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# Influence of Cr-substitution on the structural, magnetic, electron transport, and mechanical properties of $Fe_{3-x}Cr_xGe$ Heusler alloys



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## ABSTRACT

We performed combined experimental and theoretical studies of the effect of Cr substitution for Fe on the structural, magnetic, transport, electronic, and mechanical properties of  $Fe_{3-x}Cr_xGe$  ( $0 \le x \le 1$ ) intermetallic alloys. Single phase microstructures are observed for  $x \le 0.70$ . Higher Cr concentrations x > 0.70 are multi-phased. A hexagonal  $D0_{19}$  structure is found for all Cr concentrations, with the lattice parameters increasing systematically with an increasing Cr content. All the alloys in the series are found to be ferromagnets with large magnetization values of about 6  $\mu_B/f.u.$  and high Curie temperature above room temperature. The low-temperature saturation magnetic moments agree fairly well with our theoretical results and also obey the Slater-Pauling rule. The density functional theory calculation reveals that Cr substitution energetically favours one of the Fe sites in Fe<sub>3</sub>Ge. The electrical resistivity measured over the temperature range from 5 K to 400 K shows metallic behavior, with a residual resistivity ratio that decreases with Cr content. Vicker's hardness values are observed to increase with increasing Cr content to approximately 5 GPa.

# 1. Introduction

Heusler compounds include a large family of interesting materials exhibiting a wide range of properties of both fundamental and potential technological interest such as half metallic ferromagnets, high perpendicular magnetic anisotropy materials, shape-memory alloys, spingapless semiconductors, skyrmions, topological insulators, and magnetocalorics [1-9]. Half metallic Heusler alloys are the most suitable materials in the field of information storage and spintronics as well as many other areas [1,10–12] because the electrical current is perfectly spin polarized in these materials. For applications in magnetics and spintronics [1], the inherently low magnetocrystalline anisotropy in cubic Heusler alloys can be limiting factor [13]. Identifying a hexagonal Heusler analogue [10] that exhibits a high magneto-crystalline anisotropy may be very attractive for applications such as perpendicular media, current perpendicular to plane giant magnetoresistance (CPP-GMR), and spin-torque-transfer RAM (STT-RAM) [14-17].

The extensive tunability of the Heusler compounds through chemical substitutions makes the family especially interesting. The intermetallic

compound Fe<sub>3</sub>Ge is an iron rich ferromagnet, well known to crystallize in two crystal structures, a cubic L1<sub>2</sub> phase (Cu<sub>3</sub>Au type, *Pm*3*m*, space group No. 221 [18,19]) at low temperatures (< 700°C) and hexagonal D0<sub>19</sub> phase (Mg<sub>3</sub>Cd type, P6<sub>3</sub>/mmc, space group No. 194 [18,19]) at higher temperatures (> 700°C) [20,21]. High magnetizations, with moments of about  $2\mu_B$ /Fe, high Curie temperatures of 640 K along with crystallographic anisotropy, makes the hexagonal phase of Fe<sub>3</sub>Ge substantial interest as a permanent magnet [18,22]. As 3d transition metals exhibit large magnetic moments and high Curie temperatures, and compounds in cubic phase generally exhibit weak magnetocrystalline anisotropy, identifying magnetic compounds with high Fe concentrations in hexagonal or tetragonal crystal structures is very helpful to discover new potential permanent magnets.

To our best knowledge, in spite of investigations aimed at understanding the magnetocrystalline anisotropy by substituting nominal Cr (x = 0.099) in hexagonal  $Fe_{3.3}$ Ge [23], there is not yet a detailed report of the structural, magnetic, electron transport, and mechanical properties of  $Fe_{3-x}Cr_x$ Ge in the bulk form, neither experimentally nor theoretically. Our interest in this compound stems from a recent theoretical

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prediction that Fe<sub>2</sub>CrGe has the high density-of-state at the Fermi energy in the majority-spin state and exhibits high spin polarization (almost 100%) insensitive to Fe–Cr chemical disorder [24]. In this paper, we present our systematic experimental investigation of the microstructure and phase purity, magnetic properties, electrical transport, and hardness in addition to structure determination to understand the structure–property relationships in this interesting family of Heusler-like compounds and compare the experimental data with results of first principles calculation. Particular attention has been paid to metallography and microstructural analysis to determine which regions of the phase diagram yield single phase specimens.

