

# Hyperfine properties of $\text{La}(\text{V}_{1-x}\text{Fe}_x)\text{O}_3$ compounds

L. F. S. Tupan<sup>1</sup> · F. F. Ivashita<sup>1</sup> · R. Barco<sup>1</sup> ·  
B. Hallouche<sup>2</sup> · A. Paesano Jr.<sup>1</sup>

© Springer International Publishing Switzerland 2017

**Abstract**  $\text{LaV}_{1-x}\text{Fe}_x\text{O}_3$  perovskites were synthesized in the vanadium-rich concentration range (i.e.,  $x < 0.5$ ) and characterized structurally and for the hyperfine properties of the iron nuclear probe. The aim of this investigation was to better understand the physical transformations that take place in the undoped compound ( $\text{LaVO}_3$ ) at low temperatures. For that, X-ray diffraction analysis and, more extensively,  $^{57}\text{Fe}$  Mössbauer spectroscopy were applied. The results revealed that the  $\text{LaV}_{1-x}\text{Fe}_x\text{O}_3$  vanadium-rich perovskites are orthorhombic at RT, and their lattice parameters decrease with increasing vanadium concentration. Lowering the temperature, the system becomes magnetic, with the iron moment freezing progressively. The presence of two magnetic subspectral components obtained at the lowest measurement temperatures suggests that the vanadium-rich samples, including  $\text{LaVO}_3$ , undergo a phase transition from an orthorhombic to a monoclinic structure at low temperatures.

**Keywords**  $\text{LaVO}_3$  · Anomalous diamagnetism · Iron doped · Rietveld refinement · Mössbauer spectroscopy

## 1 Introduction

$\text{LaVO}_3$  is an orthorhombic and paramagnetic compound at room temperature (RT) known for presenting the striking anomalous diamagnetism effect in the temperature range around

---

This article is part of the Topical Collection on *Proceedings of the 15th Latin American Conference on the Applications of the Mössbauer Effect (LACAME 2016), 13-18 November 2016, Panama City, Panama*  
Edited by Juan A. Jaén

---

✉ A. Paesano Jr.  
paesano@wnet.com.br

<sup>1</sup> Universidade Estadual de Maringá, Maringá, Brazil

<sup>2</sup> Universidade de Santa Cruz do Sul, Santa Cruz do Sul, Brazil

135 K [1]. Although a model has been proposed for explaining it [2], there is no consensus about the true nature of the reversal magnetization observed for this perovskite [3]. An orthorhombic ( $Pnma$ ) to monoclinic ( $P2_1/a$ ) crystallographic transition is also attributed to this orthovanadate at low temperatures ( $\sim 147$  K), but this phase transformation is also being questioned. In orthorhombic symmetry, the  $V^{3+}$  cation occupies one site, whereas in monoclinic symmetry, it would occupy two different sites [4].

In this case, if the compound could be doped with iron,  $^{57}\text{Fe}$  Mössbauer spectroscopy would tell how many sites exist and, consequently, help to decide what the real crystalline structure at low temperatures is and understand the origin of the anomalous diamagnetism. Actually, this experiment has already been tried [3], but the low doping level and the possibility of a favorite site for iron occupation in the (possible) monoclinic lattice leave this question still unsolved.

With this aim in mind,  $\text{LaV}_{1-x}\text{Fe}_x\text{O}_3$  perovskites were synthesized in the vanadium-rich concentration range (i.e.,  $x < 0.5$ ) and characterized structurally and for the hyperfine properties of the  $^{57}\text{Fe}$  nuclear probe. Earlier, we investigated compounds of this system prepared in the  $x \geq 0.5$ -concentration range [5, 6]. However, only with the results of the present investigation we can offer evidence in favor of the crystallographic transition pointed out above.

