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Crystal structure and high temperature X-ray diffraction study of thermoelectric chimney-ladder FeGe_γ ($\gamma \approx 1.52$)

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Abstract

The crystal structure of Nowotny chimney-ladder phase FeGe_γ with $\gamma \approx 1.52$ was studied by X-ray diffractometry from 300 K to 850 K. The diffraction patterns were fitted by Rietveld refinement considering an incommensurate composite crystal structure. The refined crystal structure of FeGe_γ is described in details and compared to MnSi_γ , a thermoelectric material with $\gamma \approx 1.74$. The lattice parameters a , c_{Fe} and c_{Ge} were found to increase with the temperature following a polynomial law, while the modulation vector component γ remained constant up to the peritectoid decomposition into FeGe and FeGe_2 . Within the temperature range considered, the linear and volumetric thermal expansion parameters increased from about $3 \times 10^{-6} \text{ K}^{-1}$ to $10 \times 10^{-6} \text{ K}^{-1}$ and from $9.6 \times 10^{-6} \text{ K}^{-1}$ to $31.5 \times 10^{-6} \text{ K}^{-1}$, respectively.

Keywords:

X-ray diffraction, Intermetallics, Thermoelectric materials, Crystal structure, Thermal expansion

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1. Introduction

Heat losses are omnipresent in modern societies. In combustion engines heat losses occur through the exhaust, in electronics there are heat losses due to Joule heating, even the human body experiences heat loss due to thermoregulation. The direct conversion of thermal energy from these heat losses into electricity by an all-solid-state thermoelectric (TE) generator is a promising way to supply power to the ever more numerous and autonomous sensors and microelectronic devices pervading society [1, 2, 3]. The most common design of generator is an assembly of n - and p -type TE materials connected electrically in series and thermally in parallel between two electrically insulating and thermally conducting ceramic plates [4, 5]. The conversion efficiency of the TE materials is directly related to the adimensional figure of merit ZT , which is defined at a given temperature T (K) as:

$$ZT = \frac{\alpha^2 T}{\rho \kappa} \quad (1)$$

where α (V K^{-1}) is the Seebeck coefficient, ρ ($\Omega \text{ m}$) the electrical resistivity and κ ($\text{W m}^{-1} \text{ K}^{-1}$) the thermal conductivity.

The Nowotny chimney-ladder compound MnSi_γ with $\gamma \approx 1.74$ often referred to as higher manganese silicide (HMS), is a highly promising p -type TE material because it is composed of inexpensive and non-toxic elements [6, 7]. Its incommensurate composite crystal structure [8] results in a relatively low thermal conductivity of about $2.5 \text{ W m}^{-1} \text{ K}^{-1}$ and ZT of 0.4 at 800 K [9, 10]. However, the large scale development of mid-temperature TE generators (600 - 800 K) based on this material remains limited due to the lack of an n -type counterpart with comparable thermoelectric and mechanical properties [11]. Among the other silicides, the current best options are n -type Co-doped FeSi_2 whose ZT only reaches about 0.2 in the same conditions [12] or Sn-doped Mg_2Si which

27 has much lower mechanical and chemical resistance properties [13].

28

29 In 2000, a new Nowotny chimney-ladder Fe-Ge compound with a composi-
30 tion close to Fe_2Ge_3 was discovered by Gerasimov *et al.* [14]. The late discov-
31 ery of this compound is explained by its slow peritectoid formation below 850
32 K from the kinetically stable FeGe and FeGe_2 . Later, Li *et al.* demonstrated by
33 electron diffraction that it crystallizes in an incommensurate composite struc-
34 ture with modulation wave vector $\mathbf{q} = \gamma\mathbf{c}^*$, which is isostructural to HMS [15].
35 The crystal structure is composed of two interpenetrating [Fe] and [Ge] tetrag-
36 onal subsystems with common a but different and incommensurate c_{Fe} and c_{Ge}
37 lattice parameters (see Figure 1). As both subsystems have 4 atoms per unit
38 cell, the modulation wave vector component, $\gamma = c_{\text{Fe}}/c_{\text{Ge}}$, dictates the stoi-
39 chiometry of the compound. For this reason, the phase is better described by
40 the chemical formula FeGe_γ with γ close but not exactly equal to 1.52. The TE
41 properties of FeGe_γ were first reported for a bulk polycrystalline sample by Sato
42 *et al.* who established an n -type conductivity and a high ZT of approximately
43 0.6 at 700 K [16]. As for HMS, the low thermal conductivity of $2.5 \text{ W m}^{-1} \text{ K}^{-1}$
44 at 700 K is attributed to the complex crystal structure which efficiently scat-
45 ters heat-carrying phonons. This material has garnered much interest in recent
46 years and is now considered as a promising high-performance n -type counter-
47 part to HMS. Verchenko *et al.* first managed to grow FeGe_γ single crystal by
48 a chemical transport method [17]. Surprisingly, single crystal X-ray diffraction
49 (XRD) data indicates a commensurate structure Fe_2Ge_3 isostructural to Ru_2Sn_3
50 with space group $P\bar{4}c2$ (no. 116) and lattice parameters of $a = 5.5848(8) \text{ \AA}$ and
51 $c = 8.9400(18) \text{ \AA}$. However, this structural model was not supported by powder
52 XRD and electron diffraction patterns which clearly indicate incommensurabil-
53 ity. Despite these divergent results, no detailed structural analysis of polycrys-
54 talline FeGe_γ has been reported. A better description of the FeGe_γ structure is of
55 the highest importance to gain a better understanding of the structure-property
56 relationships in Nowotny chimney-ladder compounds.

57

58 In this article, the crystal structure of polycrystalline FeGe_γ is studied by
59 powder XRD and refined by the Rietveld method considering a composite crystal
60 model in (3+1) dimension. The discussion is focused on the structure and mi-
61 crostructure of FeGe_γ in comparison with the better-known MnSi_γ. The thermal
62 behavior of the structure is also investigated up to the decomposition tempera-
63 ture around 850 K. The evolution of the lattice parameters at high temperatures
64 and the thermal expansion coefficients are determined and discussed as they are
65 of practical importance for TE generator design and manufacturing.