## 2. Experimental details

 $Fe_{3-x}Cr_x$ Ge (0≤x≤1) bulk samples were prepared by arc melting of stoichiometric amounts of the constituents in an argon atmosphere at  $10^{-4}$  mbar (see details in Supplementary). Care was taken to avoid oxygen contamination. As an oxygen getter, Ti was melted inside the vacuum chamber separately before melting the compound to avoid oxygen contamination. The as-cast ingots were examined repeatedly using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis in a JEOL 7000 Field Emission Scanning Electron Microscope (FESEM) to confirm homogeneity and correct composition. After confirming the anticipated target composition, the polycrystalline ingots were then annealed in an evacuated quartz tube at different temperatures ranging from 650 °C to 1000 °C for different dwell times (5 days to 25 days), and at the end of each annealing cycle, the samples were cooled slowly in the furnace to get optimum crystallization.

Annealed ingots were polished for spectroscopic investigations (see details in Supplementary). The polishing was done, first grinding using silicon carbide abrasive discs (120 through 1200 grit size) followed by diamond suspension polishing. Colloidal silica suspension of grit size 0.02  $\mu$ m was used at last for the finest polishing. After obtaining a smooth and reflective surface, the samples were etched with Adler etchant (9 g of CuNH<sub>3</sub>Cl, 45 g of hydrated FeCl<sub>2</sub>, 150 mL of HCl and 75 mL of DI Water) [25]. The purpose of etching is that etchant attacks different phases present in the samples at different rates, and provides high quality surface contrast for microstructure characterization.

Structural analyzes were carried out by means of X-ray diffraction (XRD) using a Bruker D8 Discover X-ray diffractometer equipped with monochromatic Co-K $\alpha$  ( $\lambda$  = 0.179 nm) radiation. The polished samples were rotated around the  $\phi$  axis during the XRD measurement to minimize surface effects. CaRIne crystallography 4.0 software [26] as well as in-house PYTHON code [27] including the dispersive corrections to the atomic scattering factors were used to simulate the XRD patterns to compare with the experimental XRD patterns. XRD analysis (Rietveld refinement) was done using the CRYSTAL IMPACT MATCH! software based on the FULLPROF algorithm [28] that uses the least-square refinement between experimental and calculated intensities. The low temperature magnetic and electrical transport properties were studied in Quantum Design Physical Properties Measurement System (PPMS), while the high temperature magnetization was measured using the Lakeshore VSM 7407. DC electrical resistivity measurements were carried out using van der Pauw method [29]. Al wire bonding was used to make the contacts. The mechanical properties were studied in terms of Vicker's hardness by using Buehler model 1600-6100 micro-hardness tester.

# 3. Experimental results and discussions

# 3.1. Microstructural and compositional analysis

Optical microscopy and SEM of polished and etched samples are the most direct ways to characterize micro-structure by revealing grain

boundaries, phase boundaries, and inclusion distribution as XRD is not always sufficient to confirm the phase purity if the impurity phase content is less than 5% of the overall volume [30–33]. We can speculate the presence of impurity phases observing different contrast in optical images, and SEM with EDS/EBSD can be used to directly quantify whether areas of different contrast represent impurity phases or possible different crystallite orientations.

Starting from the full stoichiometric  $Fe_2$ CrGe, multi-phase microstructure was obtained in every heat treatments performed at 650, 800, 900, or 1000 °C for different dwelling times; 3, 5, 7, 15 or 25 days. However, with the substitution of Fe for Cr, the secondary phase began to disappear and uniform single phase behaviour was observed in the Cr composition range ( $0 \le x \le 0.70$ ). All other higher Cr concentration produced multiphase behaviour (see details in Supplementary Information). Fig. 1 shows microstructure of all single phase samples heat treated at 1000 °C for 15 days. The microstructure of the high temperature (> 700 °C) phase for x = 0 *i.e.*, the parent Fe<sub>3</sub>Ge compound is presented in Fig. 1(a) already known to be stable, annealed under similar conditions [21,34].

The composition of all the stable single phase samples in the series are confirmed to be close to the target composition within  $\sim 5\%$  instrumental uncertainty range using EDS (see details in Supplementary information). SEM images displaying the microstructure are shown in Fig. 2, all annealed at 1000 °C for 15 days.

