

Crystallographic, Magnetic and Mössbauer Study of Phase Transition in LaVO_3

Sunghyun Yoon*

Department of Physics, Gunsan National University, Gunsan 573-701, Korea

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Nature of phase transition in LaVO_3 has been studied using X-ray diffraction, SQUID magnetometer, and Mössbauer spectroscopy with 1% of ^{57}Fe doped sample. The crystal structure was orthorhombic with space group $Pnma$. Antiferromagnetic phase transition temperature T_N was 140 K, below which a weak ferromagnetic trace has been found. Mössbauer spectra below T_N were single set of hyperfine sextet, which enabled us to discard the possibility of two inequivalent magnetic sites or uncompensated antiferromagnetism. Hyperfine magnetic field abruptly disappeared as low as about 90 K, much below T_N .

Keywords : LaVO_3 , 1% ^{57}Fe doping, Mössbauer spectroscopy, weak ferromagnetism

1. Introduction

LaVO_3 exhibits many exciting properties which can be related to orbital or spin rearrangements. Most outstanding points of dispute concern its structures above and below the transition temperature, nature of two phase transitions, and anomalous diamagnetism.

LaVO_3 was known as a simple antiferromagnetic semiconductor, undergoing a structural transition at the Nel temperature $T_N \sim 137$ K [1, 2]. Subsequently, Borukhovich *et al.* [3, 4] observed two consecutive λ points separated by about 2 K in the temperature dependence of the specific heat, which suggested that the antiferromagnetic transition occurred at a temperature different from the structural phase transition. The lower one corresponded to a magnetostrictive crystallographic distortion setting in below $T_1 < T_N$ and the upper one to a Nel temperature T_N . Bordet *et al.* [5] performed a comprehensive crystallographic diffraction study and concluded that at room temperature LaVO_3 was orthorhombic (space group $Pnma$) while it was monoclinic (space group $P2_1/a$) below the phase transition temperature. They also observed a ferromagnetic component in the low temperature neutron diffraction analysis and attributed it to a magnetic moment generated by two sets of inequivalent V sites originate from the monoclinic distortion. Previously, Shirakawa *et al.* [6] first reported that under a magnetic field of a few

hundred Oe the structural transformation was accompanied by a magnetic transition into an abnormally large diamagnetic state below 135 K. They thought that a structure of lower symmetry in low temperature brought about the weak ferromagnetic moment due to canting of spins through Dzialoshinsky-Moriya interaction and that this resultant magnetic moment changed its sign during cooling down.

However, there are two different opinions concerning the origin of the weak ferromagnetism. Several groups [5, 7, 8] speculated that the monoclinic distortion produced two independent vanadium sites, leading to uncompensated antiferromagnetism (ferrimagnetism). On the other hand, Goodenough [9] ruled out the possibility of two inequivalent magnetic sites and suggested another mechanism by which the weak ferromagnetic component rotates antiparallel to external field, giving rise to the anomalous diamagnetism. Predicating the essence of the phase transition to be first-order phase change between a localized-electron and an itinerant-electron antiferromagnetism, he claimed that both reversal of persistent atomic current responsible for vanadium angular momentum and strong spin-orbit coupling caused a diamagnetism on traversing T_1 .

Therefore, a correct answer for this controversy can be found by directly verifying whether there are two distinct crystallographic sites for transition metals in the sample. To the knowledge of author, however, there are no precedent study about this. The present experiments were undertaken to clarify the nature of phase transitions in

*Corresponding author: Tel: +82-63-469-4562,
Fax: +82-63-469-4561, e-mail: shyoon@kunsan.ac.kr

LaVO₃ mainly by measuring the Mössbauer spectra of ⁵⁷Fe doped in the specimen. The ⁵⁷Fe Mössbauer spectroscopy is an effective and decisive tool to look into the nature of magnetic transition. It is quite useful for the study of LaVO₃ as long as a small quantity of ⁵⁷Fe can substitute V in LaVO₃ without any disturbance to the intrinsic properties. This assumption was found to be correct by the crystallographic and magnetic investigations throughout this work. Moreover many previous works also confirmed that doped Fe can be regarded as a reliable probe to manifest the nature of a magnetic transition.

