

**This presentation is a part of my oral presentation in Annual Conference  
on Magnetism and Magnetic Materials (MMM) held in Las Vegas from  
Nov 4-8, 2019.**



# Experimental and Theoretical study of influence of mixing the low-valent transition metal atoms ( $Y = V$ , and $Cr$ ) on the structural, magnetic, transport, and mechanical properties of the Heusler alloys $Fe_{3-x}Y_xGe$

Rabin Mahat

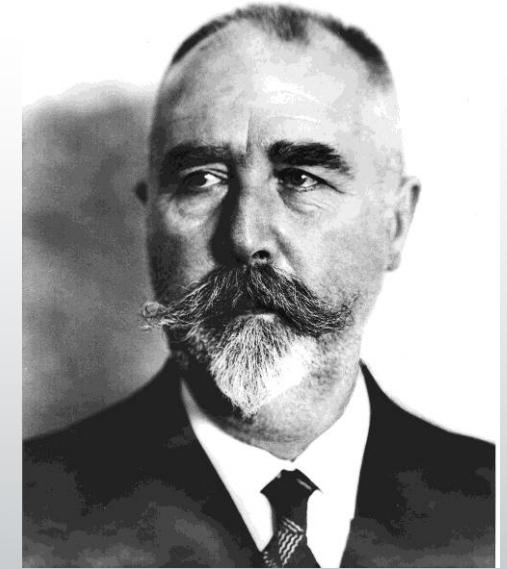
Department of Physics and Astronomy

11/05/2019

# The Heusler System



Cu      Mn      Al

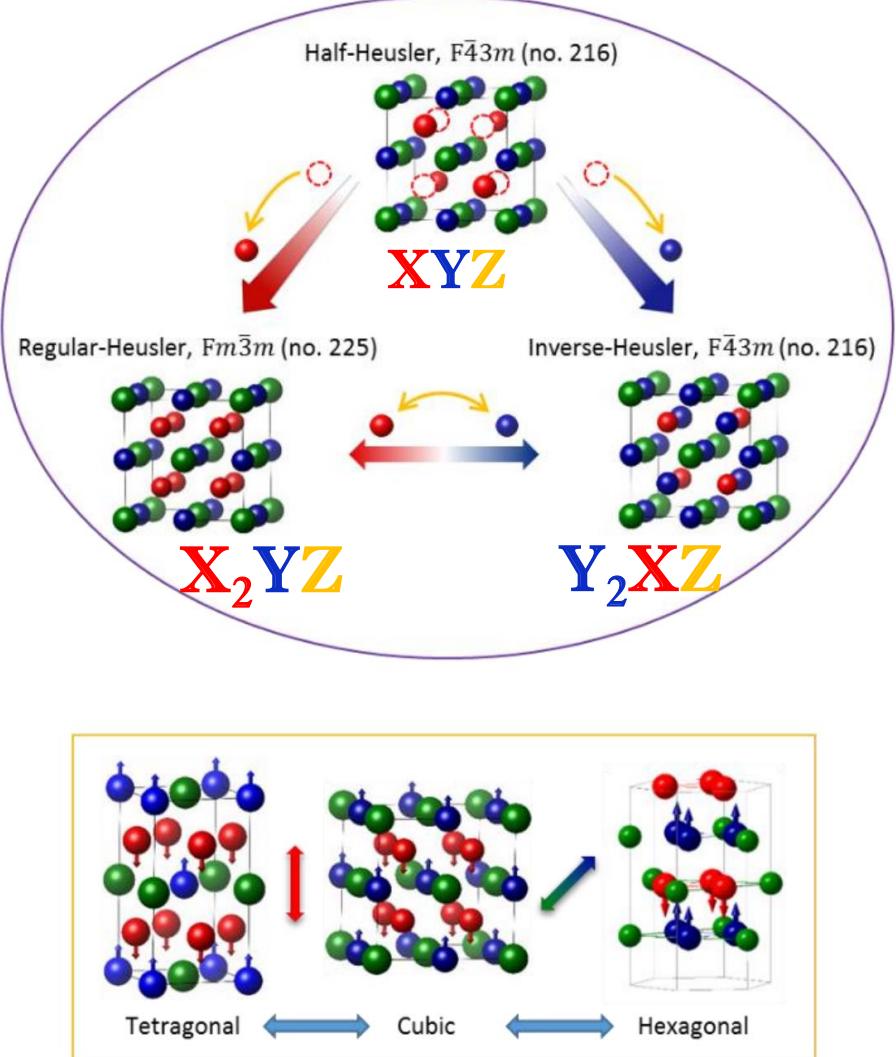


Friedrich Heusler

125 years Heusler alloys



# The Heusler System



$X_2YZ$ Heusler compounds																	
H	2.20																He
Li	0.98	Be	1.57														Ne
Na	0.93	Mg	1.31														
K	0.82	Ca	1.00	Sc	1.36	Ti	1.54	V	1.63	Cr	1.66	Mn	1.55	Fe	1.83	Ni	Cu
Rb	0.82	Sr	0.95	Y	1.22	Zr	1.33	Nb	1.60	Mo	2.16	Tc	1.90	Ru	2.20	Rh	Pd
Cs	0.79	Ba	0.89									Ag	1.93	Cd	1.69	In	Sn
Fr	0.70	Ra	0.90									Ge	1.81	As	2.01	Br	Kr
				Hf	1.30	Ta	1.50	W	1.70	Re	1.90	Os	2.20	Ir	2.20	Pt	Au
																Hg	Tl
																Pb	Bi
																Po	At
																	Rn
La	1.10	Ce	1.12	Pr	1.13	Nd	1.14	Pm	1.13	Sm	1.17	Eu	1.20	Gd	1.20	Tb	Dy
Ac	1.10	Th	1.30	Pa	1.50	U	1.70	Np	1.30	Pu	1.28	Am	1.13	Cm	1.28	Bk	Cf
																	Es
																Fm	Md
																No	Lr

Graf et al., *Progress in solid state chemistry*, 39(1), pp.1-50



# The Heusler System



## Half metallic Ferro-magnetics (HFM)

- Band gap in one spin channel at Fermi level
- Integer magnetic moment : Slater-Pauling rule

### Types:

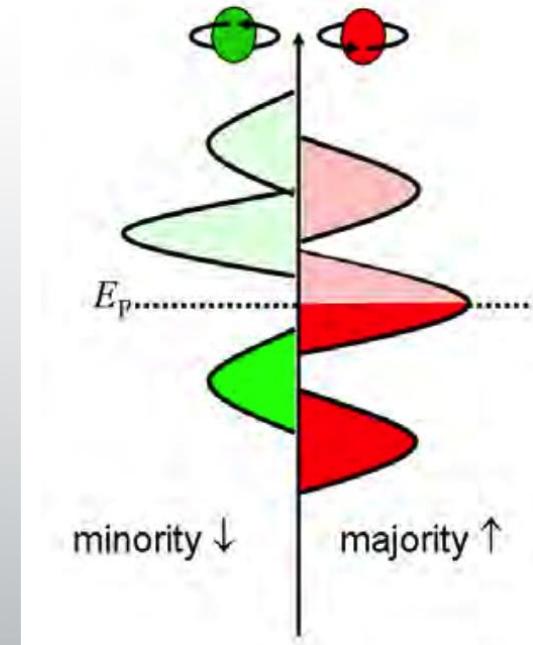
- Oxide compounds (Rutile  $\text{CrO}_2$  ; spinel  $\text{Fe}_3\text{O}_4$ )
- Perovskites  $[(\text{La},\text{Sr})\text{MnO}_3]$
- Zinc-blende compounds (zb-GaAs)
- Heusler alloys ( $\text{Ni}_2\text{MnSb}$ )

### What do we need???

- High curie temperature
- Adjusted  $E_f$
- Low magnetic moment
- High spin polarization of conduction electrons

$$P = \frac{n\uparrow(E_f) - n\downarrow(E_f)}{n\uparrow(E_f) + n\downarrow(E_f)} = 100\%$$

- Highly Ordered crystal structure



# The Heusler System



Goal : Directed Design of new multifunctional materials

$X_2YZ$ Heusler compounds																		He		
H 2.20																		He		
Li 0.98	Be 1.57																	He		
Na 0.93	Mg 1.31																	He		
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00			
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.60	Mo 2.16	Tc 1.90	Ru 2.20	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe 2.60			
Cs 0.79	Ba 0.89		Hf 1.30	Ta 1.50	W 1.70	Re 1.90	Os 2.20	Ir 2.20	Pt 2.20	Au 2.40	Hg 1.90	Tl 1.80	Pb 1.80	Bi 1.90	Po 2.00	At 2.20	Rn 2.27			
Fr 0.70	Ra 0.90					La 1.10	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.20	Gd 1.20	Tb 1.10	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.10	Lu 1.27
						Ac 1.10	Th 1.30	Pa 1.50	U 1.70	Np 1.30	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.30	Cf 1.30	Es 1.30	Fm 1.30	Md 1.30	No 1.30	Lr 1.30