## 3.2. Crystal structure and atomic order analysis

XRD patterns taken from the  $Fe_{3-x}Cr_xGe$  alloy series annealed at 1000 °C for 15 days after polishing and etching, using a Co-K<sub>a</sub> radiation source at room temperature are shown in Fig. 3(a). All the diffraction peaks can be indexed as corresponding to the hexagonal D0<sub>19</sub> structure for all single phase specimens, though as noted below texturing effect makes it difficult to rely on XRD peak intensities. Lattice parameters of all stable phases, both along a-axis and c-axis, extracted using Cohen's method with a Nelson–Riley extrapolation function [35], are observed to increase systematically with increasing Cr content which leads to an overall increase in the unit cell volume (see Fig. 3(c)). The reason for the increase in unit cell is in accordance to Vegard's law [36] as the atomic radius of Cr (200 pm) is comparatively larger compared with that of the Fe atom (156 pm) [37]. The lattice parameters of all stable samples in  $Fe_{3-x}Cr_xGe$  alloy series are presented in Table 2.

Considering the fact that Heusler-like compounds can crystallize in a number of structures, particularly the ordered L2<sub>1</sub> ( $Fm\overline{3}m$ , space group



**Fig. 1.** Optical micrograph of  $Fe_{3-x}Cr_xGe$  ( $0 \le x \le 1$ ) heat treated at 1000 °C for 15 days showing the grain structures. The samples were etched for 1 min using the Adler etchant.



**Fig. 2.** SEM micrograph of  $Fe_{3-x}Cr_xGe$  ( $0 \le x \le 1$ ) heat treated at 1000 °C for 15 days.

No. 225 [18,19]) and its possible disordered phases  $DO_3$  (*Fm*3*m*, space group No. 225 [18,19]),  $DO_{19}$  (P6<sub>3</sub>/mmc, space group No. 194 [18,19]) [38–40], and  $DO_{22}$  (I4/mmm, space group No. 139 [18,19]), structure assignment should be undertaken carefully. The structural deformation through compression or elongation along one of the cubic (100) axes forms a tetragonal lattice while a similar deformation along the (111) direction results in a hexagonal structure [41]. In order to avoid a selection bias, we first determined the crystal class from the XRD data alone, following the procedure in Ref. [35]. From the observed XRD peaks, the values of  $\sin^2\theta$  were tabulated. If the structure is in the cubic system, then these values, when properly normalized, will yield a set of integers. Omissions in the list of integers distinguish the type of cubic

lattice (*sc*, *bcc*, *fcc*). If there is no overall normalization of the values that results in only integral values, the system is not cubic. For the  $Fe_{3-x}Cr_xGe$  alloy series shown in Fig. 3(a), We easily ruled out the possibility of cubic L2<sub>1</sub>, Xa and complete A2 and B2 disordered structures due to the presence of more number of reflection peaks than those required for cubic structures. A similar but slightly more involved procedure [35] can be used to test the XRD data against hexagonal systems. We observed that the XRD data presented in Fig. 3(a) derive from a hexagonal crystal system, and after indexing all peaks, lattice parameters (see Table 2) were extracted for all alloys in the series using Cohen's method with a Nelson–Riley extrapolation function [35]. So, from our initial list of structures, only D0<sub>19</sub> structure is remained to be a plausible crystal structure.

As a secondary check, all above postulated crystal structures L2<sub>1</sub> and its possible disordered phases (e.g., D0<sub>3</sub>), the hexagonal D0<sub>19</sub>, and the tetragonal D0<sub>22</sub> were simulated using either CaRIne 4.0 simulations or CRYSTAL IMPACT MATCH, or an in-house PYTHON code [27] including both the real and imaginary dispersive corrections to the atomic scattering factors [42]. The simulated XRD patterns using CaRIne 4.0 for different crystal structures are presented in Fig. 3(b) with details including their prototypes and Wyckoff positions listed in Table 2. Again, among all the simulated XRD patterns, only the hexagonal  $D0_{19}$ structure provides a good match to the experimental XRD pattern observed for all single phase compositions in the alloy series. There is some variation in experimental XRD peak intensities than those generated from simulations, which might be due to texturing effects, given the large grain size we observe ( $\sim 300 \, \mu m$ ). As the crystal structure of parent Fe<sub>3</sub>Ge is hexagonal D0<sub>19</sub> at higher temperature (>700 °C) and cubic  $(L1_2, Pm\overline{3}m, space group No. 221 [18,19])$  at lower temperature (< 700 °C), the L1<sub>2</sub> crystal structure was also simulated, but none of the intensities and peak positions matched with the experimental pattern (see Fig. 3).