## 2 Experimental

$\text{LaV}_{1-x}\text{Fe}_x\text{O}_3$  compounds (with  $x = 0.0, 0.05, 0.10, 0.20$  and  $0.40$ ) were prepared by arc-melting under argon atmosphere the mechanical mixture of  $\text{La}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  powders pressed in cylindrical shape. The hematite was  $^{57}\text{Fe}$  enriched to 50 %. The resulting ceramic buttons were sieved and heat treated in a hydrogen atmosphere for 40 min, at  $800^\circ\text{C}$ . Then, the samples were characterized by X-ray powder diffraction (XRPD) and by  $^{57}\text{Fe}$  Mössbauer spectroscopy (MS).

Characterization by XRPD was done with a conventional diffractometer in Bragg-Brentano reflection geometry, using  $\text{Cu K } \alpha$  radiation ( $\lambda = 1.5418\text{ \AA}$ ). The data were obtained between  $20^\circ$  and  $80^\circ$  ( $2\theta$ ), in steps of  $0.02^\circ$  and 6 s per step. The diffractograms were refined by the Rietveld method, using the FULLPROF program [7]. Zero shift, background, isotropic temperature factors, unit cell and profile parameters were refined using a pseudo-Voigt function.

The MS was conducted at RT and low temperatures, using a  $^{57}\text{Co}(\text{Rh})$  source, with 50 mCi of nominal starting activity. For the low temperature Mössbauer measurements, a closed cycle helium cryostat was used. The spectrometer was calibrated with the 14.4 keV gamma rays emitted by the source and using a metallic iron foil as absorber at RT. The Mössbauer transmission spectra were analyzed with a non-linear least square routine, with a Lorentzian line shape. The isomer shift ( $\delta$ ), quadrupole splitting ( $2\varepsilon$ ), hyperfine magnetic field ( $B_{\text{hf}}$ ) and linewidth ( $\Gamma$ ) were free to vary. A hyperfine magnetic field distribution (histogram) was applied for some spectra.

## 3 Results and discussion

Figure 1 shows the refined X-ray diffractogram for the  $\text{LaV}_{0.9}\text{Fe}_{0.1}\text{O}_3$  compound. It reveals that the compound crystallized with the orthorhombic structure ( $Pnma$ ). Other diffractograms of the  $\text{LaV}_{1-x}\text{Fe}_x\text{O}_3$  system basically reproduced this result though small amounts

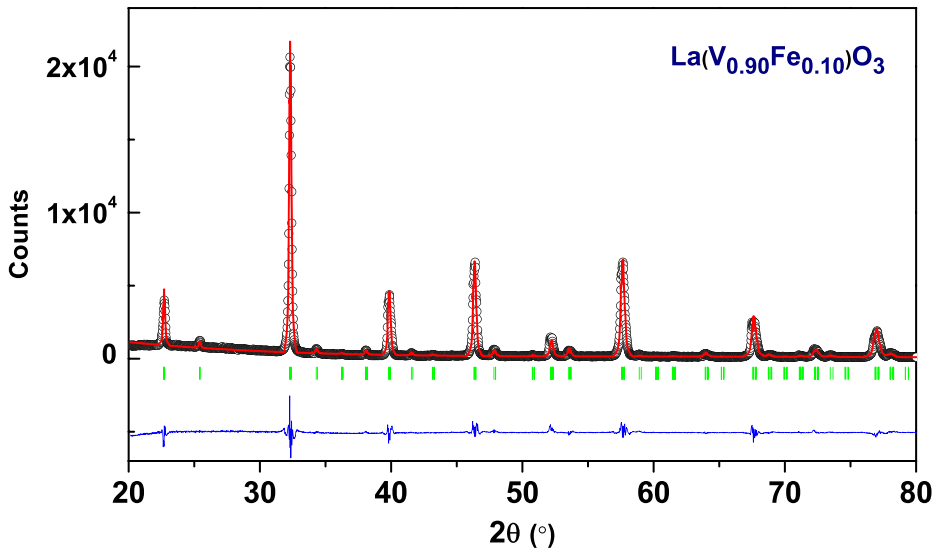


Fig. 1 Refined diffractogram for the  $\text{LaV}_{0.9}\text{Fe}_{0.1}\text{O}_3$  compound