Our tool box : The periodic table

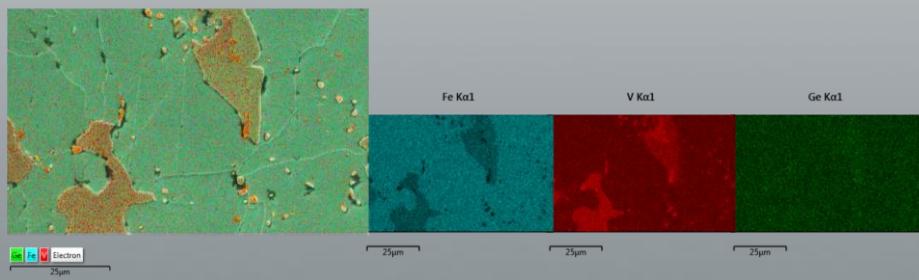


# $\text{Fe}_2\text{YGe}$ ; Y = Mn, Cr, V, Ti & Sc

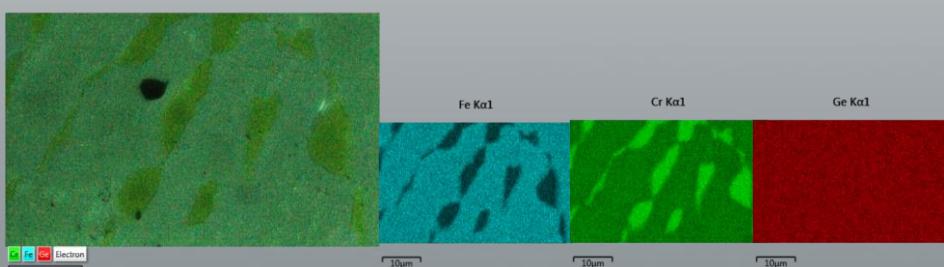
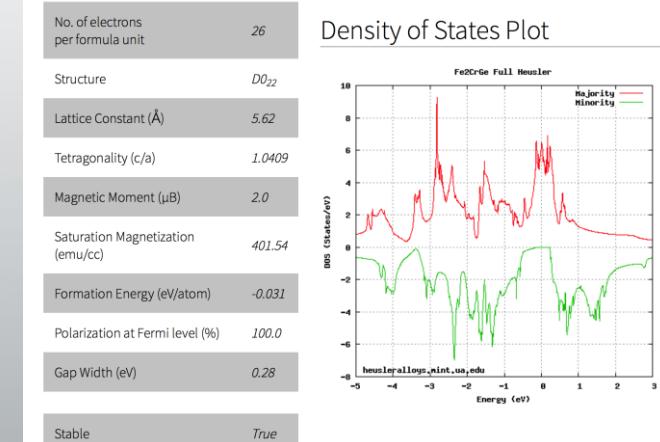


- More than 1000 heusler compounds in <http://heusleralloys.mint.ua.edu/search/>
- New candidates for stable half-metallic Heusler compounds were selected for experimental investigations.

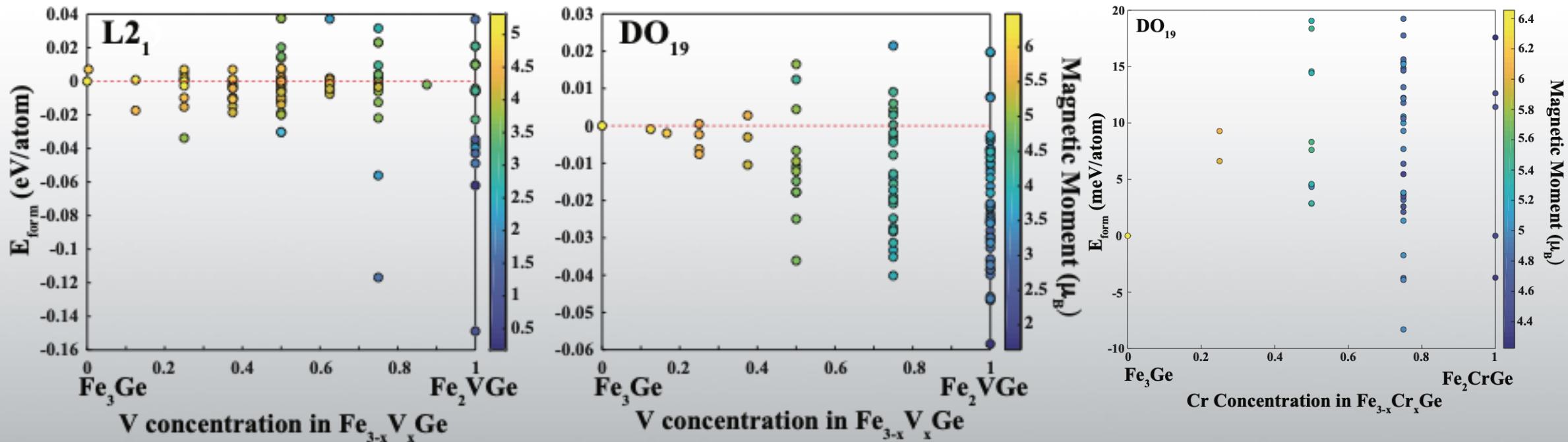
$\text{Fe}_2\text{VGe}$



$\text{Fe}_2\text{CrGe}$



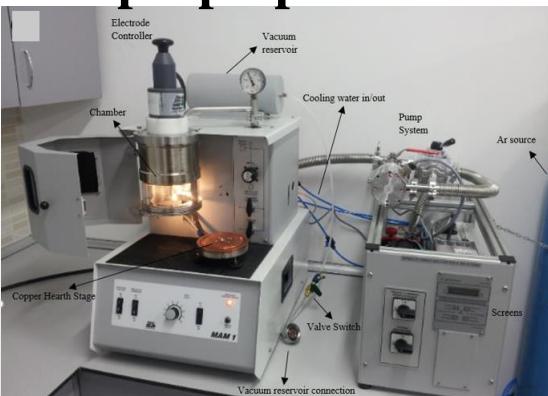
# $\text{Fe}_{3-x}\text{Y}_x\text{Ge}$ : Ground states



- The formation energy (in eV/atom) as a function of V/Cr concentration for the L2<sub>1</sub> and DO<sub>19</sub> alloys created with the Special Quasirandom Structures (SQS) method.