XRD is a powerful analytical tool to determine the structures and phases present, however, the unknown degree of texturing as evident



**Fig. 3.** (a) Experimental XRD patterns of  $Fe_{3-x}Cr_xGe$  alloy series annealed at 1000°C for 15 days, here, \* and + correspond to the secondary cubic phase and unknown impurity phase, respectively. The first from bottom is simulated XRD pattern for D0<sub>19</sub> structure. (b) The simulated powder XRD patterns considering different crystal structures using CaRIne, and (c) The composition dependent lattice parameters a and c and unit cell volume of  $Fe_{3-x}Cr_xGe$  (x = 0, 0.25, 0.50, 0.70) alloys investigated at room temperature.

from larger grains ( $\sim$ 300  $\mu$ m) (in our case) alters the relative intensities of the XRD peaks and makes it difficult to rely only on the experimental XRD to determine the exact chemical order. In an attempt to determine the possible atomic ordering, we have performed Rietveld refinement. Fig. 4 shows the Rietveld refinement for x = 0.50 (see Supplementary information for x = 0, x = 0.25 and x = 0.70). Rietveld refinement showed reasonably good agreement (reduced  $\chi^2 = 4.8$  and weighted average Bragg *R*-factor = 12.2) between the observed XRD pattern and the calculated pattern for the hexagoanl  $DO_{19}$  structure with the experimental lattice parameters a = 5.1934 Å and c = 4.2269 Å. However, slightly higher fitting parameters than those expected for a perfect fit can be attributed to the sample texture altering the relative intensities of the peaks compared to the calculated pattern. According to Rietveld refinement, the 6h sites (with the parameter y = 5/6) are shared by Fe and Cr with occupancy 0.833 and 0.167, respectively, in agreement with the nominal composition, and the 2c sites are occupied by Ge. Here, with no evidence to the contrary, we presume that Fe and Cr mix randomly on the 6h sites. This D0<sub>19</sub> structure is shown in Fig. 6 (b). The proposed site assignments are summarized for  $DO_{19} Fe_{3-x}Cr_xGe$ in Table 1 [40].

Five hour continuous EBSD scan of  $Fe_{2.50}$ Cr<sub>0.50</sub>Ge sample with the step size of ~0.5  $\mu$ m was performed to determine the degree of texturing and purity of phase considered. Relatively large grains with some preferred orientation is revealed from IPF color map as shown in Fig. 5 (a). The different color assigned is based on the orientation of grains. Almost 96% of the selected microstructure is observed to match the proposed structure (red color in the EBSD map (see Fig. 5(b)) with some zero solution regions (approximately 4%, black spots) which seem to be from the sudden changes in the roughness of the sample at grain boundaries or from artifacts caused by the metallography and chemical etching procedures. This indicates that the phase present in  $Fe_{2.50}$ Cr<sub>0.50</sub>Ge is proposed D0<sub>19</sub> phase. All these experimentally observed facts support that the crystal structure of all stable samples  $0 \le x \le 0.70$  could be D0<sub>19</sub>.

#### 3.3. Magnetic characterization

Bulk magnetic properties of all single-phase samples, measured using the VSM module of a Quantum design PPMS Dynacool are presented in Fig. 7 and the main parameters are summarized in Table 2. Fig. 7(a) shows the field dependent magnetization M(H) curves of all stable samples in the  $Fe_{3-x}Cr_xGe$  series at 5 K. All the samples appeared to be ferromagnetic at 5 K. The saturation magnetizing field is observed to decrease with increasing Cr concentration consistent with the Slater-



**Fig. 4.** The Rietveld refinement of XRD pattern for x = 0.50 showing a signature of good fit with the proposed crystal model D0<sub>19</sub>.

## Table 1

Proposed site	assignment for	the	hexagonal	D019	$Fe_{3-x}Cr_xGe$	e.
			~			

	Wyckoff position	Coordinates	Occupancy
Fe	$6h, y = \frac{5}{6}$	$(y, 2y, \frac{1}{4})(-2y, -y, \frac{1}{4})(y, -y, \frac{1}{4})(-y, -2y, \frac{3}{4})$	$\frac{3-x}{3}$
Cr	$6h, y = \frac{5}{6}$	$(2y,y,\frac{3}{4})(-y,y,\frac{3}{4})$ (y, 2y, $\frac{1}{4}$ )(-2y, -y, $\frac{1}{4}$ )(y, -y, $\frac{1}{4}$ )(-y, -2y, $\frac{3}{4}$ )	$\frac{x}{3}$
Ge	2c	$(2y, y, \frac{3}{4}) (-y, y, \frac{3}{4}) (\frac{1}{3}, \frac{2}{3}, \frac{1}{4}) (\frac{2}{3}, \frac{1}{4}, \frac{3}{4})$	1







(b)