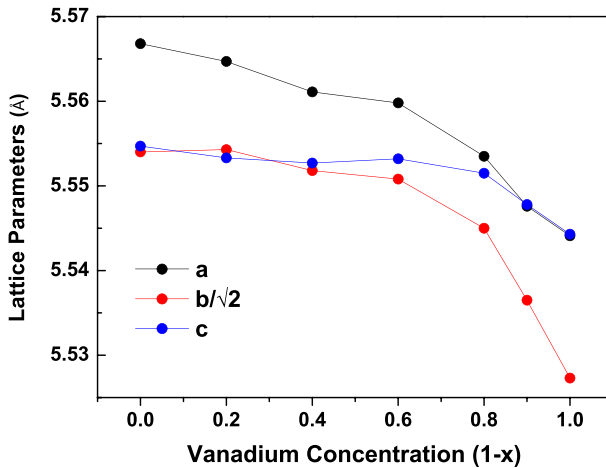
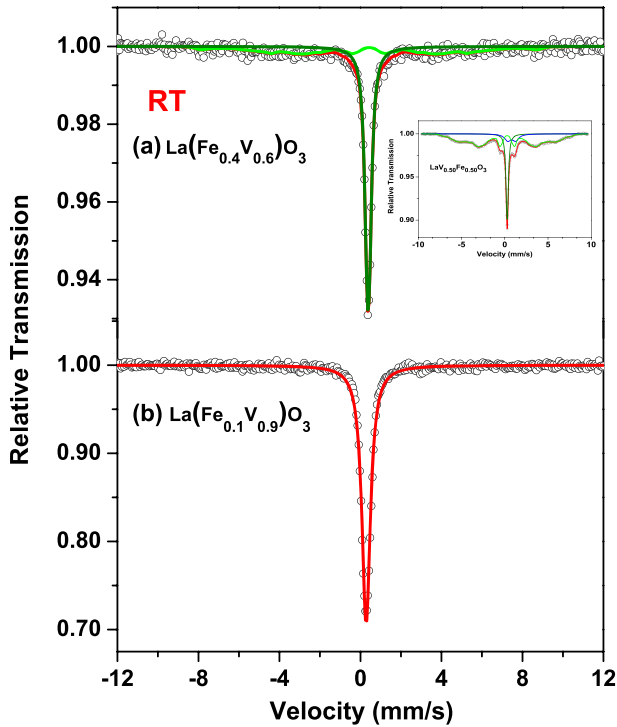


Fig. 2 Lattice parameters vs vanadium concentration, for the  $\text{LaV}_{1-x}\text{Fe}_x\text{O}_3$  system. Data for  $x \geq 0.5$  were compiled from Ref. 5

of secondary phases were detected in some samples. The variation in the lattice parameters with vanadium concentration is shown in Fig. 2.

The lattice parameters of the pseudo-ternary compounds are shown to decrease monotonically with the progressive substitution of iron by vanadium. Along the vanadium-richest concentration range, the decrease is linear. This happens because the ionic radius of  $\text{V}^{3+}$  (0.640 Å) is smaller than that of  $\text{Fe}^{3+}$  (0.645 Å) [8], with the assumption that the ferric ion enters substitutional in the orthovanadate lattice.



**Fig. 3** RT Mössbauer spectra for the  $x = 0.40$  (a) and  $0.10$  (b) samples. The insert is the  $x = 0.50$  sample spectrum, taken from Ref. 5

Some representative RT Mössbauer spectra obtained for the  $\text{LaV}_{1-x}\text{Fe}_x\text{O}_3$  samples are shown in Fig. 3. The hyperfine parameters for these and other samples are listed in Table 1. We see that the spectra do not alter significantly with increasing vanadium concentration; they change from a combination of a hyperfine magnetic field distribution in a minor fraction, and a singlet, for  $x = 0.4$ , to a unique singlet, for  $x \leq 0.20$ . The  $x \geq 0.5$  spectra obtained before [5, 6] are more magnetic and complex, as shown in the insert of Fig. 3.a.