67 2. Experimental section

68 For the synthesis of FeGe_γ, first, elemental powders of Fe (> 99.99 %) and Ge
69 (> 99.99 %) were mixed in a nominal molar ratio of 2:3. 5 g of the powder
70 mixture was then ball-milled in a 400 mL WC vial with Ø=1 cm WC balls for
71 1 h at 400 rpm under Ar atmosphere. The mixture was then cold pressed and
72 annealed in an evacuated silica tube for 1 month at 773 K.

73
74 Powder XRD was realized using a θ -2 θ Rigaku SmartLab diffractometer
75 equipped with a Cu rotating target, a Ge(111) monochromator set at incident
76 beam side selecting the Cu K_{α1} radiation (1.54056 Å) and a D/teX Ultra 250 de-
77 tector. The measurements were performed from 20° to 120° with a step width
78 of 0.020° using variable slits. High temperature measurements were performed
79 at 300 K, 400 K, 500 K, 600 K, 700 K, 800 K and 850 K under dynamic vacuum
80 ($\approx 7 \times 10^{-3}$ Pa). The X-ray powder patterns were fitted using the JANA2006
81 software [18]. The peak shapes were modeled using Thompson-Cox-Hastings
82 pseudo-voigt functions [19]. Berar's factors were applied to the estimated stan-
83 dard deviation to obtain more realistic values [20]. The mass fractions of impu-
84 rities were determined by quantitative Rietveld refinement.

85
86 Details about the lattice vectors setting and refinement procedure used in
87 the present work will be discussed briefly here. More general information about

88 incommensurate crystallography can be found in ref. [21]. In real space, the
 89 subsystems [Fe] and [Ge] present conventional 2D periodicity along the a and
 90 b directions but are incommensurate along the c direction. The diffraction pat-
 91 tern of FeGe_γ is constructed as the superposition of the diffraction patterns of
 92 the two incommensurately modulated [Fe] and [Ge] subsystems. Two sets of
 93 four reciprocal lattice vectors, M_{Fe} and M_{Ge} , are thus required to fully index
 94 the reciprocal lattice of the subsystems. Each set contains three linearly inde-
 95 pendent basic vectors corresponding to the basic structure and one additional
 96 modulation wave vector. Because of the mutual interaction, the modulation of
 97 the [Fe] subsystem is determined from the basic reciprocal lattice vectors of the
 98 [Ge] subsystem and *vice versa*. Furthermore, the two subsystems share a com-
 99 mon reciprocal lattice plane. Only one set of four reciprocal lattice vectors $M =$
 100 $(\mathbf{x}_1^*, \mathbf{x}_2^*, \mathbf{x}_3^*, \mathbf{x}_4^*)$ is thus required to fully index the composite crystal diffraction
 101 patterns. The reciprocal lattice vector sets M_{Fe} and M_{Ge} are defined from the
 102 set M by application of the following W matrices :

$$W_{Fe} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad W_{Ge} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad (2)$$

103

104 In this setting, the FeGe_γ reciprocal lattice parameters are $a^* = \|\mathbf{x}_1^*\| = \|\mathbf{x}_2^*\|$, c_{Fe}^*
 105 $= \|\mathbf{x}_3^*\|$, $c_{Ge}^* = \|\mathbf{x}_4^*\|$. Since the reciprocal lattice vectors \mathbf{x}_3^* and \mathbf{x}_4^* are collinear,
 106 the modulation vector component γ is equal to $\|\mathbf{x}_4^*\| / \|\mathbf{x}_3^*\|$. Four Miller indices
 107 $hklm$ are required to index all the Bragg reflections of FeGe_γ pattern. In the
 108 present settings, the reflections $hk00$ are common to both subsystems, $hk10$ cor-
 109 responds to the [Fe] subsystem main reflections, $hk0m$ corresponds to the [Ge]
 110 subsystem main reflections and $hklm$ ($l \neq 0, m \neq 0$) are satellite reflections re-
 111 sulting from the modulations of both subsystems. Satellite reflections up to the
 112 second order were considered for structural refinements.

113

114 The modulation function $u(\mathbf{v})$ describing the displacement of atoms from
115 their average positions in modulated crystals is periodic along the forth super-
116 space direction \mathbf{v} [22, 23]. In the case of FeGe_γ , \mathbf{v} is defined for the subsystems
117 [Fe] and [Ge] as:

$$\begin{aligned}v_{Fe} &= t + \gamma \cdot x_3 \\v_{Ge} &= t + 1/\gamma \cdot x_4\end{aligned}\quad (3)$$

118

119 where t is a constant. The modulation functions can be decomposed using a
120 Fourier series:

$$u(\mathbf{v}) = \sum_{k=1}^k A^k \sin(2\pi k\mathbf{v}) + B^k \cos(2\pi k\mathbf{v}) \quad (4)$$

121

122 where the Fourier terms A^k and B^k were refined against the diffraction pattern
123 up to $k = 2$ and $k = 4$ for Fe and Ge modulations, respectively. The following
124 restraints apply to the Fourier terms of the [Ge] subsystem due to superspace
125 symmetry: $A_x^1 = A_y^1 = B_x^1 = -B_y^1$ and $A_x^3 = A_y^3 = -B_x^3 = B_y^3$. Similarly, only the
126 Fourier term B_z^2 is allowed by symmetry in the [Fe] subsystem.

127 Differential scanning calorimetry (DSC) analysis was performed using a Rigaku
128 DSC 8270 apparatus and using Al_2O_3 reference. The analysis was performed
129 from 300 K to 1000 K at a rate of 10 K min^{-1} in a Pt-Rh crucible under N_2
130 atmosphere.

131

132 3. Results and discussion

133 3.1. Crystal structure of FeGe_γ at 300 K

134 The sample used for diffraction measurement contained 86.1 wt.% of FeGe_γ as
135 well as 4.5 wt.% of FeGe ($P2_13$), 5.9 wt.% of FeGe_2 ($I4/mcm$) and 3.5 wt.% of

136 FeGe₂O₄ ($Fd\bar{3}m$) as determined by quantitative Rietveld analysis. Single phase
137 sample is very challenging to synthesize because of the slow peritectoid forma-
138 tion of FeGe_γ which requires long annealing time. However, the present sample
139 was considered of sufficient quality for XRD analysis as the diffraction peaks of
140 the impurities are well-defined and do not overlap with the phase of interest.

