

Table 2. Parameters obtained from the Mössbauer spectra collected at 77 K and 170 K.

Samples	I. S. (mm/s)/ α -Fe	Hyperfine field (T)	Relative %	Charge state
LSF20 at 77 K	0.47	56.0	34	Fe ³⁺
	0.44	53.8	55	Fe ³⁺
	-0.07	26.3	11	Fe ⁵⁺
LSFC2010 at 77 K	0.47	55.5	24	Fe ³⁺
	0.43	53.2	63	Fe ³⁺
	-0.073	26.1	13	Fe ⁵⁺
LSFC2010 at 170 K	0.45	54.7	24	Fe ³⁺
	0.41	52.2	62	Fe ³⁺
	-0.06	25.2	12.5	Fe ⁵⁺
	0.41	-	1.5	Fe ³⁺

The Mössbauer results indicate: (i) the presence of two sextets with isomer shifts corresponding to Fe³⁺, (ii) the presence of one sextet with isomer shift corresponding to Fe⁵⁺, (iii) hyperfine parameters typical of Fe³⁺ and Fe⁵⁺ ions with octahedral coordination, (iv) the relative percentage of the two Fe³⁺ is different for different compositions, while Fe⁵⁺ poorly increases with the Cu content, and (v) while no structure related to Fe⁴⁺ is observed, above and below T_s, the amount of Fe³⁺ and Fe⁵⁺ does not vary. These data exclude charge disproportion for LSFC2010 in the range 77-170 K.

4 Conclusions

The coexistence of antiferromagnetic and weak ferromagnetic behavior at room temperature was determined by NPD and the magnetic hysteresis loop, respectively. The room temperature magnetic moment of the Fe/Cu atoms is $\mu_x = 2.43(3)\mu_B$ for LSFC2010. In addition, the nanosized LSF20 and LSFC2010 powders exhibit an interesting low temperature jump (at 70-80 K) in the ZFC magnetization curves versus temperature. In order to elucidate their complex magnetic behavior several hypotheses have been investigated: (i) magnetic hysteresis loops at 5 K excluded a Morin-like transition from a room temperature weak ferromagnetism to a low temperature antiferromagnetism; (ii) ⁵⁷Fe Mössbauer spectroscopy measurements indicated that Fe³⁺ and Fe⁵⁺ ions coexist in both compounds, but the relative percentage of Fe⁵⁺ is almost the same at 77 and 170 K, rejecting a charge disproportion mechanism. Further work will be required to ascertain whether a low temperature structural transition takes place, and to investigate a possible size effect on magnetic behavior.

References

1. J. Pérez-Ramírez, B. Vigeland, Catal. Today. **105**, 436 (2005)
2. V.A. Sadykov, L.A. Isupova, I.S. Yakovleva, G.M. Alikina, A.I. Lukashevich, S. Neophytides, React. Kinet. Catal. Lett. **2**, 393 (2004)
3. D. Mescia, J.C. Caroca, N. Russo, N. Labhsetwar, D. Fino, G. Saracco, V. Specchia, Catal. Today. **137**, 300 (2008)
4. S. Furfori, S. Bensaid, N. Russo, D. Fino, Chem. Eng. J. **154**, 348 (2009)
5. H. Kishimoto, N. Sakai, T. Horita, K. Yamaji, M.E. Brito, H. Yokokawa, Solid State Ionics. **178**, 1317 (2007)
6. D. Burnat, P. Ried, P. Holtappels, A. Heel, T. Graule, D. Kata, Fuel Cells. **10**, 156 (2010)
7. L. T. Wilkinson, J. H. Zhu, J. Electrochem. Soc. **156**, 905 (2009)
8. J.S. Yoon, J. Lee, H.J. Hwang, C.M. Whang, J. Moon, D. Kim, J. Power Sources. **181**, 281 (2008)
9. J. Wang, F. Wu, G. Song, N. Wu, J. Wang, Ferroelectrics **323**, 71 (2005)
10. A. Cavalieri, T. Caronna, I. Natali Sora, J.M. Tulliani, Ceramics International, **38**, 2865 (2012)
11. Dann, S. E.; Currie, D.B.; Weller, M.T. J. Solid State Chem. **109**, 134 (1994)
12. H. Kong, C. Zhu, Appl. Phys. Lett. **88**, 041920 (2006)
13. SK. Park, T. Ishikawa, Y. Tokura, JQ Li, Y. Matsui, Phys. Rev. B **60** 10788 (1999)
14. I. Natali Sora, T. Caronna, F. Fontana, C. De Julián Fernández, A. Caneschi, M. Green, J. Solid State Chem. **191**, 33 (2012)
15. T. Caronna, F. Fontana, I. Natali Sora, R. Pelosato, Mater. Chem. Phys. **116**, 645 (2009)