2. Experiments

Polycrystalline LaVO₃ sample was prepared by a two-step solid state reaction [10]. For the Mössbauer measurement, 1% of the vanadium sites were replaced by iron. Stoichiometric mixture of La₂O₃, V₂O₃ and Fe₂O₃ (97% enriched in ⁵⁷Fe) powders was intimately ground and fired at 900°C for 5 hours for calcination. After re-grinding, followed by press-molding into a pellet, the precursor was sintered at 1100°C in air for 30 hours. LaVO₃ was obtained by grinding and heating this at 950°C under a flow of H₂/Ar balance gas for 1 day.

Powder X-ray diffraction (XRD) pattern of the sample was obtained with Cu K α radiation. The pattern was taken at room temperature over the range of $10^\circ \leq 2\theta \leq 80^\circ$ with a slow scanning speed of 0.5° advance in 2θ per min. to enhance the resolution. Rietveld profile refinement was carried out using the GSAS program package [11]. The dc magnetic moment was measured in a temperature range $5 \text{ K} \leq T \leq 300 \text{ K}$ using a SQUID magnetometer. The measurements were done both after cooling the sample under zero field [zero-field-cooled (ZFC) case] and after cooling in the measuring field [field-cooled (FC) case]. A Mössbauer spectrometer of a conventional transmission type was used with the constant acceleration mode over a temperature range from 4.2 K to 300 K. A ⁵⁷Co source in a Rhodium matrix was used at room temperature.

3. Results and Discussion

The measured XRD pattern of the sample showed a single phase with no trace of impurity. The diffraction pattern was analyzed by Rietveld method using the orthorhombic space group *Pnma*, isostructural with GdFeO₃. At first, only profile parameters were refined until a convergence was attained. A profile function formed by a convolution of pseudo-Voigt shape (CW profile function

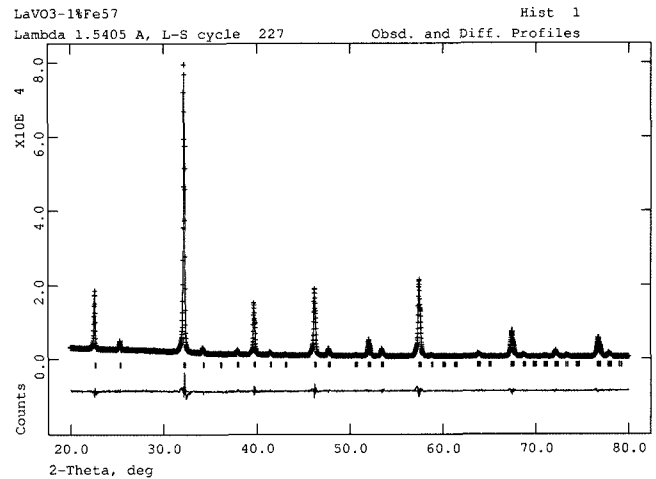


Fig. 1. Observed (···), calculated (—), and difference curves in the XRD profile for 1% ⁵⁷Fe-doped LaVO₃ at room temperature.

No. 3 provided in the package) was used. Once a minimum had been reached for a set of profile parameters, then atomic parameters such like positions and isotropic thermal factors were varied in the next process of refinement. The fractions of the atoms were fixed to a full occupancies under the assumption that there were no vacancies in either metal sites or oxygen sites. Consequently, 39 variables were refined simultaneously. The final observed and calculated XRD profile is illustrated in Fig. 1, and the corresponding crystallographic data are given in Table 1. Close look at the bond angles indicates that

Table 1. Structural parameters, bond lengths and bond angles for 1% ⁵⁷Fe-doped LaVO₃ powder at room temperature. (space group: *Pnma*)

Bond lengths (Å)		Bond angles (°)	
V - O1	1.991×2	O1 - V - O1	179.98
V - O2	1.85×2	O1 - V - O2	69.4×2
V - O2	2.18×2	O1 - V - O2	75.6×2
		O1 - V - O2	104.4×2
La - O1	2.48	O1 - V - O2	110.6×2
La - O1	2.572	O2 - V - O2	86.7×2
La - O1	3.025	O2 - V - O2	93.3×2
La - O1	3.10	O2 - V - O2	180.0×2
La - O2	2.44×2		
La - O2	2.645×2	V - O3 - V	160.0
La - O2	2.831×2	V - O4 - V	154.0
lattice constants (Å)		a = 5.5487	
		b = 7.8439	
		c = 5.5583	
fitted wRp = 8.59%			
fitted Rp = 6.24%			
Rb = 6.06%			