141

142 A first attempt to fit the diffraction pattern was made by considering the
143 commensurate Fe₂Ge₃ (or FeGe_γ with $\gamma = 1.5$) structure determined by Verchenko
144 *et al.* on single crystalline sample [17]. This structural model (see Table SI. 1)
145 could not, however, satisfactorily fit the data, showing large discrepancies be-
146 tween observed and calculated 2θ positions for many Bragg reflections. As a
147 result, the Rietveld refinement is unstable and high discrepancy values were ob-
148 tained, *e.g.* $\chi^2 > 100$.

149

150 A better agreement with the experimental data was obtained by considering
151 FeGe_γ as an incommensurate composite crystal with γ close to but slightly dif-
152 ferent than 1.5. The (3+1)D space group $I4_1/amd(00\gamma)00ss$ used to describe
153 the structural symmetry [24]. The [Fe] and [Ge] subsystems were generated by
154 placing Fe and Ge atoms in position $x = y = z = 0$ and $x = y = z = 0.25$,
155 respectively. Three lattice parameters, a , c_{Fe} and γ , are refined against the
156 diffraction pattern (see experimental section). The lattice parameter c_{Ge} was
157 deduced from the relation $c_{Fe}/\gamma = c_{Ge}$. Rietveld refined patterns and refined
158 structural parameters can be found in Figure 2 and Table 1, respectively. The
159 fact that only the (3+1)D superspace approach lead to satisfactory agreement
160 with the data is clear evidence of the structural incommensurability of FeGe_γ.
161 Interestingly, the full width at half maximum of some $hk0m$ ([Ge] subsystem)
162 and $hklm$ (satellite) diffraction peaks are significantly broader than the other
163 reflections. Such anisotropic peak broadening was taken into account in the
164 refinement procedure using the Stephens method [25]. This anisotropic peak
165 broadening is consistent with the high defect concentration evidenced by TEM
166 on the [Ge] subsystem [17]. Similar observations have also been reported in

167 MnSi $_{\gamma}$ [26] where the broader $hk0m$ reflections is also attributed to high den-
 168 sity of defects on the ladder [Si] subsystem [27, 10]. However, it should be
 169 noted that no peak shape asymmetry is observed for FeGe $_{\gamma}$, contrarily to HMS
 170 [28, 10].

171

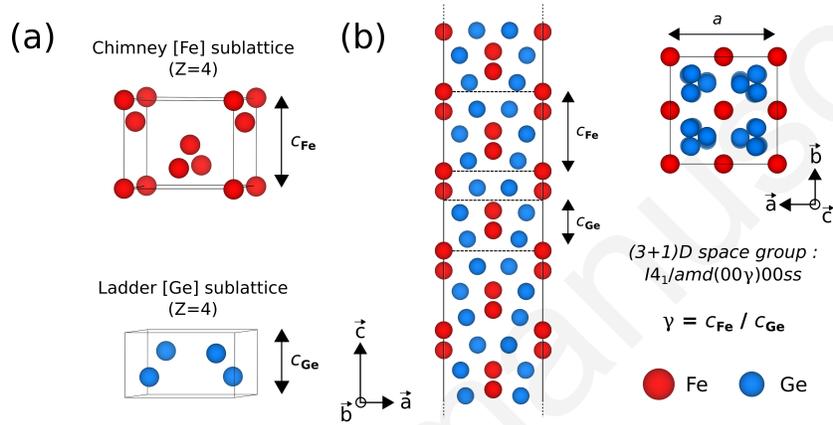


Figure 1: Representations of (a) the structure of the chimney [Fe] and ladder [Ge] subsystems, and (b) the structure of FeGe $_{\gamma}$ after interpenetration of the two subsystems.

172 The Rietveld refinement converged to the lattice parameters $a = 5.5924(3)$
 173 Å, $c_{Fe} = 4.4948(3)$ Å and $\gamma = 1.5190(1)$. Table 1 compares these values to the
 174 lattice parameters of isostructural HMS reported by Kikuchi *et al.* [29]. The [Fe]
 175 chimney subsystem has a and c parameters 1.2 % and 2.9 % larger, respectively,
 176 than the [Mn] subsystem in HMS. This corresponds to a 5.5 % increase of the
 177 unit cell volume. The main difference between the two compounds is the 12.6
 178 % smaller γ in FeGe $_{\gamma}$. As $\gamma = c_{Fe}/c_{Ge}$, it is a direct consequence of the larger c_{Ge}
 179 = 2.959(1) Å compared to $c_{Si} = 2.5108(1)$ Å. This causes a 20.7% expansion
 180 of the [Ge] ladder unit cell volume that can be explained by the larger atomic
 181 radius of Ge (1.25 Å) compared to Si (1.10 Å) [30]. The important volume
 182 increase of the ladder unit cell caused by the replacement of Si by Ge manifests
 183 predominantly through an expansion of the [Ge] subsystem along the c direc-
 184 tion and has only a limited impact on the (a, b) -plane.