# Sample preparation &characterization

## Sample preparation



## Sample characterization

### Microstructure Analysis

- ❖ Grain Formation
- Optical Microscope & SEM

### Compositional Analysis

- ❖ Stoichiometry & phase distribution
- EDX/EBSD

### Structural Analysis

- ❖ Crystal Structure and atomic ordering
- XRD

### Magnetometry & Transport

- ❖  $M_s$  at low temperature,  $T_c$ ,  $R(T)$ .
- PPMS

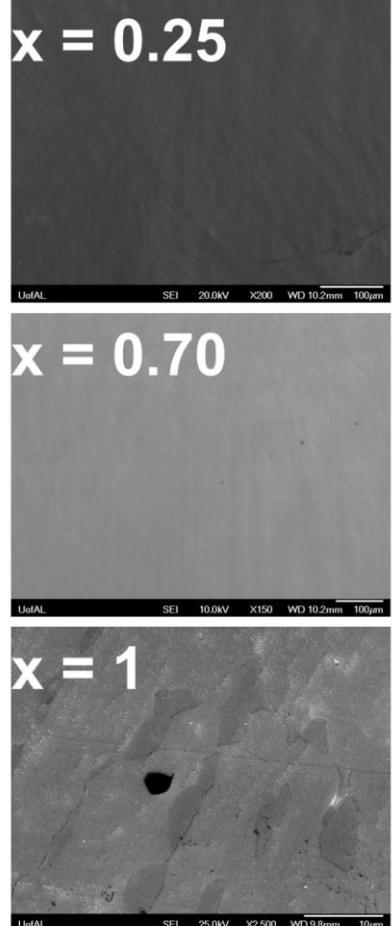
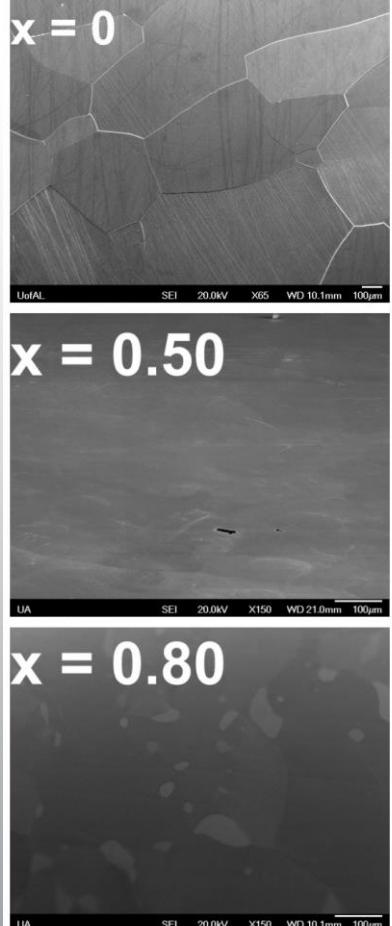
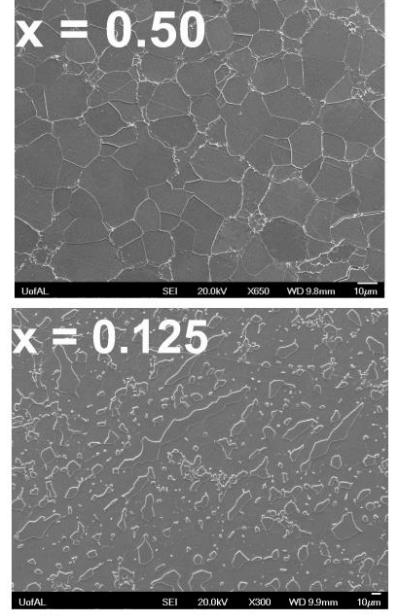
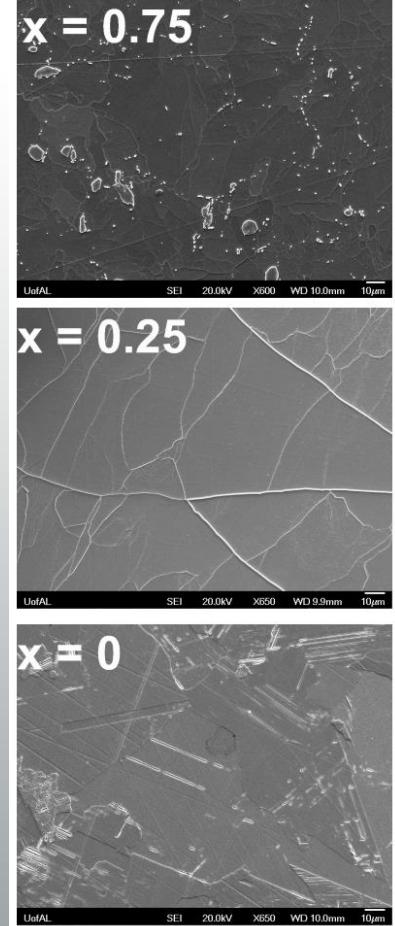
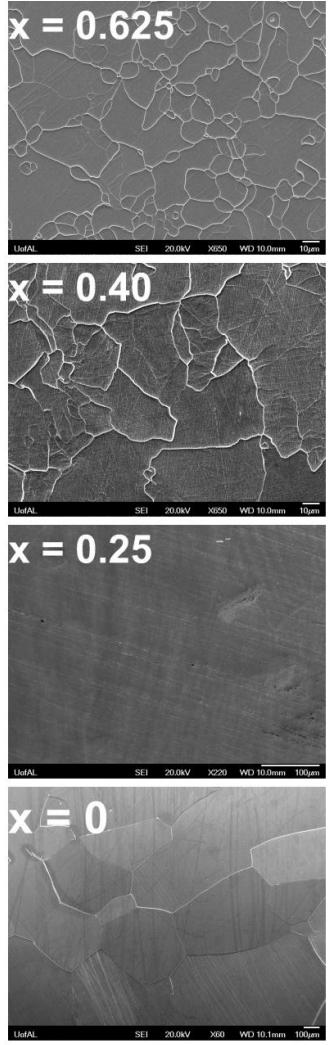
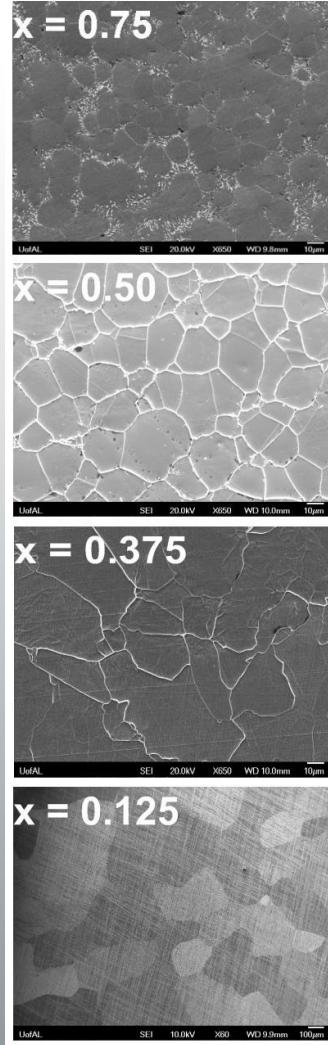


Arc  
Melting

Heat  
Treatment

Metallography

# $\text{Fe}_{3-x}\text{Y}_x\text{Ge}$ : Microstructure and Composition



$\text{Fe}_{3-x}\text{V}_x\text{Ge}$  : 7D 950C

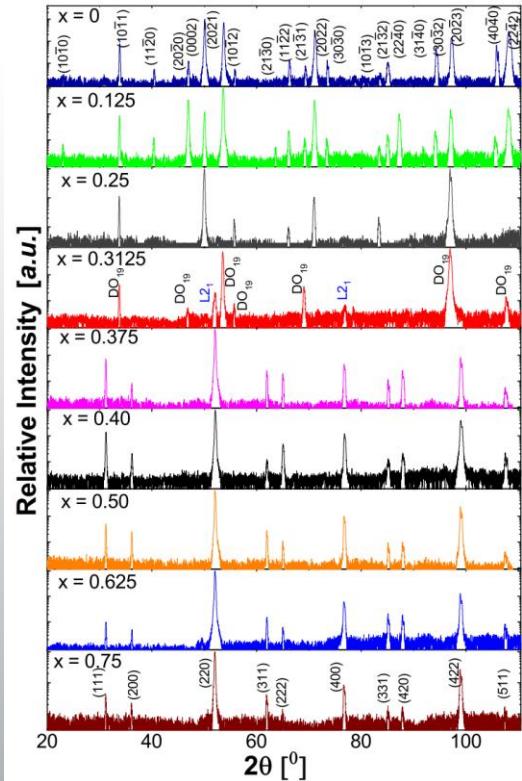
$\text{Fe}_{3-x}\text{V}_x\text{Ge}$  : 25D 650C