**Fig. 5.** (a) Inverse pole figure (IPF) color map of x = 0.50 taken using EBSD in SEM showing grain orientation with preferred texture. The insert shows the color map of crystallographic orientation. (b) The corresponding EBSD phase map of the same area showing single-phase behavior. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Pauling rule, though all samples are magnetically very soft. The Slater-Pauling rule describes the dependence of the magnetic moment on the valence electron concentration [43,44]. The saturation magnetic moments ( $M_s$ ) were extracted from an Arrot plot [45], *i.e.*, by extrapolating the linear part of  $M^2$  versus H/M to H/M = 0 (see inset to Fig. 7 (a)). The obtained values of saturation magnetic moment ( $M_s$ ) versus Cr



Fig. 6. Crystal structures (a) L1<sub>2</sub>, and (b) D0<sub>19</sub>.

concentration plot presented in Fig. 7(b) shows linear behavior for all stable  $D0_{19}$  phases, in good agreement with those obtained from first principles calculations (shown in green data points).

The high temperature magnetization was measured by means of a vibrating sample magnetometer (LakeShore VSM 7407) equipped with a high temperature stage. The temperature of the sample was ramped at 5 K/min and measurements were taken in heating mode under an applied field of 100 Oe. The plots of Fig. 7(c) show the temperature dependence

of magnetization M(T) curves for  $Fe_{3-r}Cr_rGe$  alloy series showing the ferro-paramagnetic transition. As shown in Fig. 7(c), the sample with x = 0.25 shows two magnetic transitions (see details in Supplementary information). The magnetic transition at 546 K corresponds to the Curie temperature but the origin of the transition at 436 K is not clear. One possible reason could be order-disorder phase transition introduced by the substitution of Cr on parent Fe<sub>3</sub>Ge. Although the possibility of secondary phase formation (small amount) due to vacuum annealing cannot be completely ruled out, the composition measured using EDS was within  $\sim$  5% instrumental uncertainty range. The extracted Curie temperature is observed to decrease linearly with the increase of Cr content (see Fig. 7(d)). The change in interatomic spacing in Fe<sub>3</sub>Ge due to the substitution of a third element Cr leads to change in magnetic interaction. The increase in lattice parameter with Cr concentration is expected to change the distance between magnetic ions leading a weak exchange interaction between Fe-(Fe,Cr) sublattices and hence giving lower T<sub>c</sub> values compared to parent Fe<sub>3</sub>Ge (640 K) [34]. The inset in Fig. 7(d) shows the first-order derivative of magnetization as a function of temperature.

The saturation magnetic moments at 5 K and corresponding Curie temperature of all stable samples in  $Fe_{3-x}Cr_xGe$  alloy series are presented in Table 2.



**Fig. 7.** (a) The field-dependent magnetization at 5 K of  $Fe_{3-x}Cr_x$ Ge alloy series annealed at 1000 °C for 15 days. The inset shows the Arrot plot for x = 0.50. (b) The magnetic moment versus Cr concentration both experimental and theoretical. (c) Temperature dependence of magnetization M at 1000e. The green arrow shows possible order–disorder phase transition at 436 K for x = 0.25. (d) The variation of  $T_c$  with Cr concentration. The inset shows the first-order derivative of magnetization as a function of temperature, the minima of which is used to extract  $T_c$ .

#### Table 2

Experimental lattice parameters and saturation magnetic moments at T = 5 K, both experimental and theoretical, and Curie temperature of  $Fe_{3-x}Cr_xGe$  alloy series, all annealed at 1000 °C for 15 days (D0<sub>19</sub> phases). The numbers in parentheses are the uncertainty in the last digit, *e.g.*,  $6.55(9) = 6.55 \pm 0.09$ .

x	Experimental lattice	Theoretical lattice	Expt. $M_s$ at $T = 5 K$	Theor. M <sub>s</sub>	T <sub>c</sub>
	(Å)	(Å)	$(\mu_B/f.u.)$	$(\mu_B/f.u.)$	(K)
0	a = 5.1768(2)	<i>a</i> = 5.134	6.55(9)	6.48	640 [34]
	c = 4.2246(3)	c = 4.222			
0.25	a = 5.1885(2)	<i>a</i> = 5.144	5.79(5)	5.98	546
	c = 4.2260(3)	c = 4.202			
0.50	a = 5.1934(2)	a = 5.153	5.11(5)	5.52	446
	c = 4.2269(2)	c = 4.195			
0.70	a=5.1958(1)	a = 5.155	4.44(7)	4.98	364
	c=4.2275(3)	c = 4.195			