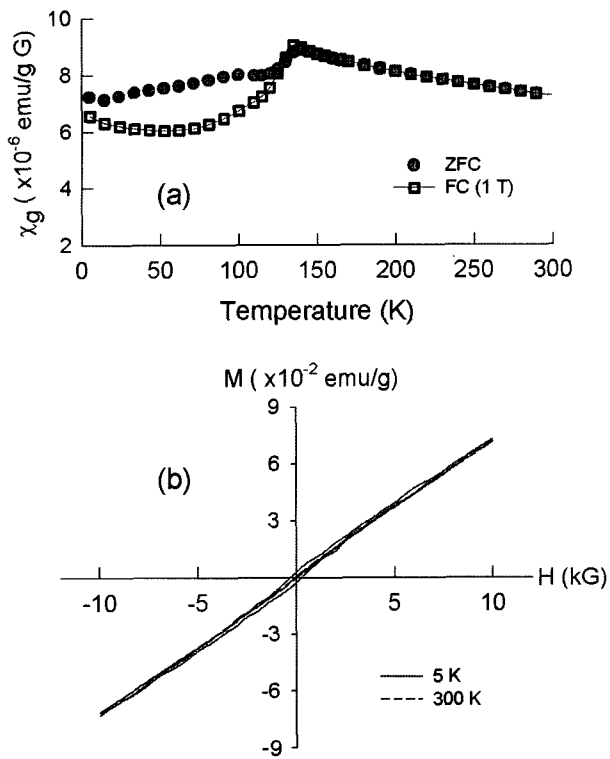


Fig. 2. (a) Measured susceptibility as a function of temperature taken upon 1 T FC and ZFC, and (b) $M(H)$ hysteresis curves at 300 K and 5 K (ZFC) for 1% ⁵⁷Fe-doped LaVO₃.

rhombohedral distortion within a VO₆ octahedron is slightly less than the bending between two adjacent octahedra [12]. It is clear from the lattice constants that a relation $b/\sqrt{2} < a \leq c$ holds for this sample. This is classified as an O'-orthorhombic $Pnma$ structure; this can be encountered when a deformation of the VO₆ octahedra is superimposed on a cooperative rotation of the VO₆ octahedra. On the other hand, if the VO₆ octahedra remain undistorted, the cooperative distortion result in a conventional O-orthorhombic $Pnma$ structure in which the relation $c \leq a < b/\sqrt{2}$ is normally found. Goodenough [9] insisted that this O'-orthorhombic nature of LaVO₃ was a potential origin for the first-order magnetostrictive distortion which brought about a spin canting.

Since the low-temperature XRD was not available, we went over the temperature dependence of magnetic susceptibility in order to verify the sample. Fig. 2(a) shows the magnetic susceptibility of 1% ⁵⁷Fe-doped LaVO₃ taken upon both cooling in magnetic field of 1 T and zero field cooling. It exhibits a peak at $T_N \sim 140$ K, indicative of antiferromagnetic-paramagnetic phase transition. The FC and ZFC curves well overlap above T_N . However, a divergence of FC from ZFC data can be seen below the transition temperature, reminding the magnetism of spin