10

$\text{Fe}_{3-x}\text{Cr}_x\text{Ge}$  : 15D 1000C

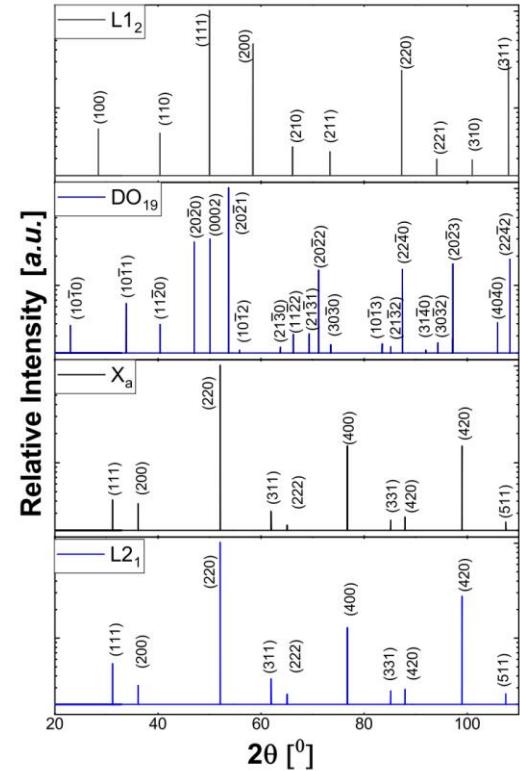


# $\text{Fe}_{3-x}\text{Y}_x\text{Ge}$ : Crystal structure and atomic order

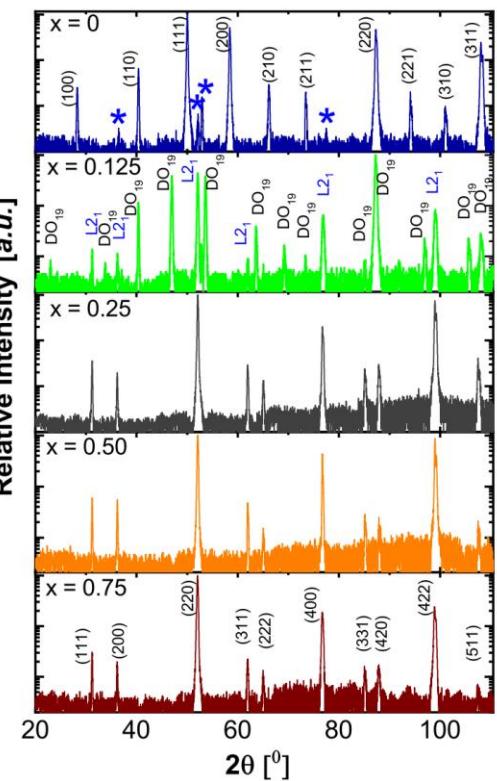


# Fe<sub>3-x</sub>V<sub>x</sub>Ge : 7D 950C

- $0 \leq x \leq 0.25$  : Hexagonal
  - $0.375 \leq x \leq 0.625$  : Cubic

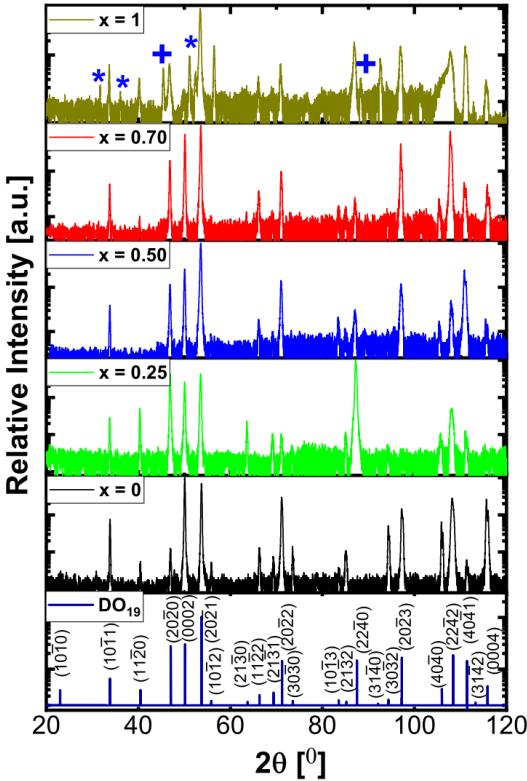


-  Cubic



## Fe<sub>3-x</sub>V<sub>x</sub>Ge : 25D 650C Fe<sub>3-x</sub>Cr<sub>x</sub>

- ## Hexagonal

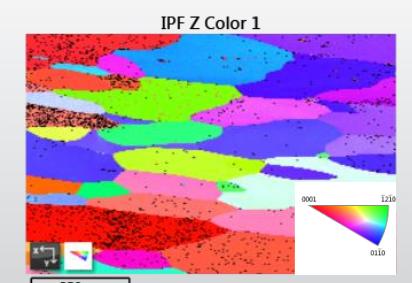
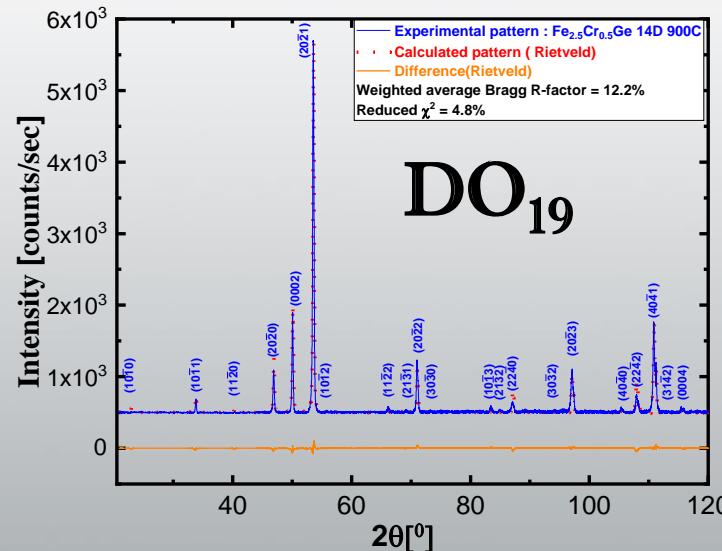
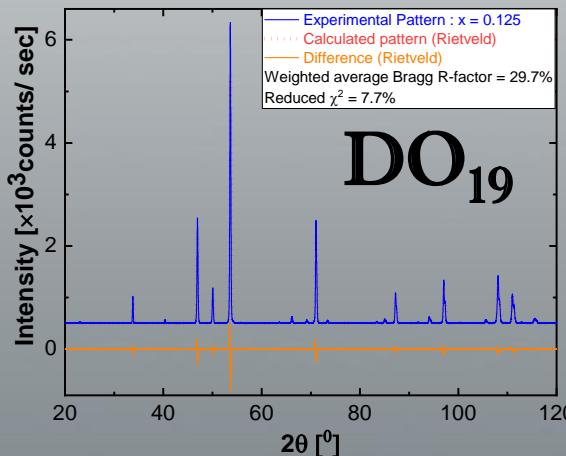
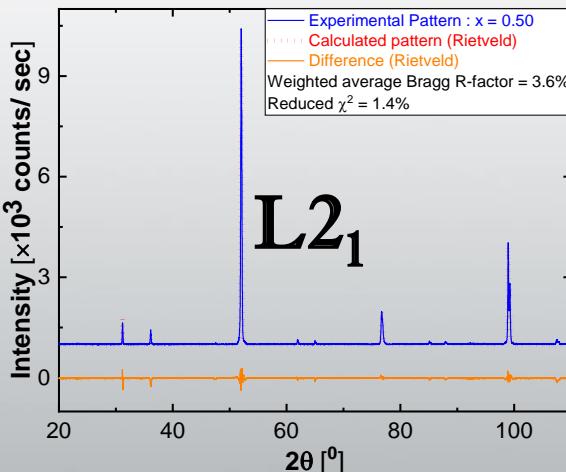


# $\text{Fe}_{3-x}\text{Cr}_x\text{Ge}$ : 15D 1000C

# $\text{Fe}_{3-x}\text{Y}_x\text{Ge}$ : Crystal structure and atomic order

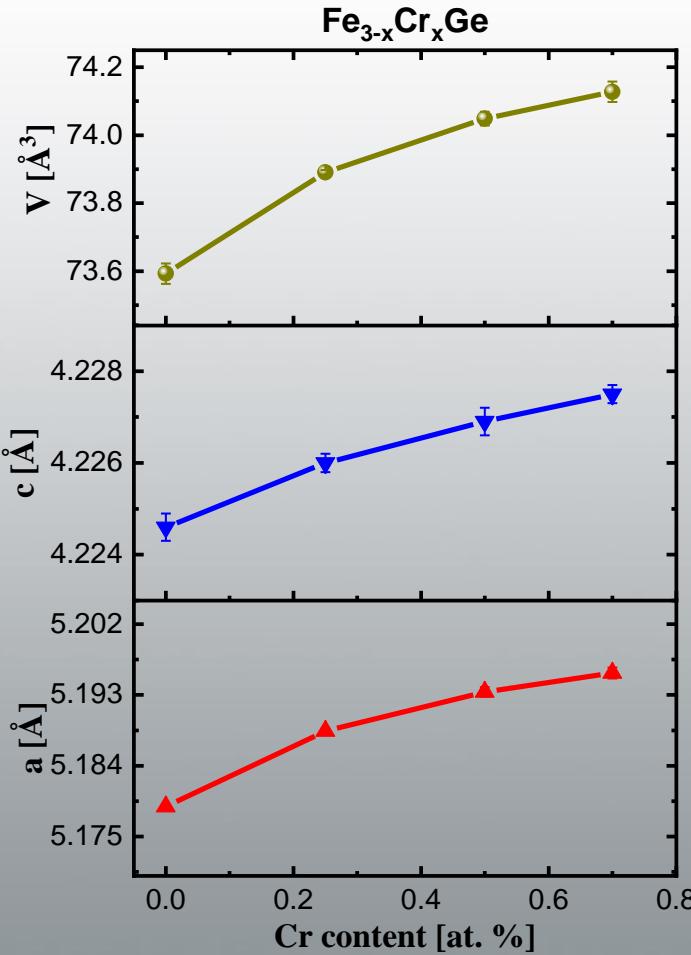
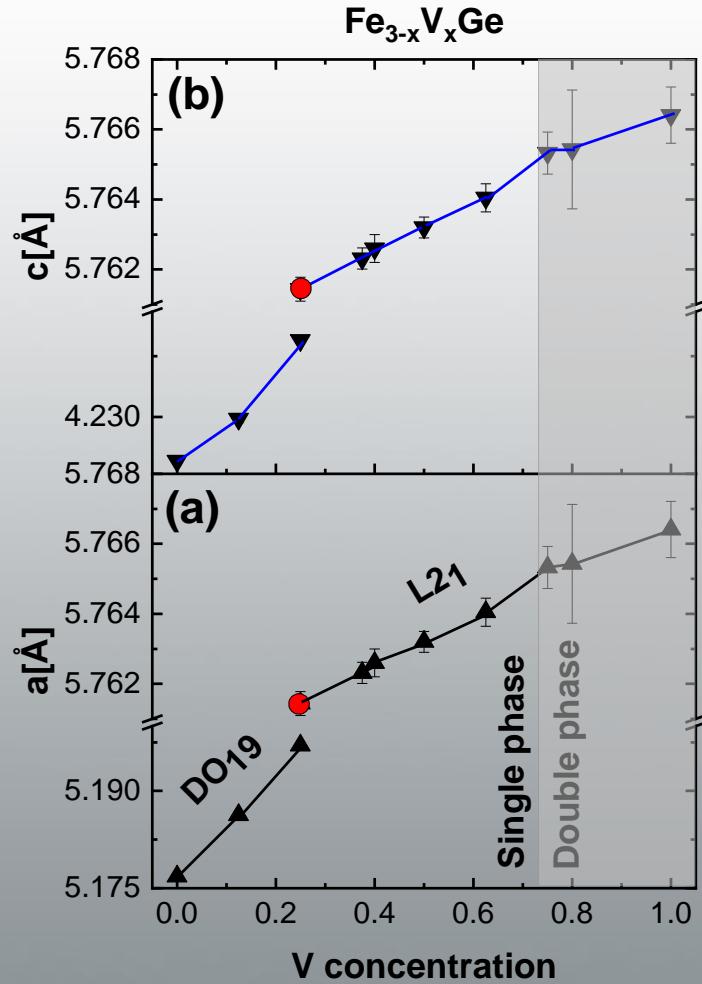