## 3.4. Electrical resistivity

Temperature dependence of electrical resistivity  $\rho$  of the  $Fe_{3-x}Cr_xGe$ alloy series was measured using the van der Pauw method [29] in a PPMS Dynacool for samples with approximate dimensions  $4 \times 4 \times 1.5$ mm<sup>3</sup>. Fig. 8 shows the variation of normalised electrical resistivity (in zero magnetic field) as a function of temperature for all samples measured during cooling process in the temperature range from 5 K to 400 K. The residual resistivity ratio (RRR)  $\rho_{300K}/\rho_{5K}$  for  $Fe_{3-x}Cr_xGe$  series is found to be 7.22, 4.36, 3.16, and 2.13 for x = 0, 0.25, 0.50 and 0.70 respectively. A higher RRR values usually indicate to good chemical ordering, while a lower values can be attributed to scattering from impurities or anti-site defects [46]. In the present alloys, lower RRR values after Cr substitution indicates the presence of atomic disorder. Also, an increase of Cr substitution for Fe results a substantial decrease of RRR value which suggests that the disorder increases with the increase of Cr concentration.

The resistivity up to 25 K is found to be almost independent of temperature, called residual resistivity due to lattice imperfections, impurities, *etc.* which increases with an increasing Cr content. After that, the resistivity is observed to increase with an increasing temperature and saturated at higher temperatures after Cr substitution, indicating weak variation of resistivity resulting from the parallel contribution of the intrinsic resistivity and some limiting resistivity (*e.g.*, disordered grain boundaries) known as shunting with temperature [47,48]. The details of the nonlinear least-squares fit to resistivity including shunting term is provided in Supplementary information.



Fig. 8. Variation of normalised electrical resistivity for  $Fe_{3-x}Cr_xGe$  alloys.

#### 3.5. Vickers micro hardness

Most previous studies on mechanical properties of Heusler alloys are theoretical in nature [49-52] and only few are verified experimentally. Therefore, we decided to investigate the Vickers hardness of our alloy series as evidenced by the polishing time required during specimen preparation. The variation of Vickers micro hardness of our alloy series (all annealed at 1000 °C for 15 days) with Cr concentration is presented in Fig. 9 with corresponding values in Table 3. Hardness values reported are the averages of data taken from at least 12 different regions of each sample with 0.2 kg load and 10 s loading time. Fe<sub>3-x</sub>Cr<sub>x</sub>Ge system is observed to be softer than those reported for Heusler systems in the literatures [53-55,33,32,56], respectively. The hardness is observed to increase almost linearly with increasing Cr concentration and depend on grains size and phases present as reported in the literature [57]. An enhancement of hardness is expected with the substitution of atoms with larger atomic radius for the atoms with lower atomic radius, consistent with our substitution of Cr for Fe [58]. The observed hardness values are found to agree well with those calculated theoretically (see details in Supplementary information). From the microstructure analysis of all single phase compositions, a decrease in grain size was observed with the increase of Cr concentration. We argue that grain size reduction was one key factor in the enhancement of hardness.

# 4. Theoretical calculations

# 4.1. Computational methodology

We performed first-principle calculations within the density functional theory (DFT) framework as implemented in the Vienna Ab-initio Simulation Package (VASP) [59]. We used potentials from the projector augmented-wave (PAW) method and used the Perdew-Burke-Ernzerhof (PBE) functional [60–62]. The valence states of the atoms are as follows: Fe:  $3d^7 4s^1$ , Ge:  $4s^2 4p^2$ , Cr:  $3d^5 4s^1$ . To sample the Brillouin zone, The Monkhorst–Pack scheme was used with a  $9 \times 9 \times 9$ k-point grid for cubic structures and a  $9 \times 9 \times 5$  grid for hexagonal structures in addition to a plane wave basis set with a cutoff energy of 400 eV [63]. Self-consistent field calculations of the total and projected electronic density of states were carried out with a Gaussian-type Fermi-level smearing width of 0.05 eV. In order to generate  $Fe_{3-x}Cr_xGe$  structures with varying Cr concentrations, we used the Special Quasirandom Structures (SQS) method implemented in the ATAT package [64–66]. The formation



**Fig. 9.** Vickers hardness versus Cr concentration in  $Fe_{3-x}Cr_xGe$ , all annealed at 1000 °C for 15 days, with imprint of the indenter with radial cracks [bottom right]. The black data points represent the single phase compositions and diamond shaped solid red data point represent the hardness of low temperature  $L1_2$  phase of parent Fe<sub>3</sub>Ge annealed at 650 °C for 25 days. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 3**Vickers micro-hardness of the  $Fe_{3-x}Cr_xGe$  alloy series.

