-spin Fe^{4+} one. The calculated hf value and isomer shift are similar to those obtained in the previous investigations of the $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ and SrFeO_3 systems.

Based on the XAS measurements of the $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ system [28], we suppose that the electronic configuration of the Fe and Co ions should include a contribution from the charge transfer configurations. So, the Fe^{4+} high-spin electronic state in the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}^{57}\text{Fe}_{0.022}\text{O}_3$ is rather formal. This means that the ionic state of the Fe and Co ions is not really $4+$, but rather that the charge state is compensated by oxygen 2p holes. Due to the strong delocalization of the e_g electrons, the Mössbauer parameters obtained resemble those observed for binary alloys and metals [29], and one can conclude that the tetravalent Fe state suggests metallicity. This assumption is confirmed by the hf value obtained for Fe^{4+} ions ~ 30 T, whereas in the case of localized d electrons the estimated hf value should be near to 38–43 T.

The calculated $P(H)$ distribution (figure 4) near the magnetic transition temperature has two components: one of them lies in the low hf area, and the other one is disposed in the high-field range. Only the high-field component remains at the lowest temperatures, whereas the low-field component vanishes at 100 K. With decreasing temperature the high-field component shifts slowly to a high-field range revealing the hf values of 13 T at 210 K and about 30 T at 100 K. But besides the field value shifting, this component demonstrates a splitting of the hf magnitude at 100 K. The four new components have nearly the same hf values (see table 1). Such splitting can be explained by an inequality in the distribution of the surrounding ions: whether they are neighbouring Co ions with different valence or different combination of La and Sr ions. According to the Goodenough theory [2], the presence of a Co^{4+} ion causes a quick reversible reconstruction of wavefunctions of the neighbouring Co^{3+} ions with rates higher than the Mössbauer spectroscopy sensitivity.

So we cannot observe such phenomena using the Mössbauer technique. The different La/Sr surroundings of the Mössbauer probe ions is a more reliable reason for the hf splitting. The possible probe ion surroundings giving such hf splitting should contain the following $\text{La}^{3+}/\text{Sr}^{2+}$ ions ratios: 5 Sr^{2+} ions + 3 La^{3+} ions; 4 Sr^{2+} + 4 La^{3+} ; 3 Sr^{2+} + 5 La^{3+} and 2 Sr^{2+} + 6 La^{3+} . Regions with Sr ions predominant in the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ compound are excluded by the sample preparation conditions.

We should note that together with ferromagnetism the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ compound exhibits a paramagnetic component present over the entire temperature range. This fact is clearly evidenced by the Mössbauer measurements. Starting from RT, all Mössbauer spectra contain a single-line component specified by the nonmagnetic surroundings of the Fe probe ions. Several possible reasons for such sample behaviour are discussed below. Most likely, such nonmagnetic inhomogeneities, enriched with La ions, should contain the low-spin Co^{3+} ions and probably exhibit a low-dimension structure (like planes or one-dimension structures). In favour of a low-dimension structure of such inhomogeneities is the fact that three-dimensional paramagnetic regions should stabilize Fe^{3+} ions, as occurs in LaCoO_3 samples [24]. However, this is in disagreement with the Mössbauer parameters obtained. In the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ compound the Fe probe ions, embedded in such inhomogeneity, have surroundings most probably consisting of 7 La^{3+} ions and only 1 Sr^{2+} ion. So, a single-line component in the Mössbauer spectra has an isomer shift value which can be ascribed to Fe^{4+} ions. These data are consistent with the NMR study of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ systems [18, 19], where even at the doping level up to $x = 0.5$ a signal from LS Co ions remains.

Another possible reason for a paramagnetic inhomogeneity presence can be oxygen vacancies. It is commonly known that $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system is inclined to oxygen vacancy creation at high Sr concentrations. In the works [7, 22] it is claimed that $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-d}$ samples ($0.4 < x < 0.5$) have an oxygen content about 2.97 ± 0.03 . So, the possible oxygen

vacancy should stabilize the Co ions in the 3+ valence state. However, the Co ions surroundings containing the oxygen vacancy presence should be a pentahedral instead of octahedral one. And under these conditions the Co^{3+} ions tend to change spin state into the high-spin one [30]. However, the high-spin Co^{3+} ions should cause strong antiferromagnetic interactions similar to $\text{SrCoO}_{2.5}$ [31], which are not consistent with the magnetization data for the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ sample. Besides, vacancies should stabilize the Fe^{3+} state of iron probe ions, which also does not agree with the Mössbauer data obtained.