- Rietveld Refinements to determine the crystal structure and crystal imperfections
- EBSD IPF and phase map to confirm the degree of texturing and the purity of phase considered



# $\text{Fe}_{3-x}\text{Y}_x\text{Ge}$ : Crystal structure and atomic order

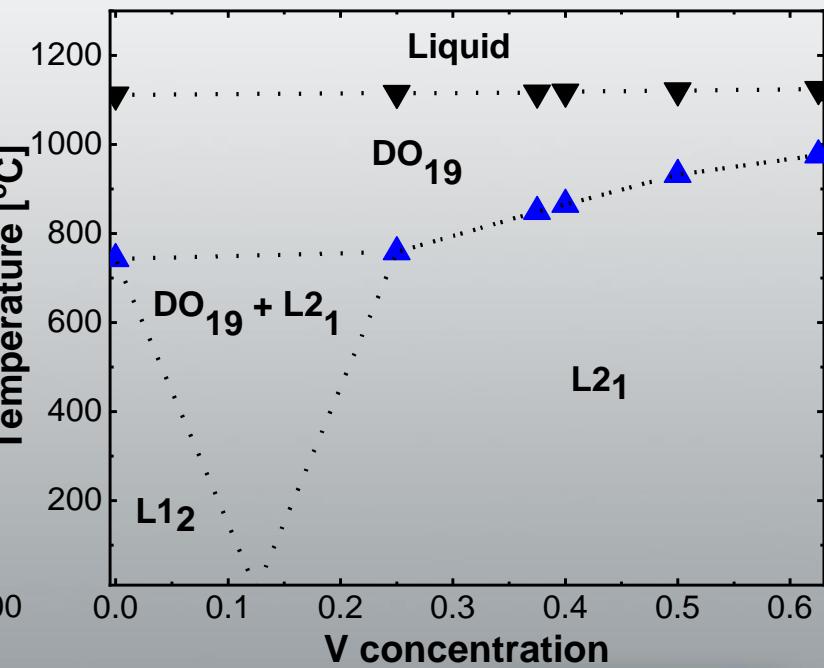
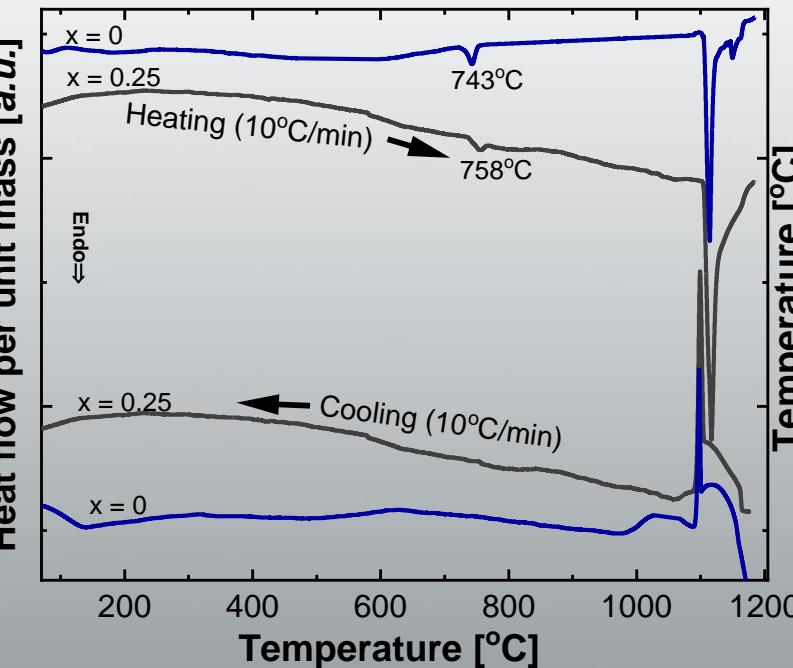
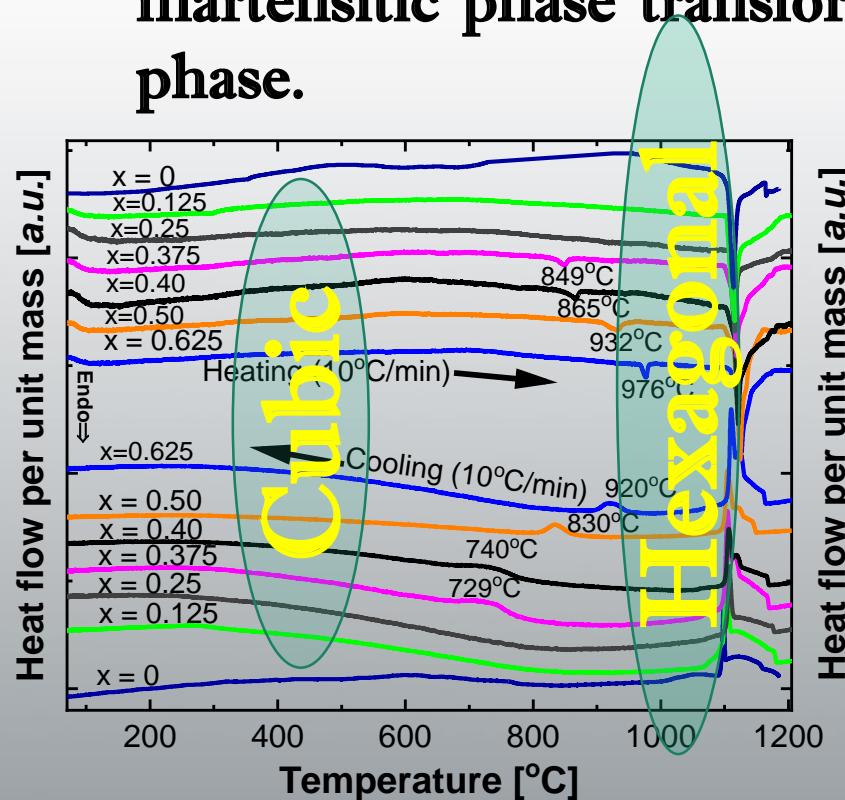
- Lattice parameters increase systematically with the increase of V/Cr concentration



# $\text{Fe}_{3-x}\text{V}_x\text{Ge}$ : Phase transformation and thermal stability



- Differential scanning calorimetry (DSC) : V substitution systematically shifts the martensitic phase transformation temperature to higher values stabilizing the L<sub>2</sub><sub>1</sub> phase.