The singlet observed in both spectra of the figure corresponds to the singlet found by Yoon [3], in spite of the difference in the iron doping level applied by the author (i.e., 1 %). Essentially, this pattern reflects the cubic symmetry of the cationic site  $4b$ , in the orthorhombic lattice.

The Mössbauer spectroscopy results obtained at low temperatures (LT) for the  $\text{LaV}_{0.90}\text{Fe}_{0.10}\text{O}_3$  compound are shown in Fig. 4. When the temperature decreased the pattern became gradually magnetic, revealing a well-defined split in the lowest temperature spectrum.

The  $x = 0.10$  LT spectra were fitted changing the component number and nature, according to the measurement temperature: from 100 K down to 80 K, a singlet was used plus a magnetic hyperfine field distribution; a discrete sextet was added for the 60 K spectrum; the singlet was removed for 40 K; finally, at 18 K, two discrete sextets composed the theoretical spectrum. For the fit of the sextet with the smallest field obtained at 18 K, the linewidths  $\Gamma_{1,6}$  and  $\Gamma_{2,5}$  were free to vary relatively to the  $\Gamma_{3,4}$ . The hyperfine parameters respective to the LT spectra are also presented in Table 1.

**Table 1** Hyperfine parameters and subspectral areas for the  $\text{LaV}_{1-x}\text{Fe}_x\text{O}_3$  samples

Sample (x)	T(K)	Site	$\delta$ (mm/s)	$2\varepsilon$ (mm/s)	$B_{\text{hf}}^*$ (T)	$\Gamma$ (mm/s)	Area (%)
0.40	RT	Singlet	0.38	–	–	0.32	64.5
		$B_{\text{hf}}$ Dist.	0.43	0.0	33.5	0.27**	35.5
0.20		Singlet	0.40	–	–	0.30	100
0.10		Singlet	0.39	–	–	0.50	100
	100	Singlet	0.50	–	–	0.71	55.4
		$B_{\text{hf}}$ Dist.	0.54	-0.08	29.2	3.0	44.6
	80	Singlet	0.50	–	–	0.71	42.1
		$B_{\text{hf}}$ Dist.	0.50	-0.01	35.0	0.27**	57.9
	60	Singlet	0.50	–	–	0.70	26.3
		$B_{\text{hf}}$ Dist.	0.52	0.01	36.6	0.27**	53.9
		Sextet 1	0.52	0.01	47.7	0.75	19.8
	40	$B_{\text{hf}}$ Dist.	0.50	-0.02	32.1	0.27**	71.1
		Sextet	0.50	-0.04	47.7	0.75	28.9
18	Sextet 1	0.51	0.01	47.8	0.48	29.5	
	Sextet 2	0.51	0.01	43.7	0.58***	70.5	
0.05	RT	Singlet	0.40	–	–	0.46	100

\*Average value for distributions; \*\*Parameter fixed in the fitting process; \*\*\*  $\Gamma_{3,4}$ ;

Definitely, our last results are different from that reported by Yoon [3], for a  $\text{LaV}_{0.99}\text{Fe}_{0.01}\text{O}_3$  sample measured in the 4.2 K – 30 K temperature range (i.e., only one sextet).

Actually, we see two magnetic components in our lowest temperature spectra taken explicitly in the fits as field distributions or as discrete sextets (in which case, the large linewidths also indicate some degree of distribution).