185

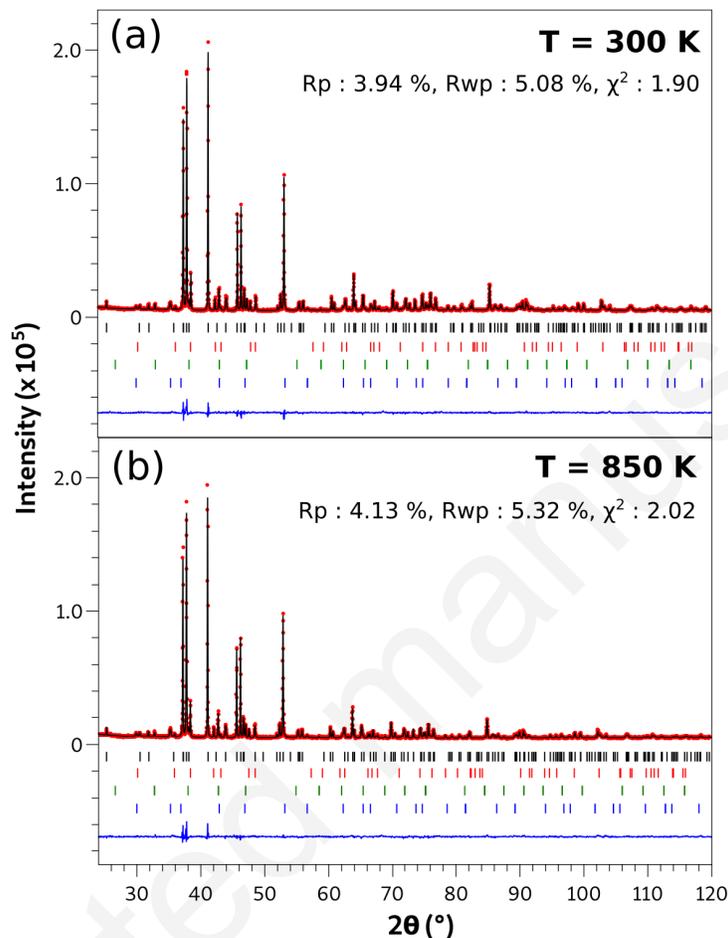


Figure 2: Rietveld refined XRD patterns of FeGe_7 measured at 300 K (top) and at 850 K (bottom). The experimental data are plotted in red symbols, the calculated pattern with a black line and the difference with a blue line. The vertical ticks indicate the theoretical Bragg positions of FeGe_7 (black), FeGe_2 (red), FeGe (green) and Fe_2GeO_4 (blue).

186 Interaction between the two interpenetrating [Fe] and [Ge] subsystems causes
 187 the atoms to be displaced incommensurately from their average positions. All
 188 information about the atomic displacements can be fully represented using t -
 189 plots which consist in plotting the modulation functions $u(\mathbf{v})$ in one superspace
 190 unit cell *i.e.* for $0 \leq t \leq 1$. Refined Fourier coefficients are displayed in Ta-
 191 ble 1 while corresponding $u(\mathbf{v})$ functions are plotted in Figure 3. On the one
 192 hand, the displacement of Fe atoms was found to be small along c ($\leq 0.015 \text{ \AA}$)

Table 1: Structural parameters obtained by Rietveld refinement of FeGe_γ XRD pattern collected at 300 K. Structural parameters reported in reference [29] for MnSi_γ and obtained by powder XRD are also shown for comparison.

	FeGe_γ	MnSi_γ
γ	1.5190(1)	1.7387(1)
a (Å)	5.5924(3)	5.5252(1)
Subsystem 1	Fe	Mn
x,y,z	0,0,0	0,0,0
c (Å)	4.4948(3)	4.3656(1)
V (Å ³)	140.57(2)	133.372(3)
B_z^2	-0.003(1)	-0.0147(7)
U_{iso} (Å ²)	0.0296(7)	0.0249(5)
Subsystem 2	Ge	Si
x,y,z	0.25,0.25,0.25	0.25,0.25,0.25
c (Å)	2.959(1)	2.5108(1)
V (Å ³)	92.54(3)	76.652(4)
A_x^1	0.0720(2)	0.0767(3)
A_x^3	-0.0041(3)	0.0092(4)
B_z^4	-0.010(2)	-0.023(2)
U_{iso} (Å ²)	0.0329(6)	0.0245(7)

193 and null along a and b . On the other hand, Ge has much larger displacement
194 amplitudes, reaching a maximum of about 0.52 Å along a and b . The effect of
195 the Ge modulation in the (a,b) -plane is clearly visible on the c -axis projection
196 of the structure in Figure 1b with the formation of Ge-helices. The displace-
197 ment amplitude of Ge atoms along the c -axis is much smaller with a maximum
198 of about 0.07 Å. The Fourier coefficients describing the modulation function of
199 [Mn] and [Si] in MnSi_γ are also shown for comparison in Table 1 and Figure
200 3 with dotted lines. The shape of the modulation functions are similar for the
201 two compounds. The only significant difference is the smaller displacements of
202 both Fe and Ge atoms along the c direction (in green in Figure 3).

203
204 A direct consequence of the incommensurability is the different coordination
205 environment of all atoms along the c -axis. However, all the possible coordina-

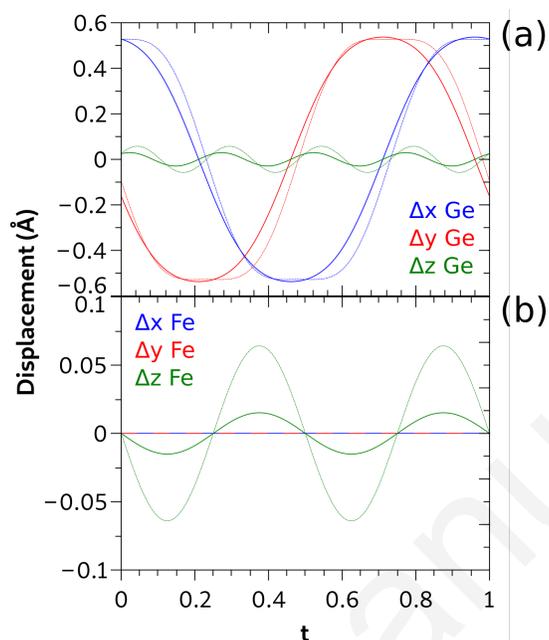


Figure 3: t -plot showing the modulated displacement of Ge (top) and Fe (bottom) atoms around their average positions in FeGe_7 (solid lines). The corresponding displacement for Mn and Si in MnSi_7 are plotted in dashed lines.

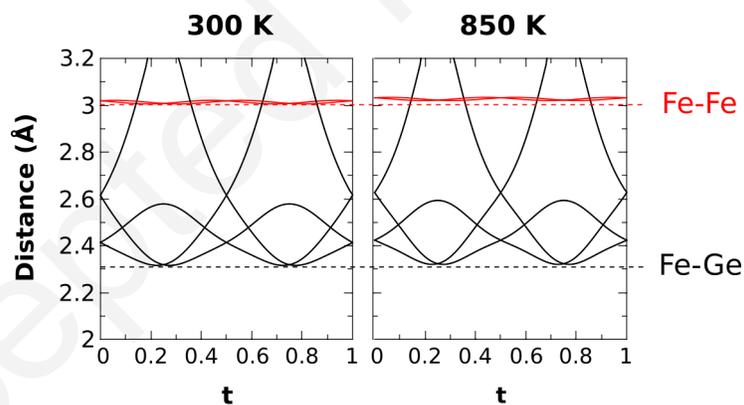


Figure 4: t -plots of the bonds distances around Fe atoms determined from Rietveld refinement at 300 K and 850 K. Fe-Fe bonds are represented in red and Fe-Ge bonds in black.