## Fe<sub>3-x</sub>V<sub>x</sub>Ge : 7D 950C

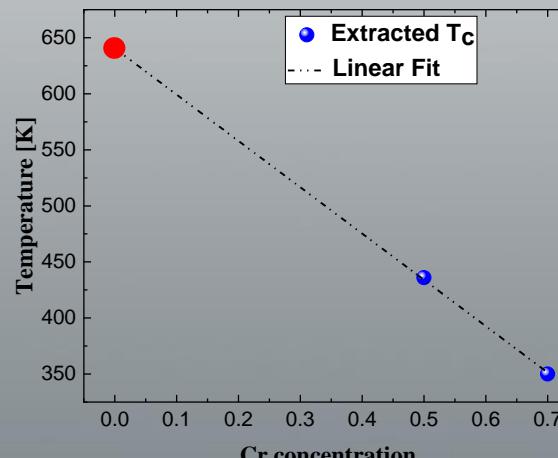
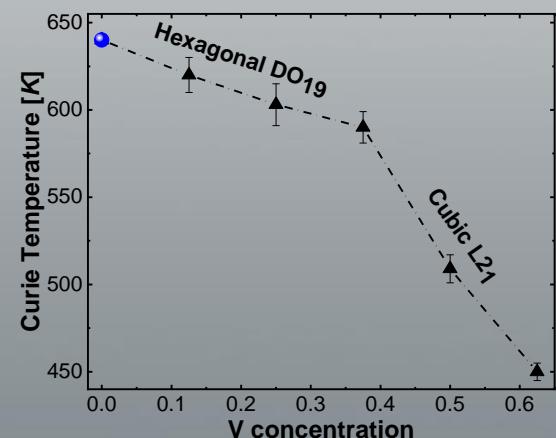
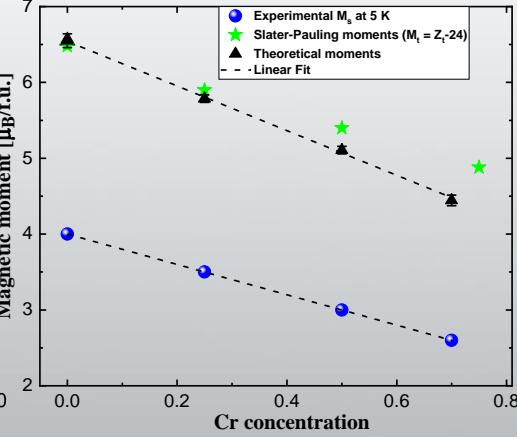
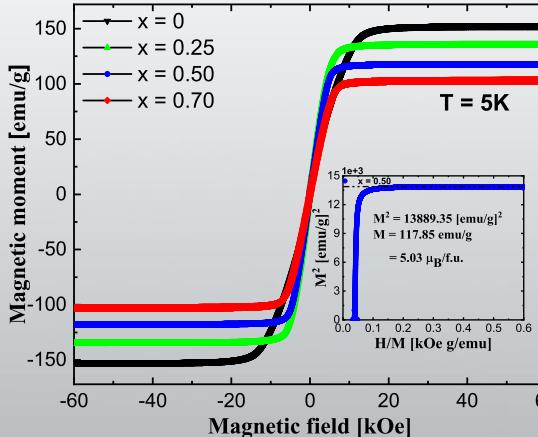
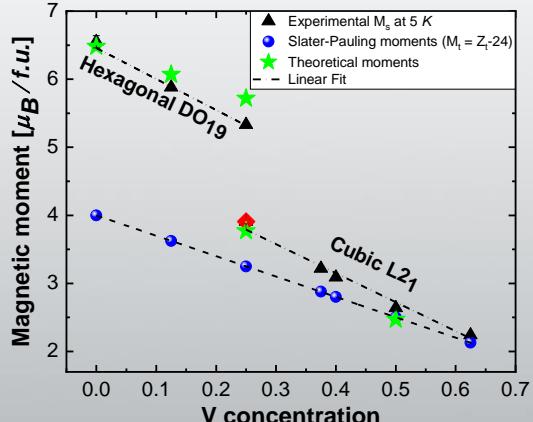
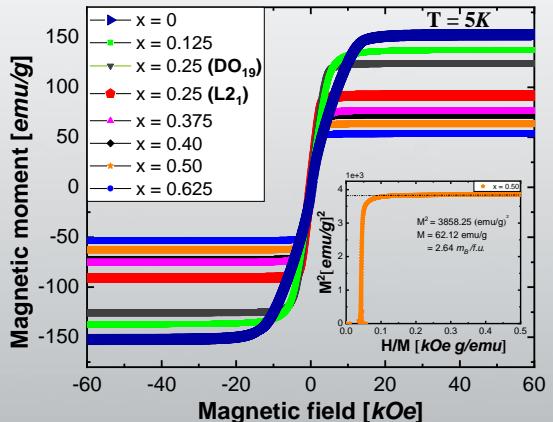
# Fe<sub>3-x</sub>V<sub>x</sub>Ge : 25D 650C



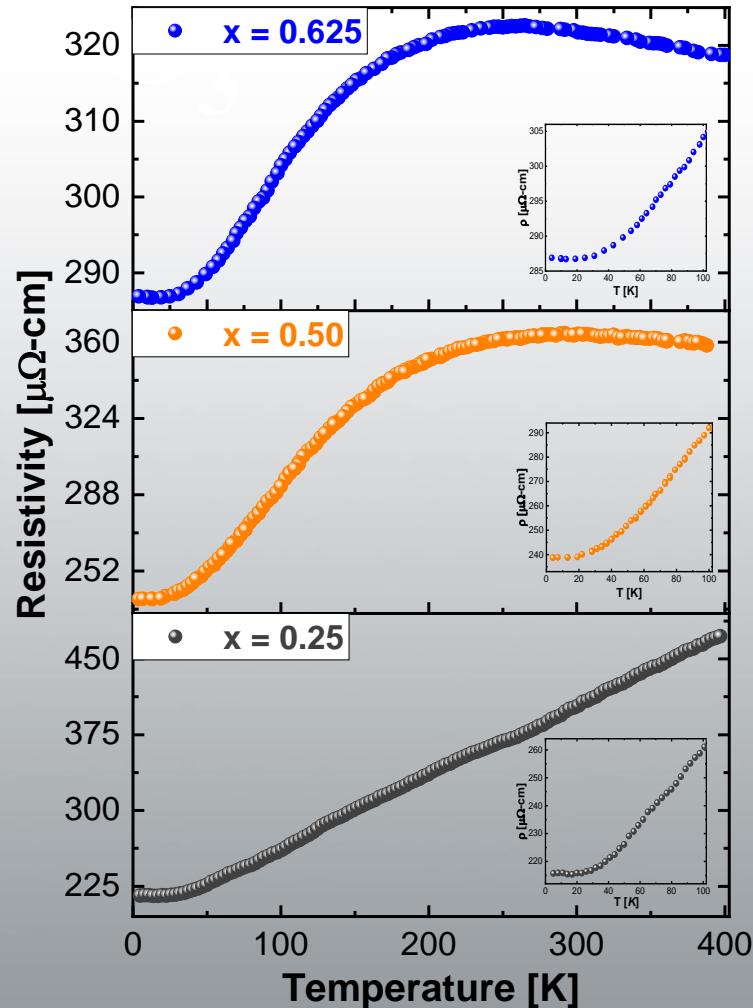
# $\text{Fe}_{3-x}\text{Y}_x\text{Ge}$ : Magnetization



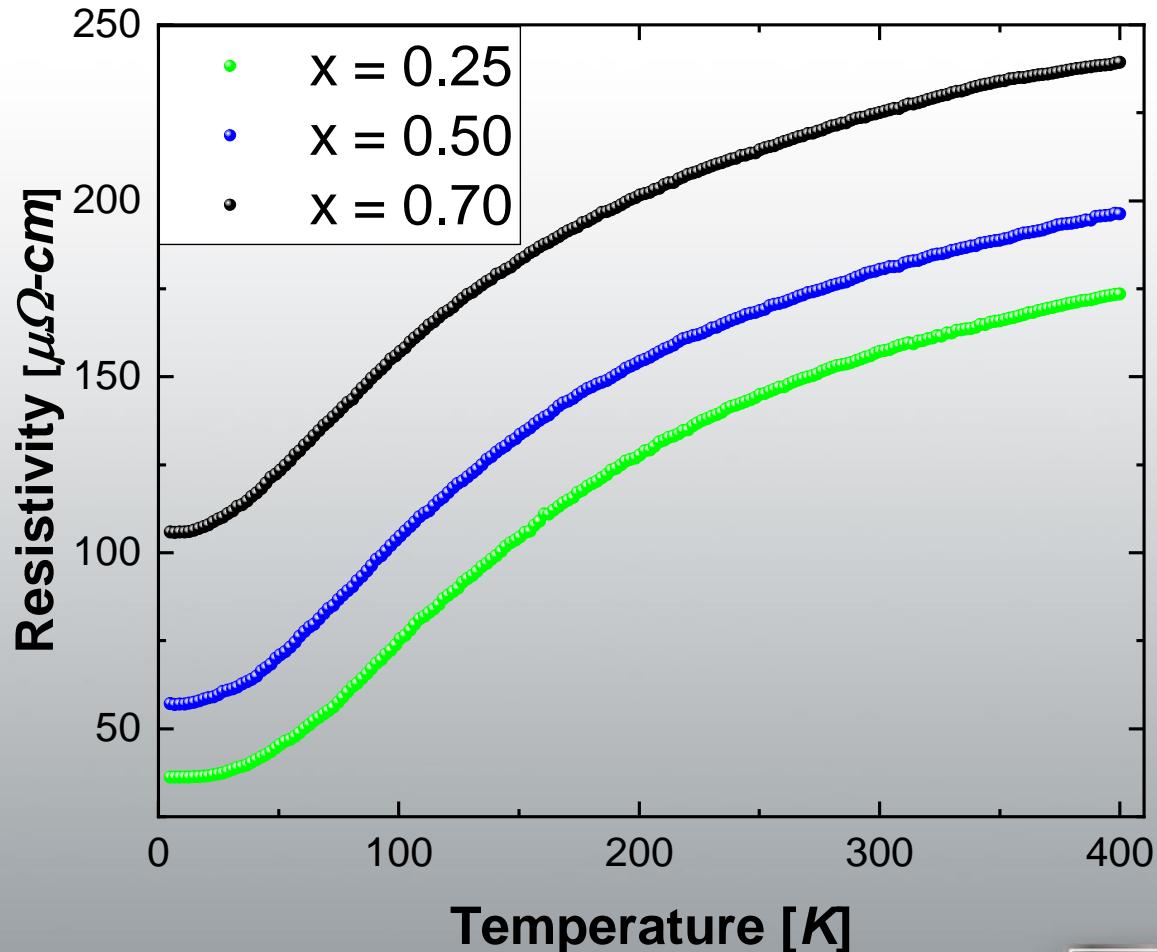
- Both magnetization and  $T_c$  decrease systematically with the increase of V/Cr concentration
- The saturation magnetizations in  $\text{DO}_{19}$  donot follow Slater-Puling rule