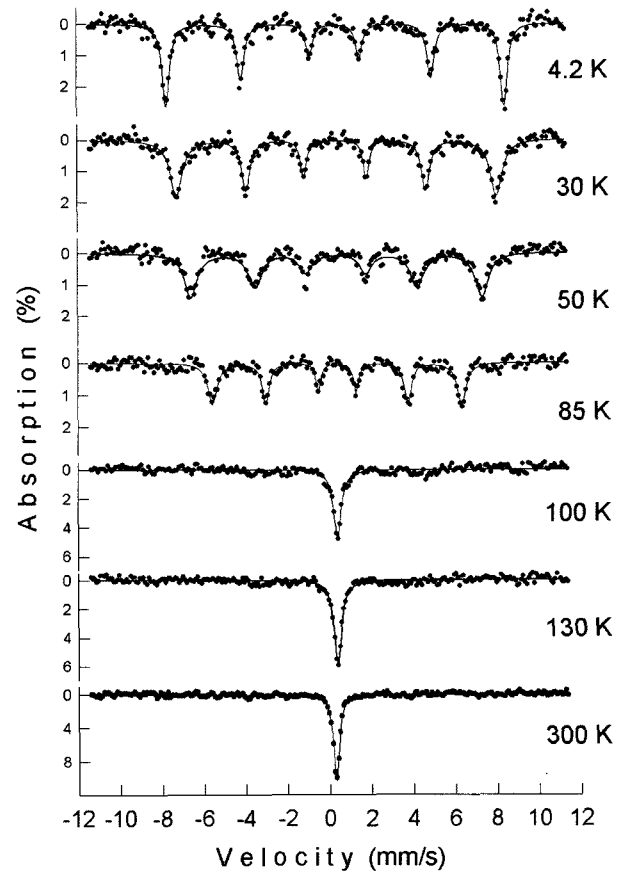


Fig. 3. Mössbauer spectra for 1% ⁵⁷Fe-doped LaVO₃ at various temperatures.

glasses. However, it is unusual in that the ZFC curve places above the FC curve. Below this transition temperature, the FC susceptibility abruptly started decreasing and reached the minimum around 50 K. This trend is consistent with that reported by Shirakawa *et al.* [6], who have first noticed a large diamagnetic anomaly in the FC susceptibility. Fig. 2(b) displays the ZFC hysteresis curves for 1% ⁵⁷Fe-doped LaVO₃ at 5 K and 300 K, which are well-below and well-above T_N , respectively. At 300 K, $M(H)$ isotherm is entirely paramagnetic and the remanent ferromagnetic moment as deduced from the curve is zero. At 5 K, however, the hysteresis curve shows faint ferromagnetic component, suggesting the presence of spin ordering due to either spin canting or uncompensated ferrimagnetism. This is consistent with the existence of magnetic peaks neutron diffraction profiles below T_N [5, 13]. No matter what might be the real cause for the tiny ferromagnetic component, that should be deeply related with the structural distortion at low temperature.

So far we have demonstrated that 1%-doping of ⁵⁷Fe into the sample did not alter the crystallographic and magnetic properties at all. Mössbauer spectra for 1%

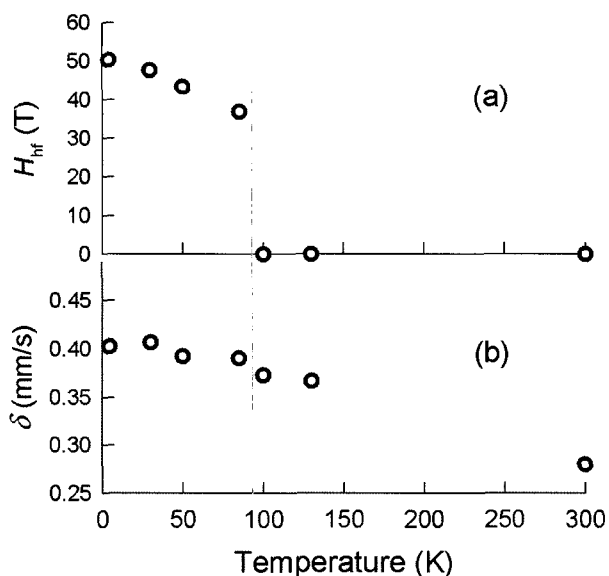


Fig. 4. Variations of hyperfine magnetic field H_{hf} and isomer shift δ for 1% ^{57}Fe -doped LaVO_3 with temperature.