206 tion spheres around Fe can be retrieved from the t -plots of the shortest Fe-Fe,
 207 Ge-Ge and Fe-Ge bond distances (Figure 4) as well as the Ge-Fe-Ge bond an-
 208 gles. In the present case, it is possible to define every existing coordination

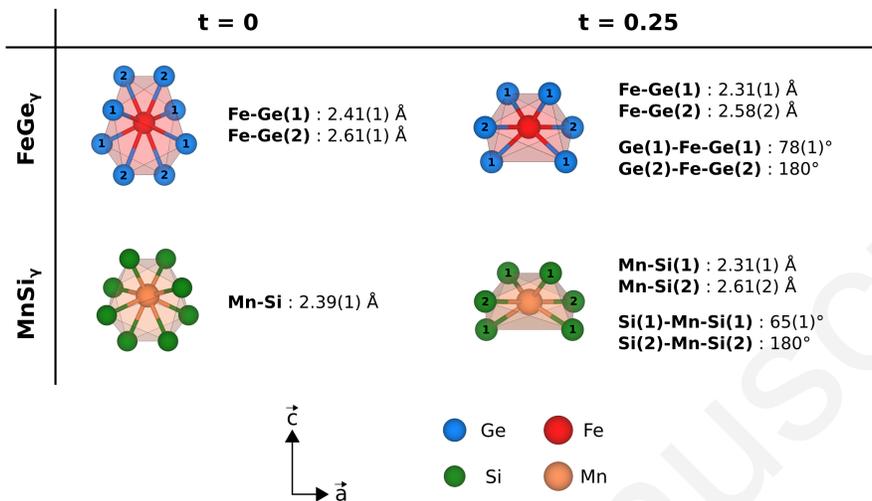


Figure 5: Comparison of the coordination sphere around Fe and Mn atoms in FeGe_γ and MnSi_γ , respectively, at $t = 0$ and $t = 0.25$.

209 sphere around a given Fe atom as an intermediate case between the two co-
 210 ordination environments found at $t = 0$ and 0.25 (Figure 5). At $t = 0$, Fe is
 211 coordinated to 4 Ge at the distance of 2.41(1) Å (labeled Ge(1) in Figure 5)
 212 and 4 Ge at 2.61(1) Å (labeled Ge(2)), resulting in a coordination number of 8.
 213 The Ge-Fe-Ge bond angles between adjacent Ge atoms are uneven but all have
 214 values between 61(1)° and 88(1)°. For $t = 0.25$, the coordination number of
 215 Fe is only 6 with 4 Ge at a distance of 2.31(1) Å (labeled Ge(1) in Figure 5)
 216 and 2 Ge at 2.58(2) Å (labeled Ge(2)). The smallest Ge(1)-Fe-Ge(1) bond an-
 217 gle is 78(1)° while Ge(2)-Fe-Ge(2) is strictly 180°. It should be noted that the
 218 reduction of the coordination number from 8 to 6, when t goes from 0 to 0.25,
 219 is compensated by a reduction of the average Fe-Ge bond distance from about
 220 2.5 Å to 2.4 Å. The length of the average Fe-Ge bond distance corresponds well
 221 to the closest Fe-Ge distances found in FeGe (2.393, 2.453 and 2.635 Å) [31],
 222 FeGe_2 (2.546 Å) [32] or $\text{Fe}_{1.75}\text{Ge}$ (2.343, 2.519 Å) [33]. Figure 5 also shows
 223 the corresponding coordination spheres around Mn in HMS determined from
 224 the structural parameters reported in Table 1 [29]. The environments of Mn in
 225 HMS are very similar to Fe in FeGe_γ with the coordination number also going

226 from 8 to 6 at $t = 0$ and 0.25, respectively. However, two significant differences
227 are : (i) there is a unique Mn-Si distance of 2.39(1) Å at $t = 0$ and (ii) the
228 shortest bond angle Si(1)-Mn-Si(1) at $t = 0.25$ is 65(1)° which is significantly
229 smaller than the respective Ge(1)-Fe-Ge(1) angle of 78(1)°. Both result in a
230 relative elongation of the Fe coordination polyhedra along the c axis compared
231 to MnSi $_{\gamma}$. These deformations of the Ge polyhedra around Fe is at the origin of
232 the longer c_{Ge} and therefore the lower γ in FeGe $_{\gamma}$.

233 3.2. High temperature XRD study of FeGe $_{\gamma}$

234 DSC analysis of the sample is presented in Figure SI. 1 and shows a large
235 exothermic peak starting around 850 K upon heating which is attributed to
236 the peritectoid decomposition of FeGe $_{\gamma}$. XRD confirms that FeGe $_{\gamma}$ decomposes
237 into FeGe and FeGe $_2$ after the thermal cycling. This result is in full agreement
238 with the accepted Fe-Ge phase diagram [17].

239
240 XRD patterns at each measured temperature were fully indexed with the
241 FeGe $_{\gamma}$ phase and FeGe, FeGe $_2$ and Fe $_2$ GeO $_4$ impurities. The mass fraction of the
242 impurities remained constant at all temperatures, as expected due to the long
243 annealing (1 month at 773 K) already undergone by the sample. The fitted pat-
244 terns are represented in Figure 2b and Figure SI. 2,3 and 4 while all the refined
245 parameters are given in Table SI 2. The thermal evolution of the parameters a ,
246 c_{Fe} , c_{Ge} , γ , the isotropic atomic displacement parameters U_{iso} for both Fe and
247 Ge and the [Fe] subsystems unit cell volume are plotted in Figure 6 and Fig-
248 ure SI 5. The expansion of lattice parameters are not linear with temperature
249 and are well described using a second order polynomial up to 850 K (Table
250 2). The a lattice parameter was the most affected with an increase of about
251 4.5 % from 300 K et 850 K. To a lesser extent, c_{Fe} and c_{Ge} both increased by
252 approximately 3.8 % in the same range. Consequently, the modulation vector
253 γ remained constant over the whole temperature range with an average value
254 of $\gamma = 1.5191 \pm 0.0001$. The atomic displacement parameter of Ge remained
255 larger than for Fe at every temperature. The thermal behaviors of U_{iso} seems to

256 follow a complex behavior which might be related to some micro-structural ef-
 257 fect occurring in the material. Figure 4 shows a comparison of the nearest Fe-Fe
 258 and Fe-Ge bond distance t -plots at 300 K and 850 K. The shortest Fe-Fe distance
 259 are from 3.006(8) Å to 3.020(8) Å (+ 0.4 %) and the shortest Fe-Ge bond from
 260 2.315(8) to 2.321(7) Å (+ 0.2 %). Except for the small increase of the bond
 261 distances, the temperature rise had negligible effect on the modulation and thus
 262 on the coordination sphere around Fe atoms.