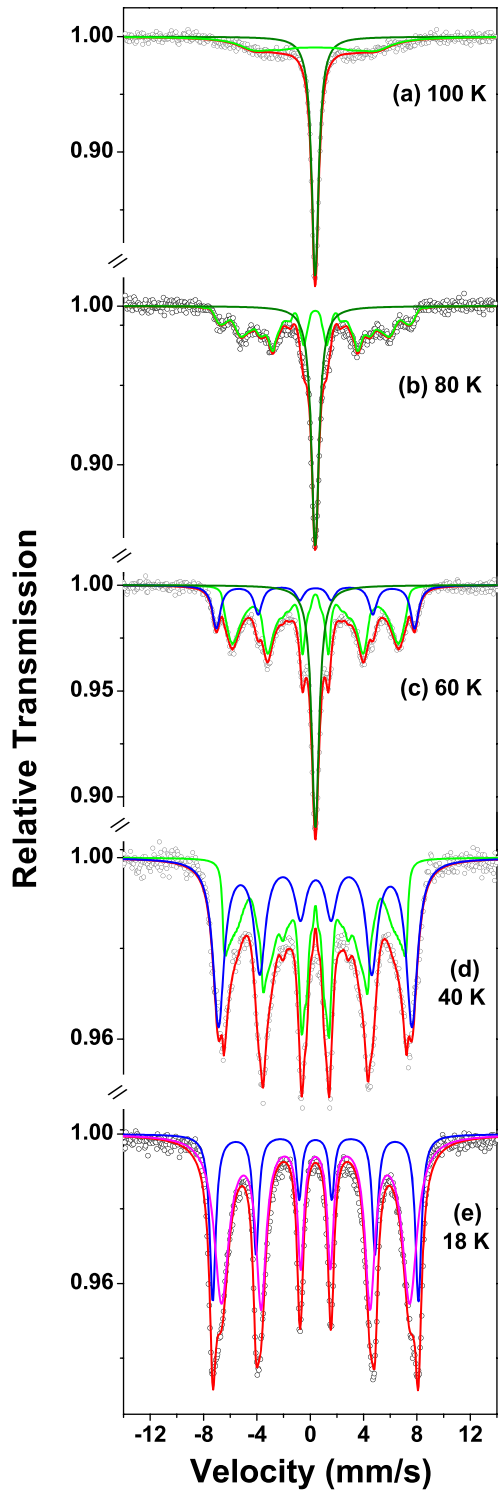
Two important questions arise at this point: (i) if the incipient freezing of the iron moment by 100 K – as observed for the  $x = 0.10$  sample (Fig. 4.a) - reflects the magnetic transition pointed out before for the  $\text{LaVO}_3$  compound (i.e.  $\text{PM} \Rightarrow \text{Weak FM}$ , by 135 K [1]), and (ii) if the two magnetic sites observed in the lowest temperature spectrum are evidence for two different crystallographic sites.

When answering these questions, it is important to recall that the doping very probably altered to some extent the “original” magnetic and structural  $\text{LaVO}_3$  properties.

From the crystallographic point of view, it was shown that no significant change was induced in the crystalline structure at RT, except a variation in the lattice parameters. Thus, it is plausible to consider that the 10 % of iron doping does not rule out the possibility of a crystallographic Orthorhombic  $\Rightarrow$  Monoclinic phase transition at low temperatures. However, the doping very probably changes the temperature of the crystallographic transition, relatively to that attributed to the  $\text{LaVO}_3$  compound.

Some analogous modification must happen in the magnetic properties of the system, since the presence of iron establishes new (super)exchange interactions, besides the original V – V (i.e. Fe-V and Fe –Fe). The relative coincidence between the temperature range of the  $\text{PM} \Rightarrow \text{AFM}$  transition of the undoped compound and the appearance of a magnetic hyperfine interaction for the iron nucleus in the  $x = 0.10$  sample is emblematic. Therefore, the two phenomena are connected and we do not see another possible origin for the  $B_{\text{hf}}$  occurrence from 100 K and below.