^{57}Fe -doped LaVO_3 taken at various temperatures are depicted in Fig. 3. At 4.2 K, the spectrum is comprised of single magnetic sextet pattern with hyperfine magnetic field of 50.3 T and isomer shift of 0.41 mm/s, respectively. This spectrum is ascribed to Fe^{3+} ions in the octahedral site. The magnetic hyperfine field value is somehow smaller than that of $\alpha\text{-Fe}_2\text{O}_3$ at 4.2 K, which is about 56.3 T. Up to 85 K, spectra are well-resolved six-line patterns. However, collapse in the hyperfine pattern takes place around about 90 K, which is much below the transition temperature $T_N \sim 140$ K deduced from above magnetic investigations. Hyperfine magnetic field and isomer shift as a function of temperature are shown in Fig. 4. The magnetic hyperfine splitting seems to collapse abruptly in the narrow temperature range of 85~100 K. The isomer shift, however, seems to decrease monotonically, not showing any significant variation at that temperature range within the experimental error. It seems that the transition concerning the disappearance of the hyperfine magnetic field does not affect the s-electron density at the nucleus. With further increasing temperature, purely paramagnetic singlet spectra were obtained. This means that Fe_2O_3 were completely dissolved in LaVO_3 matrix without clustering themselves. Furthermore, the low doping level of Fe ensures that there is no chance of direct Fe-O-Fe interaction.

It is intriguing to note that Mössbauer spectrum transforms to singlet much below the Néel temperature T_N . We can find precedent example for the similar behavior. Our result resembles the case of some vanadium oxides. V_2O_3 is the most well-known compound which exhibits metal-

Table 2. Results of Mössbauer analysis at various temperatures for 1% ^{57}Fe -doped LaVO_3 . (H_{hf} : hyperfine magnetic field; δ : isomer shift)

T (K)	H_{hf} (T)	δ (mm/s)	Γ (mm/s)	Absorption area
4.2	50.3	0.41	0.41*	0.071
30	47.6	0.40	0.47*	0.078
50	43.3	0.40	0.54*	0.073
85	37.0	0.39	0.48*	0.046
100	0	0.37	0.45	0.046
130	0	0.37	0.43	0.040
300	0	0.28	0.38	0.033

*average over six lines

semiconductor transition accompanied with an antiferromagnetic transition at $T_N \sim 150$ K at which a corundum type to monoclinic structural transition occurs as well. Shinjo *et al.* [14] found that Mössbauer spectra of ^{57}Fe -doped V_2O_3 became a paramagnetic singlet much below the Néel temperature T_N . The large difference between T_N and the temperature where hyperfine magnetic field disappears suggests that the magnetic ordering in LaVO_3 matrix is not a main origin for the transition observed by Mössbauer spectroscopy. Rather, this can be anticipated under the assumption that Fe-O-V super-exchange interaction is much weaker than that of V-O-V so that spins of Fe ion are isolated out of the LaVO_3 matrix. It is also notable from Table 2 that total absorption area decreased considerably at 85 K, which reflects the weakened atomic binding through the recoil-free-fraction of Fe ions.

If Fe is trivalent, the quadrupole splitting should have emerged in consideration of the lattice distortion in the low temperature region. There are no quadrupole splittings within experimental error. Since the magnetic hyperfine field can take random direction with respect to the principal axes of electric field gradient, the average of quadrupole splitting taken over all directions vanishes. However, the line broadening from this random distribution is not zero [15]. The averaged half line width at 85 K was 0.48 mm/s. Under the same experimental condition, that of the standard absorber was 0.28 mm/s. It is obvious that the additional line broadening is due to the distribution of quadrupole splitting from random orientation.

4. Conclusion

The nature of phase transitions in 1% ^{57}Fe -doped LaVO_3 was studied by means of structural, magnetic, and Mössbauer spectroscopic methods. The Rietveld profile analysis of room temperature XRD data showed that the sample had an orthorhombically distorted perovskite structure, isostructural with GdFeO_3 with the space group

Pnma. It showed antiferromagnetic-paramagnetic phase transition at $T_N \sim 140$ K. At 5 K, the hysteresis curve shows faint ferromagnetic component, suggesting the presence of weak ferromagnetism. As for the Mössbauer analysis, two distinguishable features can be mentioned: First, Mössbauer spectra below T_N showed single set of six-line pattern. With the assumption that Fe ions occupy different magnetic sites with equal probabilities, this indicates that two inequivalent magnetic sites or uncompensated antiferromagnetism is not identified. From this, we can conclude that Goodenough's explanation for the weak ferromagnetism is correct. However, Mössbauer spectra abruptly transforms to singlet much below the Nel temperature, meaning that the magnetic transition in LaVO₃ matrix is not a main origin for the transition observed by Mössbauer spectroscopy.

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