263

264 The stability of γ is an important characteristic that must be taken into ac-
 265 count when considering the incorporation of chimney-ladder compounds in
 266 thermoelectric generators. For example, in HMS, it was shown both theoret-
 267 ically and experimentally [9] that the valence electron count (VEC) and conse-
 268 quently the concentration of charge carriers (n) is directly linked to the γ value
 269 *via* the relation :

$$n = 4 \cdot \frac{14 - VEC}{V_{Mn}} \quad \text{with} \quad VEC = 7 + 4\gamma \quad (5)$$

270 where V_{Mn} is the volume of the chimney subsystem in HMS. Evolution of γ with
 271 the temperature thus has a direct influence on the electrical resistivity and See-
 272 beck coefficient of the material as shown experimentally by Pichon *et al.* [34].
 273 This makes optimization of the thermoelectric legs geometry difficult as well as
 274 causing high mechanical stress in the materials. As a similar relation between γ
 275 and n is expected in FeGe_γ , the absence of γ evolution suggests a good stability
 276 of the electronic properties within the temperature range of interest.

277

278 The thermal expansion is another critical property to take into account when
 279 designing mid-temperature thermoelectric generator. Indeed, it is important to
 280 match the thermal expansion of the n - and p -type thermoelectric materials as
 281 well as with the metallic contacts in order to assure to the device good mechan-
 282 ical resistance upon thermal cycling. The linear α and volumetric β thermal
 283 expansion coefficients of FeGe_γ given in Table 2 were calculated using the rela-

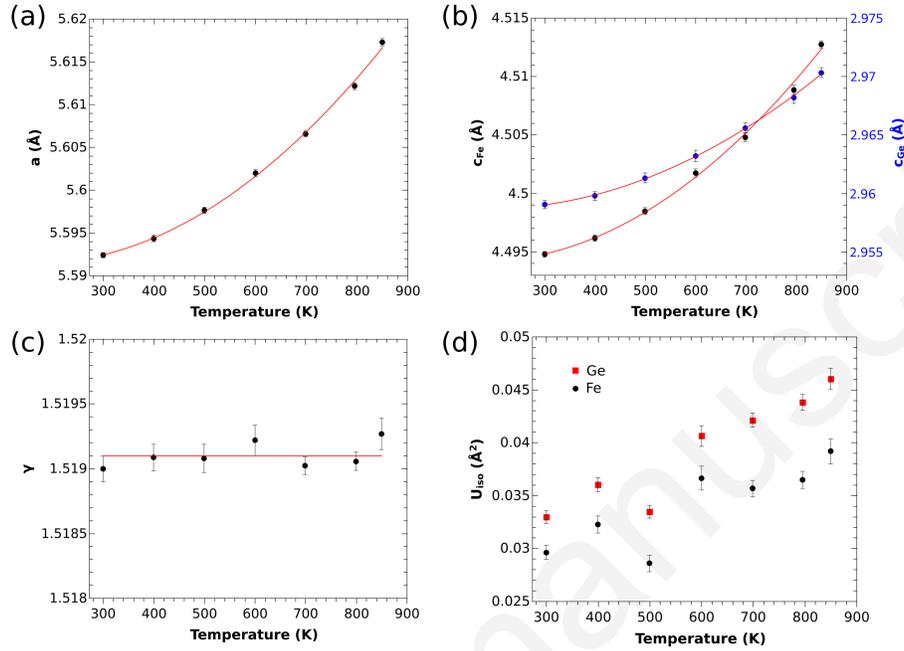


Figure 6: Thermal evolution of the lattice parameters (a) a , (b) c_{Fe} and c_{Ge} , (c) modulation vector coordinate γ and (d) Fe and Ge isotropic atomic displacement parameters U_{iso} .

284 tions:

$$\alpha_l = \frac{1}{l} \frac{dl}{dT} \quad \beta = \frac{1}{V_{Fe}} \frac{dV_{Fe}}{dT} \quad (6)$$

285

286 where l is a , c_{Fe} or c_{Ge} and V_{Fe} is the volume of the [Fe] subsystem unit cell. Due
 287 to the non-linearity of the lattice parameters' respective evolutions with temper-
 288 ature, the thermal expansion coefficients are not constant. At 850 K, the linear
 289 expansion coefficients was determined to be approximately 4 times larger than
 290 at room temperature and the volumetric thermal expansion coefficient approx-
 291 imately 3 times larger. In the same temperature range, α coefficients of p -type
 292 $MnSi_\gamma$ have constant values around $11 \times 10^{-6} \text{ K}^{-1}$ [29]. While the thermal ex-
 293 pansion coefficient of the two compounds are similar at the targeted application
 294 temperature of 800 K, the relatively large difference at lower temperatures may

Table 2: Temperature dependence of the lattice parameters, the linear expansion coefficient α and volumetric expansion coefficient β at 300 K and 850 K.

a (Å)	$5.5905(8) - 6.8(3) \times 10^{-6} T + 4.20(3) \times 10^{-8} T^2$	
c_{Fe} (Å)	$4.4935(9) - 4.9(4) \times 10^{-6} T + 3.04(3) \times 10^{-8} T^2$	
c_{Ge} (Å)	$2.9589(6) - 6.5(2) \times 10^{-6} T + 2.28(2) \times 10^{-8} T^2$	
V_{Fe} (Å ³)	$140.44(7) - 5,2(3) \times 10^{-4} T + 3.12(3) \times 10^{-6} T^2$	
	300 K	850 K
α_a (10 ⁻⁶ K ⁻¹)	3.34(9)	10.9(1)
$\alpha_{c_{Fe}}$ (10 ⁻⁶ K ⁻¹)	2.9(2)	9.7(2)
$\alpha_{c_{Ge}}$ (10 ⁻⁶ K ⁻¹)	2.5(1)	10.2(2)
β (10 ⁻⁶ K ⁻¹)	9.6(3)	31.5(5)

295 cause damages to the thermoelectric modules upon repeated thermal cycling.