# $\text{Fe}_{3-x}\text{Y}_x\text{Ge}$ : Transport properties



$\text{Fe}_{3-x}\text{V}_x\text{Ge}$



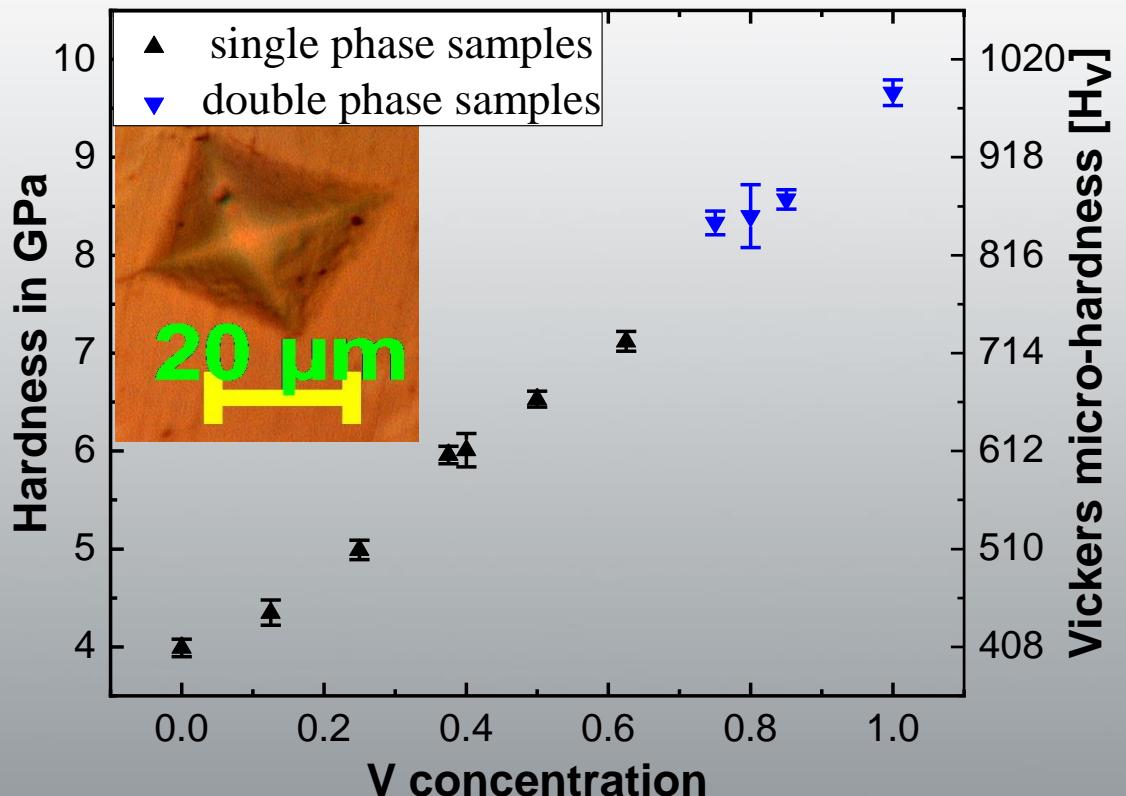
$\text{Fe}_{3-x}\text{Cr}_x\text{Ge}$



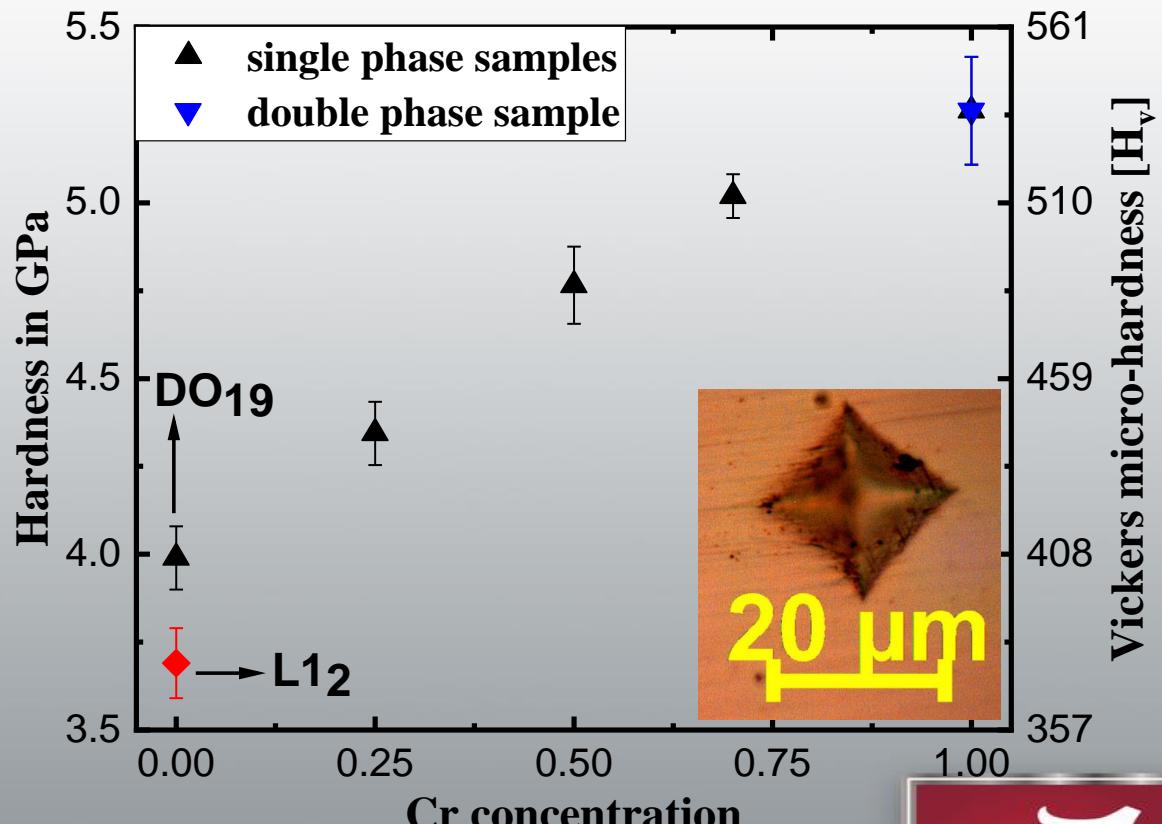
# $\text{Fe}_{3-x}\text{Y}_x\text{Ge}$ : Mechanical Hardness



- L2<sub>1</sub> phases show better toughness than DO<sub>19</sub>



$\text{Fe}_{3-x}\text{V}_x\text{Ge}$



$\text{Fe}_{3-x}\text{Cr}_x\text{Ge}$

# Summary

- Stable single phase for V/Cr substituted  $\text{Fe}_{3-x}\text{Y}_x\text{Ge}$  alloys consistent with ground states predicted from 1<sup>st</sup> principle calculations
- Strong tendency towards L2<sub>1</sub> ordering by substituting low valent transition metal atoms
- Martensitic phase transformation in V substituted alloys
- Validity of Slater-Pauling rule : only for L2<sub>1</sub> structure
- Increasing mechanical hardness with increasing atomic radius

X <sub>2</sub> YZ Heusler compounds																	
H																	He
2.20																	
Li	Be																
0.98	1.57																
Na	Mg																
0.93	1.31																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65	1.81	2.01	2.18	2.55	2.96	3.00
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.82	0.95	1.22	1.33	1.60	2.16	1.90	2.20	2.28	2.20	1.93	1.69	1.78	1.96	2.05	2.10	2.66	2.60
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.79	0.89		1.30	1.50	1.70	1.90	2.20	2.20	2.20	2.40	1.90	1.80	1.80	1.90	2.00	2.20	
Fr	Ra																
0.70	0.90																
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
1.10	1.12	1.13	1.14	1.13	1.17	1.20	1.20	1.10	1.22	1.23	1.24	1.25	1.10	1.27			
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			
1.10	1.30	1.50	1.70	1.30	1.28	1.13	1.28	1.30	1.30	1.30	1.30	1.30	1.30	1.30			



