Mössbauer effect on the FeV_2O_4 spinel nanoparticles

Chun-Rong Lin[a*](林春榮), Shao-Yi Lu [a] (呂紹亦), Yu-Jhan Siao[a] (蕭育展)
Igor S. Lyubutin[b], Yurii V. Korzetskii[b]

[a]Department of Mechanical Engineering, Southern Taiwan University of Technology, Tainan County 710, Taiwan, ROC
[b]Institute of Crystallography, Russian Academy of Sciences, Moscow 119333, Russia

The FeV_2O_4 spinel nanoparticles with average crystallite sizes *d* ranging from 3.7 to 19.6 nm were prepared by the combustion method. The magnetic properties of samples can go from paramagnetic to ferromagnetic depending on the sizes of FeV_2O_4 nanoparticles. In addition, magnetic ordering temperatures, coercivity and magnetization decrease as the crystallite size decreases. For samples with crystallite size greater than 7.4 nm, a wasp-waisted hysteresis loop and loop shift were found during the zero-field-cooled (ZFC) and field-cooled (FC) measurements, respectively. The ^{57}Fe Mössbauer spectra of samples, recorded at temperatures 80 K and 300 K, were applied to investigate the size effect on the magnetic, structural and oxidation states of iron ions in the nanoparticles. In classical presentation (for bulk material), FeV_2O_4 is a normal spinel $(Fe^{2+})_A[V^{3+}{}_2]_BO_4$, where A and B are tetrahedral and octahedral sites, respectively. However, we found that the change of magnetic behavior along with the variation of particle sizes result from the rearrangement of cation distributions in nanoparticles. In all samples, only a part of Fe ions are magnetically ordered at 80K. This part depends on the crystallite size: from 10% (in d = 3.7 nm) to 33% (in d = 19.6 nm). In the smallest particles with d =3.7 and 4.3 nm, magnetically ordered iron ions have isomer shift (*IS*) value of about 0.66 mm/s, which is at the border between Fe^{3+} and Fe^{2+} charge states, and it implies $Fe^{2.5+}$ state. Moreover, the doublet from Fe^{2+} with very large quadrupole splitting (*QS* = 2.55 - 2.67 mm/s) appears, along with another doublet with *QS* = 2.00 - 2.10 mm/s. It seems that these are due to Jan-Teller and surface effects.

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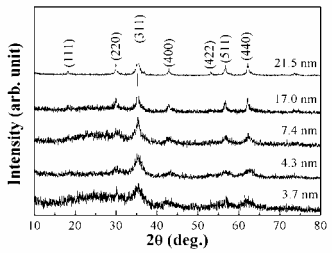

Fig. 1. XRD patterns of FeV_2O_4 nanoparticles with various crystallite sizes.

Table 1. Thermal treatment conditions, lattice constant (*a*), crystallite size (*d*), coercive force (H_C), magnetization measured at 1.1 tesla ($\sigma_{1.1\,T}$), magnetic ordering temperature (T_C) of FeV_2O_4 nanoparticles.

Samples	Thermal treatment conditions	*a* (Å)	*d* (nm)	H_C(78 K) (Oe)	$\sigma_{1.1\,T}$(78 K) (μ_B/formula)	T_C (°C)
FV1	450 °C, Ar, 2 hrs 450 °C, 10 % H_2/Ar, 2 hrs	5.898	3.7	55	0.36	–
FV2	450 °C, Ar, 2 hrs 450 °C, 10 % H_2/Ar, 2 hrs 500 °C, 10 % H_2/Ar, 4 hrs	5.898	4.3	135	0.45	–
FV3	450 °C, Ar, 2 hrs 450 °C, 10 % H_2/Ar, 2 hrs 600 °C, 10 % H_2/Ar, 4 hrs	5.896	7.4	420	0.32	112
FV4	450 °C, Ar, 2 hrs 450 °C, 10 % H_2/Ar, 2 hrs 600 °C, 10 % H_2/Ar, 10 hrs	5.895	17.3	978	0.33	117
FV5	450 °C, Ar, 2 hrs 450 °C, 10 % H_2/Ar, 2 hrs 600 °C, 10 % H_2/Ar, 16 hrs	5.894	21.6	1440	0.38	118

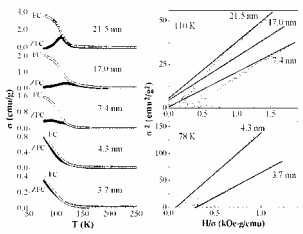

Fig. 2. Temperature dependence of the ZFC and FC magnetization curves measured under an applied field of 100 Oe (left) and Arrott plots (right) for FeV_2O_4 nanoparticles with various crystallite sizes.

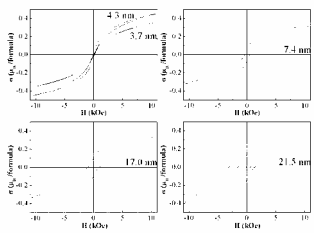

Fig. 3. Hysteresis loops measured at 78 K under FC and ZFC conditions for FeV_2O_4 nanoparticles with various crystallite sizes.