296

297 4. Conclusion

298 The crystal structure of the Nowotny chimney-ladder FeGe _{γ} with $\gamma \approx 1.52$ was
 299 studied from room temperature to its decomposition temperature at 850 K. An
 300 incommensurate composite crystal description of the structure with modulation
 301 wave vector $\mathbf{q} = (0, 0, 1.5191(1))$ was used to fit the data, clearly indicating
 302 the incommensurate nature of the polycrystalline iron germanide. The γ value
 303 is significantly smaller in FeGe _{γ} than in MnSi _{γ} . This is due to an elongation of
 304 the ladder [Ge] subsystem along the c axis caused by the larger atomic size of
 305 Ge. From room to high temperatures, the evolution of the lattice parameters a ,
 306 c_{Fe} and c_{Ge} are described with a second order polynomial up to the peritectoid
 307 decomposition into FeGe and FeGe₂ at 850 K. The linear and volumetric ther-
 308 mal expansion parameters are multiplied by 4 and 3, respectively, from 300 to
 309 850 K. Such thermal behavior is significantly different than MnSi _{γ} and suggests
 310 that thermoelectric modules made of these materials would undergo high me-
 311 chanical stress upon thermal cycling. However, the value of γ remains constant
 312 over the whole temperature range and would suggest a good stability of the

313 electronic transport properties in FeGe_γ under operating conditions.

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317 **References**

- 318 [1] T. Mori, Novel principles and nanostructuring methods for enhanced
319 thermoelectrics, *Small* 13 (2017) 1702013. doi:10.1002/smll.
320 201702013.
- 321 [2] T. Mori, S. Priya, Materials for energy harvesting: At the forefront of a new
322 wave, *MRS Bull.* 43 (3) (2018) 176–180. doi:10.1557/mrs.2018.32.
- 323 [3] S. M. Pourkiaei, M. H. Ahmadi, M. Sadeghzadeh, S. Moosavi, F. Pour-
324 fayaz, L. Chen, M. A. P. Yazdi, R. Kumar, Thermoelectric cooler and
325 thermoelectric generator devices: A review of present and potential ap-
326 plications, modeling and materials, *Energy* 186 (2019) 115849. doi:
327 10.1016/j.energy.2019.07.179.
- 328 [4] I. Petsagkourakis, K. Tybrandt, X. Crispin, I. Ohkubo, N. Satoh, T. Mori,
329 Thermoelectric materials and applications for energy harvesting power
330 generation, *Sci. Technol. Adv. Mat.* 19 (1) (2018) 836–862. doi:10.
331 1080/14686996.2018.1530938.
- 332 [5] D. Champier, Thermoelectric generators: A review of applications, *En-
333 ergy Convers. Manag* 140 (2017) 167–181. doi:10.1002/aenm.
334 201800056.
- 335 [6] W. Liu, Z. Chen, J. Zou, Eco-Friendly Higher Manganese Silicide Thermo-
336 electric Materials: Progress and Future Challenges, *Adv. Energy Mater.* 8
337 (2018) 1800056. doi:10.1002/aenm.201800056.

- 338 [7] S. LeBlanc, S. K. Yee, M. L. Scullin, C. Dames, K. E. Goodson, Material and
339 manufacturing cost considerations for thermoelectrics, *Renew. Sust. En-*
340 *erg. Rev.* 84 (2014) 313–317. doi:10.1016/j.rser.2013.12.030.
- 341 [8] Y. Miyazaki, D. Igarashi, K. Hayashi, T. Kajitani, K. Yubuta, Modulated
342 crystal structure of chimney-ladder higher manganese silicides MnSi_γ
343 ($\gamma \approx 1.74$), *Phys. Rev. B* 78 (2008) 214104. doi:10.1103/PhysRevB.
344 78.214104.
- 345 [9] Y. Miyazaki, Y. Kikuchi, Higher Manganese Silicide, MnSi_γ , Springer
346 Berlin Heidelberg, 2013, pp. 141–156 (2013). doi:10.1007/
347 978-3-642-37537-8_7.
- 348 [10] S. Le Tonquesse, V. Dorcet, L. Joanny, V. Demange, C. Prestipino, Q. Guo,
349 D. Berthebaud, T. Mori, M. Pasturel, Mesostructure - thermoelectric prop-
350 erties relationships in $\text{V}_x\text{Mn}_{1-x}\text{Si}_{1.74}$ ($x = 0, 0.04$) Higher Manganese Sili-
351 cides prepared by magnesiothermy, *J. Alloys Compd.* 816 (2020) 152577.
352 doi:10.1016/j.jallcom.2019.152577.
- 353 [11] G. Skomedal, L. Holmgren, H. M. and I.S. Eremin, G. Isachenko, M. Jae-
354 gle, K. Tarantik, N. Vlachos, M. Manoli, T. Kyratsi, D. Berthebaud, N. Y. D.
355 Truong, F. Gascoin, Design, assembly and characterization of silicide-
356 based thermoelectric modules, *Energy Convers. Manag.* 110 (2016) 13–
357 21. doi:10.1016/j.enconman.2015.11.068.
- 358 [12] S. Le Tonquesse, Z. Verastegui, H. Huynh, V. Dorcet, Q. Guo, V. Demange,
359 C. Prestipino, D. Berthebaud, T. Mori, M. Pasturel, Magnesioreduction
360 Synthesis of Co-Doped $\beta\text{-FeSi}_2$: Mechanism, Microstructure, and Im-
361 proved Thermoelectric Properties, *ACS Appl. Energy Mater.* 12 (2) (2019)
362 8525–8534. doi:10.1021/acsaem.9b01426.
- 363 [13] J. Bourgeois, J. Tobola, B. Wiendlocha, L. Chaput, P. Zwolenski, D. Berthe-
364 baud, F. Gascoin, Q. Recour, H. Scherrer, Study of Electron, Phonon and
365 Crystal Stability Versus Thermoelectric Properties in Mg_2X ($\text{X} = \text{Si}, \text{Sn}$)