**Fig. 4**  $\text{La}(\text{V}_{0.90}\text{Fe}_{0.10})\text{O}_3$  low temperature Mössbauer spectra:  $T = 100$  K (a), 80 K (b), 60 K (c), and 40 K (d) and 18 K (e). — Singlet; —  $B_{hf}$  Dist.; — Sextet 1; — Sextet 2; — Theoretical;



Regarding the second question in our opinion, the presence of two hyperfine magnetic components could indicate that iron occupies two different crystallographic sites in the (monoclinic) lattice. The two components could also be consequence of some iron clustering in the (orthorhombic) matrix, in such way that iron has two different neighborhoods. The last possibility seems to us as less probable, because a statistical distribution of 10 % of iron in the orthorhombic lattice means several different neighborhoods for iron. In this case, in a fit conducted considering only one  $B_{hf}$  Dist., the field probability would appear as a more compacted curve, instead of two separated components.

In other words, we believe that the vanadium-rich samples, including  $\text{LaVO}_3$ , effectively undergo a phase transition at low temperatures, plausibly from the orthorhombic to a monoclinic structure. Although both cationic sites (i.e., 2c, 2d) are equivalent in number in the monoclinic lattice, iron shows a preference for one of the two sites which has not been identified at this moment. More experimental work must be done to find out which site is more (or less) occupied by iron and what is the explanation for the preference.

## 4 Conclusions

Vanadium-rich  $\text{LaV}_{1-x}\text{Fe}_x\text{O}_3$  perovskites are orthorhombic at RT and their lattice parameters decrease monotonically increasing the vanadium concentration.

Iron doping the  $\text{LaVO}_3$  does not rule out the  $\text{PM} \Rightarrow \text{AFM}$  magnetic transition, characteristic of the undoped compound at low temperatures; the freezing of the iron moment is reflex of this transition.

The occurrence of two magnetic subspectral components at low temperatures is consistent with an orthorhombic  $\Rightarrow$  monoclinic phase transition, but a definitive conclusion on this aspect demands for additional Mössbauer measurements, at temperatures below 18 K, involving samples with lower iron concentrations.

## References

1. Shirakawa, N., Ishikawa, M.: Anomalous Diamagnetism of a Perovskite  $\text{LaVO}_3$ . *Jpn. J. Appl. Phys.* **30**(4B), 755–756 (1991)
2. Ren, Y., Palstra, T.T.M., Khomskii, D.I., Nugroho, A.A., Menovsky, A.A., Sawatzky, G.A.: Magnetic properties of  $\text{YVO}_3$  single crystals. *Phys. Rev. B* **62**, 6577–6586 (2000)
3. Yoon, S.: Crystallographic, magnetic and Mössbauer study of phase transition in  $\text{LaVO}_3$ . *J. Magn.* **12**(3), 108–112 (2007)
4. Bordet, P., Chaillout, C., Marezio, M., Huang, Q., Santoro, A., Cheong, S.-W., Takagi, H., Oglesby, C.S., Batlogg, B.: Structural aspects of the crystallographic-magnetic transition in  $\text{LaVO}_3$  around 140 K. *J. Solid State Chem.* **106**, 253–270 (1993)
5. Tupan, L.F.S.: Síntese e Caracterização de Perovskitas do Tipo  $\text{La}(\text{Fe}_x\text{V}_{1-x})\text{O}_3$ . Master Dissertation – Universidade Estadual de Maringá Paraná PR (2014)
6. Ivashita, F.F., Biondo, V., Bellini, J.V., Paesano Jr., A., Blanco, M.C., Fuertes, V.C., Pannunzio-Miner, E.V., Carbonio, R.E.: Synthesis, structural characterization and Mössbauer study of  $\text{LnV}_0.5\text{Fe}_0.5\text{O}_3$  perovskites (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho and Er). *Mater. Res. Bull.* **47**, 2227–2234 (2012)
7. Rodríguez-Carvajal, J.: FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis at the Satellite Meeting on Powder Diffraction of the XV IUCr Congress 127 (1990)
8. Shannon, R.D.: Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr. A* **32**, 751 (1976)