It is interesting to note that in the manganites (e.g. $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [17]) broadening of the Mössbauer spectra is also observed at low temperatures. But in contrast to the cobaltites the paramagnetic component is not revealed. This can be explained by the fact that in the La-rich regions the Jahn–Teller distortions are removed and ferromagnetic interactions between Mn^{3+} – Mn^{3+} appear [32], thus excluding the presence of paramagnetism. It should be noted that ^{57}Fe probe ions in the manganites accept the 3+ valence state, thus demonstrating different chemical bonding in comparison with cobaltites [32]. In [28] it is claimed that $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ reveals a mixed charge transfer/Mott–Hubbard regime and has a dominating $3d^n$ configuration, whereas the cobaltites have $3d^{n+1}\underline{L}$ configuration (where \underline{L} denotes a ligand hole).

As we already mentioned in the introduction section, the magnetic properties of the cobaltites are explained assuming the following approaches: (1) the ‘superexchange model’ via an oxygen ion; (2) the ‘Zener double exchange’, and (3) the ‘itinerant-electron ferromagnetism’.

We should introduce several comments against the ‘double exchange’ mechanism:

- there is no metal-to-insulator transition and essential magnetoresistance effect near T_C [7];
- the cobaltites have a 2p–hole conductivity, being negative charge transfer compounds in contrast to the manganites [8];
- the ‘double exchange’ mechanism is not operative for ferromagnetism in the $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ and $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$ systems, where 3d ions have the same valence state;
- in the polycrystalline manganites and double perovskites (like $\text{Sr}_2\text{FeMoO}_6$ [33]) strong intergranular magnetoresistance was observed at rather low magnetic fields (whereas for the ferromagnetic cobaltites the magnetoresistance at magnetic fields up to 0.5 T is less than 2–3% [34]).

This confirms a small spin polarization of the charge carriers in the cobaltites in contrast with manganites [35].

There are a number of papers describing the properties of cobaltites in terms of ‘band magnetism’ [25, 36]. This model is based on the experimental fact that all cobaltites show a clear ferromagnetic component which appears simultaneously with metallicity.

However, we should note that in the cobaltites only the e_g electrons are delocalized, whereas t_{2g} electrons have predominantly a localized character. Thus, LaCoO_3 becomes metallic only at high temperatures (~ 600 K), when the e_g band is significantly filled. The e_g electron delocalization does not lead to magnetic ordering in metallic LaNiO_3 ($\text{Ni}^{3+} t_{2g}^6 e_g^1$) [37], where LaNiO_3 is a Pauli paramagnet. The small spin polarization of the charge carriers is also in contradiction with the ‘itinerant-electron ferromagnetism’.

We propose that the more plausible mechanism, responsible for ferromagnetic properties of the cobaltites, is the ‘superexchange’ one proposed by Goodenough [2]. This model assumes the exchange interaction between localized and delocalized 3d electrons as well as 2p holes in the wide valence band. Thus, the ferromagnetism occurs due to superexchange interactions between half-filled 3d orbitals. The localized and delocalized electrons interact via the s–d exchange. The correlation between the ferromagnetism and metallicity is explained by the

fact that the onset of ferromagnetism is accompanied by delocalization of the e_g electrons and the t_{2g} holes.

5. Conclusion

The Mössbauer spectra of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.978}\text{Fe}_{0.022}\text{O}_3$ sample have been interpreted assuming that the most probable valence state of iron probe ions is a formal 4+ high-spin one. The magnetic and transport properties of the sample are explained in a model according to which the e_g electrons of the Fe and Co ions have a strongly delocalized character forming a conducting band, whereas t_{2g} ones remain localized and are not involved in the metallicity. The role of the superexchange magnetic interactions is emphasized.

The magnetic sextet broadening and the presence of the paramagnetic component in the Mössbauer spectra are explained by different $\text{La}^{3+}/\text{Sr}^{2+}$ surroundings of the iron probe ions.

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