- 366 Compounds and Their Alloys, *Funct. Mater. Lett.* 6 (5) (2013) 1340005.
367 doi:10.1142/S1793604713400055.
- 368 [14] K. Gerasimov, S. Pavlov, New equilibrium phase in the Fe-Ge system
369 obtained by mechanical alloying, *Intermetallics* 8 (4) (2000) 451–452.
370 doi:10.1016/S0966-9795(99)00113-2.
- 371 [15] W. Li, Y. Li, X. Ma, Z. Zhang, Incommensurate structure of a new Nowotny
372 phase in Fe-Ge system, *Mater. Chem. Phys.* 148 (3) (2014) 490–493. doi:
373 10.1016/j.matchemphys.2014.08.023.
- 374 [16] N. Sato, H. Ouchi, Y. Takagiwa, K. Kimura, Glass-like Lattice Thermal
375 Conductivity and Thermoelectric Properties of Incommensurate Chimney-
376 Ladder Compound FeGe_γ , *Chem. Mater.* 28 (2) (2016) 529–533. doi:
377 10.1021/acs.chemmater.5b03952.
- 378 [17] V. Y. Verchenko, Z. Wei, A. A. Tsirlin, C. Callaert, A. Jesche, J. Hadermann,
379 E. V. Dikarev, A. V. Shevelkov, Crystal Growth of the Nowotny Chimney-
380 Ladder Phase Fe_2Ge_3 : Exploring New Fe-Based Narrow-Gap Semiconduc-
381 tor with Promising Thermoelectric Performance, *Chem. Mater.* 29 (23)
382 (2017) 9954–9963. doi:10.1021/acs.chemmater.7b03300.
- 383 [18] V. Petříček, M. Dušek, L. Palatinus, Crystallographic Computing System
384 JANA2006: General features, *Z. Kristall.* 229 (2014) 345–352. doi:10.
385 1515/zkri-2014-1737.
- 386 [19] P. Thompson, D. E. Cox, J. B. Hastings, Rietveld refinement of Debye-
387 Scherrer synchrotron X-ray data from Al_2O_3 , *J. Appl. Cryst.* 20 (1987)
388 79–83. doi:10.1107/S0021889887087090.
- 389 [20] J.-F. Bérar, P. Lelann, E.s.d.'s and estimated probable error obtained in
390 Rietveld refinements with local correlations, *J. Appl. Cryst.* 24 (1) (1991)
391 1–5. doi:10.1107/S0021889890008391.

- 392 [21] S. Van Smaalen, *Incommensurate crystallography*, Oxford University
393 Press., 2007 (2007). doi:10.1093/acprof:oso/9780198570820.
394 001.0001.
- 395 [22] S. Van Smaalen, Symmetry of composite crystals, *Phys. Rev. B* 43 (1991)
396 11330–11341. doi:10.1103/PhysRevB.43.11330.
- 397 [23] V. Petříček, K. Maly, P. Coppens, X. Bu, I. Cisarova, A. Frost-Jensen, The de-
398 scription and analysis of composite crystals, *Acta Crystallogr. A* 47 (1991)
399 210–216. doi:10.1107/S0108767390012065.
- 400 [24] A. Yamamoto, Determination of composite crystal structures and super-
401 space groups, *Acta Cryst. A* 49 (6) (1993) 831–846. doi:10.1107/
402 S0108767393004404.
- 403 [25] P. W. Stephens, Phenomenological model of anisotropic peak broadening
404 in powder diffraction, *J. Appl. Cryst.* 32 (1999) 281–289. doi:10.1107/
405 S0021889898006001.
- 406 [26] L. Akselrud, R. C. Gil, M. Wagner-Reetz, Y. Grin, Disorder in the composite
407 crystal structure of the manganese ‘disilicide’ $\text{MnSi}_{1.73}$ from powder X-ray
408 diffraction data, *Acta Crystallogr. B* 71 (2015) 707–712. doi:10.1107/
409 S2052520615019757.
- 410 [27] H. G. Ye, S. Amelinckx, High-resolution electron microscopic study of man-
411 ganese silicides MnSi_{2-x} , *J. Solid State Chem.* 61 (1986) 8–39. doi:
412 10.1016/0022-4596(86)90003-4.
- 413 [28] S. Vivès, C. Navone, E. Gaudin, S. Gorsse, Improved microstructure and
414 thermoelectric properties of higher manganese silicide processed by re-
415 active spark plasma sintering, *J. Mater. Sci.* 52 (2017) 12826–12833.
416 doi:10.1007/s10853-017-1397-7.
- 417 [29] Y. Kikuchi, T. Nakajo, K. Hayashi, Y. Miyazaki, High temperature X-ray
418 diffraction study on incommensurate composite crystal MnSi_γ (3+1)-

- 419 dimensional superspace approach, *J. Alloys Compd.* 616 (2014) 263–267.
420 doi:10.1016/j.jallcom.2014.07.106.
- 421 [30] J. C. Slater, Atomic Radii in Crystals, *J. Chem. Phys.* 41 (1964) 3199.
422 doi:10.1063/1.1725697.
- 423 [31] B. Lebeck, J. Bernhard, T. Freltoft, Magnetic structures of cubic FeGe stud-
424 ied by small-angle neutron scattering, *J. Phys.: Condens. Matter.* 1 (1989)
425 6105–6122. doi:10.1088/0953-8984/1/35/010.
- 426 [32] I. Piratinskaya, R. Krentsis, A. Mikhelson, P. Geld, Magnetic susceptibility
427 of solid solutios $\text{Fe}_{x-1}\text{Co}_x\text{Ge}_2$, *Inorg. Mater.* 4 (1975) 726–728.
- 428 [33] R. Andrusyak, B. Kotur, Phase equilibriums in the Sc-Mn-Ge and Sc-Fe-Ge
429 systems at 870 K, *Russ. Metall.* 4 (1991) 204–208.
- 430 [34] P.-Y. Pichon, P. Berneron, J. Levinsky, A. Burema, G. Blake, D. Berthe-
431 baud, S. Gascoin, F. Gascoin, S. Hebert, J. Amtsfeld, T. Hommels,
432 M. Huijben, J. de Boor, E. Müller, C. Navone, A. Schönecker, Stabili-
433 ty and thermoelectric performance of doped higher manganese silicide
434 materials solidified by RGS (ribbon growth on substrate) synthesis, *J.*
435 *Alloys Compd.* (2020) 154602doi:https://doi.org/10.1016/j.
436 jallcom.2020.154602.