x	Vickers Hardness (GPa)
0	$3.99\pm0.09$
0.25	$4.34\pm0.09$
0.50	$\textbf{4.77} \pm \textbf{0.11}$
0.70	$5.02\pm0.06$
1	$5.26\pm0.15$

energy  $E_{\text{form}}$  (in eV/atom) of  $Fe_{3-x}Cr_xGe$  is defined as  $E_{\text{form}} = (E_{\text{Fe}_{3-x}Cr_xGe} - (1-x)E_{\text{Fe}_3Ge} - xE_{\text{Cr}_3Ge})$ , where  $E_{\text{Fe}_{3-x}Cr_xGe}$  is the energy of a  $Fe_{3-x}Cr_xGe$  cell,  $E_{\text{Fe}_3Ge}$  is the energy of a Fe\_3Ge cell, and  $E_{\text{Cr}_3Ge}$  is the energy of a Cr\_3Ge cell, all per formula unit. We then normalized the x axis to start from x = 0 (Fe\_3Ge) to x = 1 ( $Fe_2CrGe$ ). We used Bader charge analysis [67,68] to obtain the charge distribution on the atoms. The VESTA program was used to visualize atomic structures [69].

## 4.2. Theoretical results and discussion

For the sake of comparison, we calculated the electronic, magnetic and mechanical properties of Fe<sub>3</sub>Ge alloys for the space group of L1<sub>2</sub> and D0<sub>19</sub>. The calculated lattice constants and magnetic moments for Fe<sub>3</sub>Ge alloys in L1<sub>2</sub> and D0<sub>19</sub> phases are a = b = c = 3.638 Å,  $6.45 \mu_B$ , and a = b = 5.134 Å, c = 4.222 Å and  $6.48 \mu_B$ , respectively. These results are in good agreement with our experimental data. In order to investigate Cr atom substitution with Fe in the Fe<sub>3</sub>Ge structure, we employed the Special Quasirandom Structures (SQS) method to generate  $Fe_{3-x}Cr_xGe$ structures between x = 0 and x = 1 for the D0<sub>19</sub> phases. Fig. 10 shows the formation energy as a function of Cr concentration x of the D0<sub>19</sub> phases. The magnetic moment value is also illustrated in the color axis of Fig. 10.

As depicted in Fig. 10, the  $Fe_{3-x}Cr_x$ Ge alloys for x = 0.25 and x = 0.50 are energetically less favorable than Fe<sub>3</sub>Ge. However, some  $Fe_{2.25}Cr_{0.75}$ Ge alloys are energetically preferable structures when compared to the alloys at x = 0.25 and x = 0.50. Substitution of Cr atoms instead of Fe atoms has little effect on the lattice parameters of the  $Fe_{3-x}Cr_x$ Ge structures. For instance, for  $Fe_{2.25}Cr_{0.75}$ Ge the percent difference of the a = b lattice parameters with respect to the Fe<sub>3</sub>Ge case is



**Fig. 10.** The formation energy (in eV/atom) as a function of Cr concentration for the  $D0_{19}$  alloys created with the SQS method. Each data point represents a different structure and the color axis indicates the magnetic moment value for each structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

only 0.41% and the decrease for the c lattice parameter is 0.64%. The obtained lattice parameters are in good agreement with the experimental results (see Table 2). The obtained magnetic moment value for Fe<sub>3</sub>Ge decreases with the increasing of Cr concentration, which is in accordance with Hund's rule. We observed that for the each x = 0.25 increment of Cr concentration in the  $Fe_{3-x}Cr_xGe$  alloys results in around a 0.5  $\mu_B/f.u.$  decrease for the magnetic moment value. As can be seen in Table 2, calculated magnetic moments are also in good agreement with the experimentally measured values. The total and atomic magnetic moments in a unit cell for the  $Fe_{3-x}Cr_xGe$  alloy series are presented in Supplementary information.

For the lowest energy structure (most energetically favorable) at each experimentally observed alloying concentration, we calculated the electronic density of states (DOS). Fig. 11 depicts the atom projected DOS of the experimentally observed alloys for  $L1_2$  (x = 0) and  $D0_{19}$  (x =0, x = 0.25, x = 0.50, and x = 0.75). The spin up and spin down contributions to the DOS are indicated by the black arrows. The insets of each DOS also include the optimized geometry, the lattice constants and magnetic moment values for the considered alloys. The metallic characteristics of the D0<sub>19</sub> and L1<sub>2</sub> (for x = 0) Fe<sub>3</sub>Ge structures arise from the dominant orbital contribution of Fe atoms, while the Ge atom contribution around the Fermi level is negligible. As can be seen from the insets, increasing of the number of Cr atom inside the  $Fe_{3-x}Cr_xGe$  alloy results in Cr clusters instead of separately placed Cr atoms. Density of states calculations show that the orbital contributions of Cr atoms are similar to the Fe orbital contribution, especially for the spin-down channel. In summary, substitution of Cr does not change the electronic properties of the  $Fe_{3-x}Cr_xGe$  alloys except for the magnetic moment value.