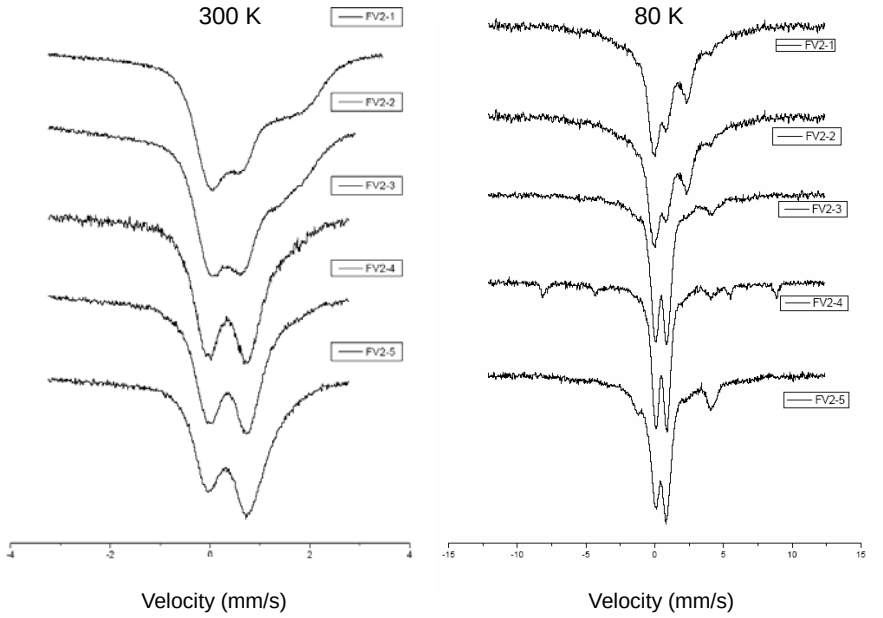

Fig. 3 Mossbauer spectra of FeV_2O_4 nanoparticles with various crystallite sizes obtained at 80 and 300 K.

Table 2. Hyperfine parameters of the ^{57}Fe-Mossbauer spectra for FeV_2O_4 nanoparticles with various crystallite sizes. H_{hf} is the hyperfine magnetic field at ^{57}Fe nuclei, *IS* is the isomer shift relative to α-Fe at room temperature, *QS* is the quadrupole shift, *S* is the area of the spectrum component, and Γ is the line width.

d = 21.5 nm						
T =300 K		H_{hf}(kOe)	*IS* (mm/s)	*QS* (mm/s)	*S* (%)	Γ (mm/s)
Doublet-1	Fe^{3+}	-	0.382	0.795	38.5	0.54
Doublet-2	$Fe^{2.5+}$	-	0.589	1.016	51.7	1.16
Doublet-3	Fe^{2+}	-	0.808	0.307	9.8	0.47
T =80 K						
Sextet-1	Fe^{3+}	172.2	1.169	0.437	36.9	1.03
Doublet-1	Fe^{3+}	-	0.304	0.907	13.1	0.46
Doublet-2	Fe^{3+}	-	0.542	0.806	50.0	0.69

d = 17.0 nm						
T =300 K		H_{hf}(kOe)	*IS* (mm/s)	*QS* (mm/s)	*S* (%)	Γ (mm/s)
Doublet-1	Fe^{3+}	-	0.363	0.756	87.6	0.66
Doublet-2	Fe^{2+}	-	0.754	1.927	4.1	0.42
Doublet-3	Fe^{2+}	-	0.955	0.358	8.3	0.57
T =80 K						
Sextet-1	Fe^{2+}	172.9	1.255	0.267	15.4	1.13
Sextet-2	Fe^{3+}	525.3	0.484	- 0.234	11.1	0.47
Doublet-1	Fe^{3+}	-	0.484	0.822	72.4	0.63
Doublet-2	Fe^{2+}	-	0.904	2.325	1.1	0.29

d = 7.4 nm						
T =300 K		H_{hf}(kOe)	*IS* (mm/s)	*QS* (mm/s)	*S* (%)	Γ (mm/s)
Doublet-1	Fe^{3+}	-	0.369	0.821	85.6	0.70
Doublet-2	Fe^{2+}	-	0.883	1.938	5.4	0.47
Doublet-3	Fe^{2+}	-	1.034	0.790	9.1	0.52
T =80 K						
Sextet-1	Fe^{2+}	181.6	1.253	0.1149	20.8	0.77
Doublet-1	Fe^{3+}	-	0.482	0.862	77.2	0.69
Doublet-2	Fe^{2+}	-	1.031	2.576	2.1	0.32

d = 4.3 nm						
T =300 K		H_{hf}(kOe)	*IS* (mm/s)	*QS* (mm/s)	*S* (%)	Γ (mm/s)
Doublet-1	Fe^{3+}	-	0.370	0.725	57.5	0.79
Doublet-2	Fe^{2+}	-	0.919	1.902	19.4	0.68
Doublet-3	Fe^{2+}	-	0.923	0.914	23.2	0.65
T =80 K						
Sextet-1	$Fe^{2.5+}$	216.0	0.653	0.126	24.6	1.36
Doublet-1	Fe^{3+}	-	0.419	0.951	34.1	0.88
Doublet-2	Fe^{2+}	-	1.076	2.474	32.2	1.28
Doublet-3	Fe^{2+}	-	1.273	2.101	9.2	1.17

d = 3.7 nm						
T =300 K		H_{hf}(kOe)	*IS* (mm/s)	*QS* (mm/s)	*S* (%)	Γ (mm/s)
Doublet-1	Fe^{3+}	-	0.340	0.731	44.7	0.68
Doublet-2	Fe^{2+}	-	0.958	1.954	27.4	0.74
Doublet-3	Fe^{2+}	-	0.878	1.004	27.9	0.78
T =80 K						
Sextet-1	$Fe^{2.5+}$	215.7	0.655	0.088	10.6	1.30
Doublet-1	Fe^{3+}	-	0.467	0.842	38.1	0.90
Doublet-2	Fe^{2+}	-	1.102	2.667	29.4	0.78
Doublet-3	Fe^{2+}	-	1.094	2.005	22.0	0.91

Chun-Rong Lin
Department of Mechanical Engineering, Southern Taiwan University,
E-mail : crlin@mail.stut.edu.tw
Tel : +886-6-2533131 ext. 3547
Fax : +886-6-2425092