*Roll Tide*

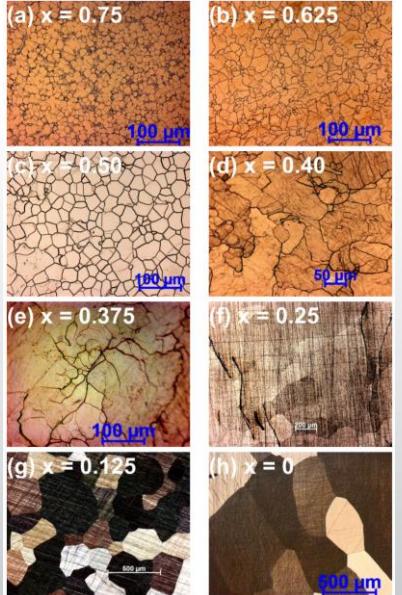




# Backup

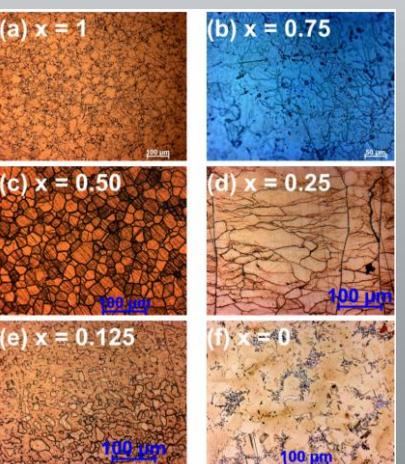


# Fe<sub>3-x</sub>V<sub>x</sub>Ge



$x$	Crystal structure	Experimental lattice (Å)	Theoretical lattice (Å)	Expt. M <sub>s</sub> at T = 5K ( $\mu_B/f.u.$ )	Theor. M <sub>s</sub> ( $\mu_B/f.u.$ )	S-P M <sub>s</sub> ( $\mu_B/f.u.$ )	T <sub>C</sub> (K)
0	DO <sub>19</sub> <sup>†</sup>	$a = 5.1768(2)$ $c = 4.2246(3)$	$a = 5.134$ $c = 4.222$	6.55(9)	6.48	4.00	640
0	L1 <sub>2</sub> <sup>‡*</sup>	$a = 3.6667(1)$	$a = 3.638$	6.55(9)	6.45	4.00	-
0.125	DO <sub>19</sub> <sup>†</sup>	$a = 5.1863(5)$ $c = 4.2298(5)$	$a = 5.146$ $c = 4.220$	5.88(2)	6.07	3.63	620(10)
0.125	L2 <sub>1</sub> + DO <sub>19</sub> <sup>‡*</sup>	-	-	-	-	-	-
0.25	DO <sub>19</sub>	$a = 5.1970(4)$ $c = 4.2395(3)$	$a = 5.159$ $c = 4.220$	5.33(3)	5.72	3.25	603(12)
0.25	L2 <sub>1</sub> <sup>‡</sup>	$a = 5.7614(3)$	$a = 5.753$	3.91(3)	3.77	3.25	-
0.375	L2 <sub>1</sub> <sup>†</sup>	$a = 5.7623(3)$	$a = 5.767$	3.18(2)	-	2.88	590(9)
0.40	L2 <sub>1</sub> <sup>†</sup>	$a = 5.7626(1)$	-	3.09(3)	-	2.80	-
0.50	L2 <sub>1</sub> <sup>†</sup>	$a = 5.7632(3)$	$a = 5.788$	2.64(3)	2.47	2.50	509(8)
0.625	L2 <sub>1</sub> <sup>†</sup>	$a = 5.7640(4)$	$a = 5.802$	2.24(2)	-	2.13	450(5)
0.75	L2 <sub>1</sub> <sup>‡*</sup>	$a = 5.7653(6)$	$a = 5.806$	-	1.62	1.75	-

<sup>†</sup> annealed at 950°C for 7 days, <sup>‡</sup> annealed at 650°C for 25 days, \* multi-phased samples.

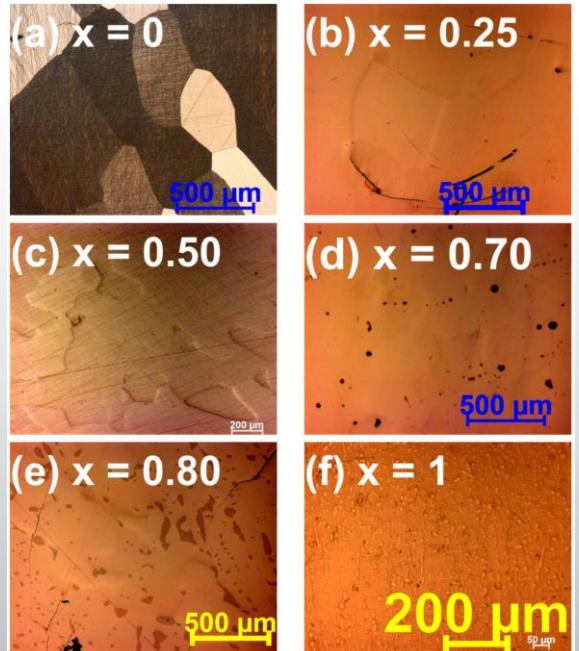


$x$	$T_1$ (°C)	$T_p$ (°C)	$\Delta S_p$ (J/g·K)	$T_m$ (°C)
0*	721	743	0.15(2)	1112
0.125	-	-	-	1115
0.25*	737	758	0.14(2)	1116
0.375	828	849	0.17(2)	1118
0.40	842	865	0.18(1)	1121
0.50	905	932	0.26(3)	1124
0.625	965	976	0.42(2)	1126

\*Samples annealed at 650°C for 25 days.



# Fe<sub>3-x</sub>Cr<sub>x</sub>Ge



$x$	$\rho_0(\mu\Omega\text{-cm})$	$\alpha(\mu\Omega\text{-cm/K})$ times $10^{-2}$	$\beta(\mu\Omega\text{-cm/K}^2) \times 10^{-3}$	$\rho_{shunt}(\mu\Omega\text{-cm})$	Reduced chi-square $\times 10^{-12}$
0.25	$39.79 \pm 0.45$	$5.68 \pm 1.40$	$7.72 \pm 0.10$	$199.56 \pm 0.40$	2.47
0.50	$71.27 \pm 0.80$	$18.60 \pm 2.56$	$10.68 \pm 0.20$	$217.05 \pm 0.49$	1.05
0.70	$105.15 \pm 0.25$	$67.95 \pm 2.01$	$15.30 \pm 0.25$	$259.18 \pm 0.45$	1.35

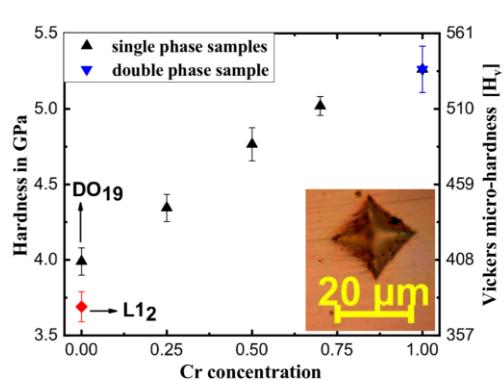
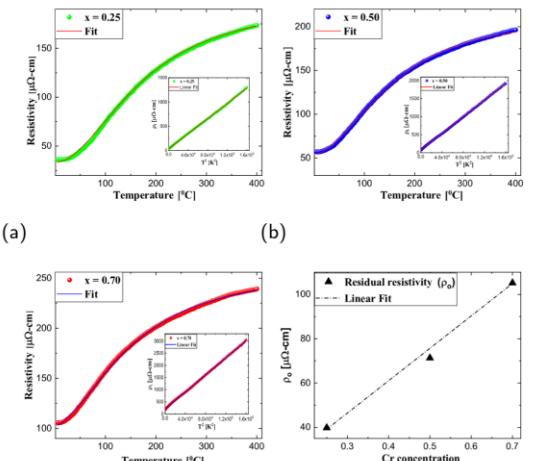


Figure 8: Vickers hardness versus Cr concentration in Fe<sub>3-x</sub>Cr<sub>x</sub>Ge all annealed at 1000°C for 15 days, with imprint of

$x$	Crystal structure	Experimental lattice ( $\text{\AA}$ )	Theoretical lattice ( $\text{\AA}$ )	Expt. $M_s$ at $T = 5K$ ( $\mu_B/\text{f.u.}$ )	Theor. $M_s$ ( $\mu_B/\text{f.u.}$ )	S-P $M_s$ ( $\mu_B/\text{f.u.}$ )	$T_C$ (K)
0	DO <sub>19</sub> <sup>†</sup>	$a = 5.1768(2)$	$a = 5.134$	$6.55(9)$	$6.48$	$4.00$	$640$
		$c = 4.2246(3)$	$c = 4.222$				
0	L1 <sub>2</sub> <sup>‡*</sup>	$a = 3.6667(1)$	$a = 3.638$	$6.55(9)$	$6.45$	$4.00$	-
0.25	DO <sub>19</sub> <sup>†</sup>	$a = 5.1885$	$a =$				<sup>†</sup>
		$c = 4.2260$	$c =$	$5.79$		$3.50$	
0.50	DO <sub>19</sub> <sup>†</sup>	$a = 5.1934$	$a =$	$5.11$		$3.00$	
		$c = 4.2269$	$c =$				
0.70	DO <sub>19</sub> <sup>†</sup>	$a = 5.1958$	$a =$	$4.44$		$2.60$	
		$c = 4.2275$	$c =$				

annealed at 1000°C for 15 days, <sup>‡</sup> annealed at 650°C for 25 days, \* multi-phased samples.