Bader charge transfer analysis for the  $Fe_{3-x}Cr_xGe$  alloys were performed to investigate the bonding type between the atoms and to gain insight on the electronic mechanism of these alloys. Bader charge analysis indicates that totally 0.30 electrons (e<sup>-</sup>) transfer to each Ge atom from Fe atoms in Fe<sub>3</sub>Ge for the D0<sub>19</sub> phase. According to the Pauling scale, the electronegativity difference between Fe and Ge atoms is 0.18, and the small amount of the charge transfer between these atoms indicate that there is non-polar covalent bonding between Fe and Ge atoms. Substitution of Cr atoms instead of Fe atoms results in a new charge distribution inside the  $Fe_{3-x}Cr_xGe$  alloys. For instance, the substituted Cr atom donates 0.39  $e^-$  and a majority of these donated electrons (0.30  $e^{-}$ ) are share by the surrounding Fe atoms for the x =0.25 ratio. This is expected because according to the Pauling scale of electronegativity, Fe has a value of 1.83 while Cr has a value of 1.66. With this charge transfer, some Fe atoms make their valence states similar to the initial non-alloyed states  $(3d^7 4s^1)$ . Increasing of the Cr concentration slightly decreases the charge transfer from Cr atoms. For instance at x = 0.50, two Cr atoms donate 0.35  $e^-$  while for x = 0.75, one Cr atom donates 0.37  $e^-$  and the remaining two Cr atoms donate 0.26  $e^-$  to the surrounding Fe and Ge atoms.

The attempt to calculate the mechanical hardness using the approaches described in references [70,71] results in a wrong dependence on the Cr composition (see details in Supplementary information).

## 5. Conclusion

In conclusion, an off-stoichiometric polycrystalline bulk  $Fe_{3-x}Cr_xGe$  intermetallic alloys series ( $0 \le x \le 1$ ) was synthesized by arc-melting and the structural, magnetic, electron transport and mechanical properties were investigated by means of theory and experiment. Single phase microstructure in the  $Fe_{3-x}Cr_xGe$  alloy series were confirmed by substituting Cr for Fe, up to x = 0.70. Cr substitution was observed to favor one of the Fe site in Fe<sub>3</sub>Ge energetically to form D0<sub>19</sub> structure, corroborated by Ab-initio simulations. All the alloys in the series were found to be soft ferromagnets at 5 K with decreasing saturation magnetic moment as the Cr concentration increases. These hexagonal samples



Fig. 11. The DOS and PDOS of the lowest energy structure at specific concentration ratios for  $L1_2$  and  $D0_{19}$ . The black arrows depict the spin up and spin down contributions and the red dotted line represents the Fermi level. The figure insets include the optimized structures, magnetic moment values and average lattice constants. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were in all cases observed to have markedly higher values of saturation moments. The ferromagnetic Curie temperature  $T_c$  was observed to decrease linearly with the addition of Cr concentration. The electrical resistivity measured over the temperature range from 5 K to 400 K showed purely a metallic behavior showing saturation at high temperatures. The residual resistivity ratio is also found to decrease with Cr substitution. Mechanical hardness values are measured to increase as Cr content increased. These findings may be interesting for magnetic applications where large saturation magnetization and high Curie temperature are desired.

# CRediT authorship contribution statement

Rabin Mahat: Conceptualization, Formal analysis, Investigation, Writing - original draft. Shambhu KC: Conceptualization, Formal analysis, Investigation, Writing - original draft. Daniel Wines: Formal analysis, Writing - original draft. Sudhir Regmi: Investigation. Upama Karki: Investigation. Zhong Li: Investigation. Fatih Ersan: Formal analysis. JiaYan Law: Investigation. Can Ataca: Conceptualization, Supervision, Project administration, Funding acquisition. Victorino Franco: Investigation. Arunava Gupta: Conceptualization, Supervision, Project administration, Funding acquisition. Patrick LeClair: Conceptualization, Supervision, Project administration, Funding acquisition, Writing - review & editing.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jmmm.2020.167398.

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